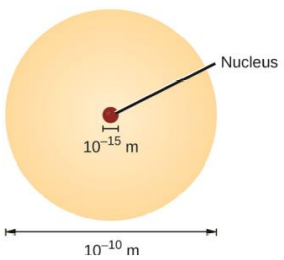
Unit 1

1. Atomic Structure and Periodicity

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m, about 100,000 times smaller.



In order to understand the structure of an atom, different types of atomic models were developed using different instruments. Some of the models are:

1.1. Democritus theory (300 BC)

The Greek philosopher Democritus expressed his own postulate and he states that:

Matter consists of very small, indivisible particles which are called as **atoms.** Atoms are derived from Greek words **ATOMOS** which mean indivisible into smaller particle. Atoms are indivisible particles. Explains certain natural occurrences such as the existence of elements

Atoms-and the protons, neutrons, and electrons that compose them—are extremely small. Atomic theory describes about the historical models of the atom, especially the external structure of atoms and how atoms combine to form molecules. This theory is a scientific theory that deals the nature of matter; states that matter is composed of discrete units which called **atoms**. Atom is the smallest particle into which an element can be divided and still be the same substance. Atoms are so small until recently, no one had ever seen it. But ideas, or theories, about atoms have been around for over 2,000 years. The theory of the atom has had a long history. The ancient Greeks postulated that matter exists in the

form of atoms. But they did not base their theory on experiment and they cannot develop additional ideas about atoms. Different scholars (researchers) give their idea on the atomic theory.

Limitation of Democritus atomic theory

- His theory does not support by experiment but only theoretical view
- Does not have any information about subatomic particles (electron, proton and neutron). Due to the lack of experiment, Democritus' idea was not accepted by many of researchers or scholars because Experimental evidence from early scientific investigations provided support for the notion of "**atomism**" and gradually gave rise to the modern definitions of elements and compounds.

1.2. Dalton's Atomic Theory

John Dalton (1766-1844), an English schoolteacher, developed the first useful atomic theory of matter around 1808. His findings were based on experiments and also from laws of chemical combination. He used fundamental laws of chemical combination just described as the basis of an atomic theory. His theory involved many assumptions:

- All substances are composed of tiny, indivisible particles which called "**atoms**".
- Atoms of the same element are identical in size, mass and properties but, atoms of different elements have different properties (**he doesn't recognize isotopes**).
- Compounds are formed by the union of two or more different elements
- Dalton model is known as the solid sphere model (like **billiard balls**)

Importance and Improvement on previous model

- Explains how atoms combine to form molecules.
- Explains chemical change better than the particle theory.
- Define conservation of mass and definite proportion.

Dalton's theory put down a corner stone for modern atomic theories since he uses the **law of chemical combination**.

1.2.1. Laws of Chemical Combination

Various chemical reactions take place according to certain laws, known as the Laws of chemical combination. There are three common laws of chemical combinations. These are:

A. Law of conservation of mass/the law of mass action: It also known as the law of

indestructibility of matter since this law states that "matter is neither created nor destroyed in the course of chemical reaction rather it may change from one form to other". The total mass of materials after a chemical reaction is same as the total mass before reaction. In short this law states that "during any physical or chemical changes, the total mass of product equal to the total mass of reactants". For example, in an experiment **63.5g** of copper combines with **16g** of oxygen to give **79.5g** of cupric oxide (a black oxide of copper).

$$\underset{48.6g}{2Mg(s)} + \underset{32g}{O_2(g)} \longrightarrow \underset{80.6g}{2MgO} \text{ and } \underset{100g}{CaCO_3} \xrightarrow{heat} \underset{56g}{CaO} + \underset{44g}{CO_2}$$

$$2Na + Cl2 \rightarrow 2NaCl,$$

$$2x23+2x35.5=117=2(23+35.5)=117$$

B. Law of constant or definite composition: According to this law, in a given compound, the constituent elements are always combined in the same proportions by mass, regardless of the origin or mode of preparation of the compound. What this law means is that when elements react chemically, they combine in specific proportions, not in random proportions. A sample of pure water which obtains river, sea, well, spring whatever the source, always contains 88.9% by mass of oxygen and 11.1% by mass of hydrogen.

C. Law of multiple proportions: According to this law, when two elements **A** and **B** combine to form more than one chemical compounds then different weights of **A**, which combine with a fixed weight of **B**, are in proportion of simple whole numbers. Or when two/more elements combine to form two/more compounds, the mass of one element combines with a fixed mass of another element. Example: Carbon monoxide (CO): 12 parts by mass of carbon combines with 16 parts by mass of oxygen. Carbon dioxide (CO_2): 12 parts by mass of carbon combines with 32 parts by mass of oxygen. Ratio of the masses of oxygen that combines with a fixed mass of carbon (12 parts) is 16: 32 or 1: 2

Limitations of Dalton's atomic theory

- Does not include the existence of the nucleus
- Does not explain the existence of ions or isotopes

- Does not have any information on subatomic particles (electron, proton and neutron).

Example 1. A nitrogen-oxygen compound is found to have an oxygen-to-nitrogen mass ratio of 1.142 g oxygen for every 1.000 g of nitrogen. Which of the following oxygen-to-nitrogen mass ratio(s) is/are possible for different nitrogen-oxygen compound(s)? a 2.285 c 0.571 b 1.000 d 2.500 2. Determine, which of the following oxygen-to-nitrogen mass ratio(s) is/are also possible for nitrogen-oxygen compound. (Refer Example 2.1 No. 1 for required information) a 0.612 c 1.713 b 1.250 d 2.856

Solution: 1. The given compound has 1.142 g of oxygen and 1.000 g of nitrogen. Response (a) has 2.285 g of oxygen for the same 1.000 g of nitrogen. The ratio of the masses of oxygen, 2.285:1.142, is almost exactly 2:1. Response (a) seems to be correct possibility, so is response (c). Here the ratio is 0.571:1.142 = 0.500 = 1:2. Responses (b) and (d) are not possibilities. They yield ratios of 1.000:1.142 = 0.875 and 2.500: 1.142 = 2.189, respectively. Neither of these can be expressed as a ratio of small whole numbers. 2. By the same method, a 0.612:1.142 = 0.536:1 is not possible b 1.250:1.142 = 1.095:1 is not possible c 1.713:1.142 = 1.5:1 or 3:2, is possible d 2.856:1.142 = 2.5:1 or 5:2 is possible

Exercise 1

1. List the postulates of Dalton that continue to have significance (are retained in modern atomic theory). 2. Match the atomic theory statements in part A with the matching items in part B.

Part A	Part B
I All matter is composed of extremely small, indivisible particles called atoms.	a Although graphite and diamond have different properties (due the nature of interatomic bonding) they are composed only of carbon. The carbon atoms are identical.
II All atoms of a given element are identical in mass and other properties, but atoms of one element differ from the atoms of every other element.	b $2H_2 + O_2 \rightarrow 2H_2O$, not CS_2 or NaCl.
III Atoms are not created, destroyed or converted into other kinds of atoms during chemical reactions. They are simply rearranged into new compounds.	c There are 6.02×10^{23} atoms in 55.85 g of iron.

3. How does the atomic theory account for the fact that when 1.00 g of water is decomposed into its elements, 0.111 g of hydrogen and 0.889 g of oxygen are obtained regardless of the source of the water?
4. Hydrogen peroxide is composed of two elements: hydrogen and oxygen. In an experiment, 1.250 g of hydrogen peroxide is fully decomposed into its elements.
   a If 0.074 g of hydrogen are obtained in this experiment, how many grams of oxygen must be obtained?
   b Which fundamental law does this experiment demonstrate?
   c How is this law explained by the atomic theory?
5. A 15.20 g of nitrogen will react with 17.37 g, 34.74 g, or 43.43 g of oxygen to form three different compounds.
   a Calculate the mass of oxygen per gram of nitrogen in each compound.
   b How do the numbers in part (a) support the atomic theory?

1.3. The concept of the atom

2.3.1. Discoveries of subatomic particles

Name	location	Charge(C)	Unit charge	Mass(amu)	Mass(g)	Discovered by
Electron	Outside nucleus	-1.602×10^{-19}	-1	0.00055	0.00091×10^{-24}	Joseph John Thomson
Proton	Nucleus	1.602×10^{-19}	+1	1.00727	1.67262×10^{-24}	
Neutron	Nucleus	0	0	1.00866	1.67493×10^{-24}	James Chadwick

A. Cathode Rays

In 1879, the English scientist William Crookes (1832-1919) experimented with gas discharge tubes. When a very high electrical potential (~ 10,000 volts) is applied across a gas taken in a discharge tube of a very low pressure (~ 0.001 torr) some radiations are emitted from cathode. These radiations are called cathode rays. Fig 2.1, shows emission of cathode rays in a discharge tube. At this stage the glass walls of the discharge tube opposite to the cathode starts glowing with a faint greenish light. It is now known that this greenish glow on the walls is due to the bombardment of the glass wall with the cathode rays.

Cathode rays normally travel in straight lines, but are deflected when a magnet is brought nearby (Figure 2.1b).

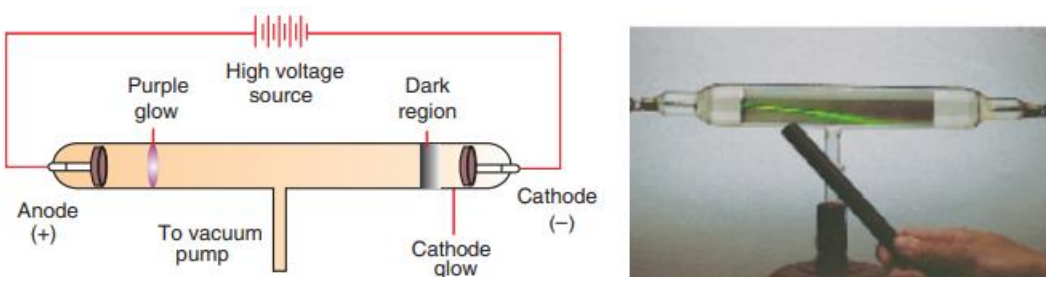


Figure 1 (a) Electric discharge in an evacuated tube (b) The cathode ray is bent. in the presence of a magnet.

An English physicist Joseph John Thomson (1856-1940) in 1897 studied the behaviour of cathode rays in electric and magnetic fields, Thomson established clearly that the rays consist of negatively-charged particles. Moreover, his experiments showed that the particles were identical, regardless of the materials from which the belectrodes were made or the type of gas in the tube. Thomson concluded that these negatively charged particles were constituents of every kind of atom. We now call these particles electrons, a term that had been coined by the Irish Physicist George Stoney in 1891 to describe the smallest unit of electric charge. Cathode rays are beams of electrons. In 1909, Robert A. Millikan, an American physicist, determined the charge on the electron by observing the behaviour of electrically-charged oil drops in an electric field. Based on careful experiments, Millikan established the charge on an electron as $e = -1.602 \times 10^{-19}$ C. From this value and the value for me/e, we can calculate the mass of an electron.

$$m_e = \frac{m_e}{e} \times e = -5.686 \times 10^{-12} \text{ kg C}^{-1} \times -1.602 \times 10^{-19} \text{ C}$$

$$= 9.109 \times 10^{-31} \text{ kg}$$

B. Radioactivity and Discovery of Nucleus

I. Radioactivity

Radioactivity is the spontaneous emission of radiation from the unstable nuclei of certain isotopes. Isotopes that are radioactive are called radioactive isotopes or radioisotopes. For example,

$^{55}_{24}Cr$, $^{226}_{88}Ra$, $^{14}_{6}C$, $^{238}_{92}U$

are radioactive isotopes. Radioactive decay is defined as a nuclear breakdown in which particles or (electromagnetic) radiation is emitted. Shortly after the discovery of radioactivity, three types of rays were identified in the emanations from radioactive substances. One type called alpha (α) particles which consist of particles that have a mass that is about four times that of a hydrogen atom. They also have a charge twice the magnitude of an electron but positive rather than negative. An alpha particle is now known to be a doubly-ionized helium atom, that is, He^{2+}.

A second type of radiation was shown to consist of negatively-charged particles, identical to cathode rays. These particles are called beta (β) particles, which are electrons, coming from inside the nucleus.

The third type of radiation, called gamma (γ) rays, is a form of electromagnetic radiation much like the X-rays but of even higher energy. Like X-rays, but unlike alpha and beta particles, gamma rays are a form of energy and not a form of matter.

II. Discovery of Nucleus

In 1910, the New Zealand chemist and physicist, Ernest Rutherford, who had studied with J.J. Thomson decided to use α-particles to probe the structure of atoms.

Together with his associate Hans Geiger, Rutherford carried out a series of experiments using very thin foils of gold and other metals as targets for α-particles from a radioactive source.

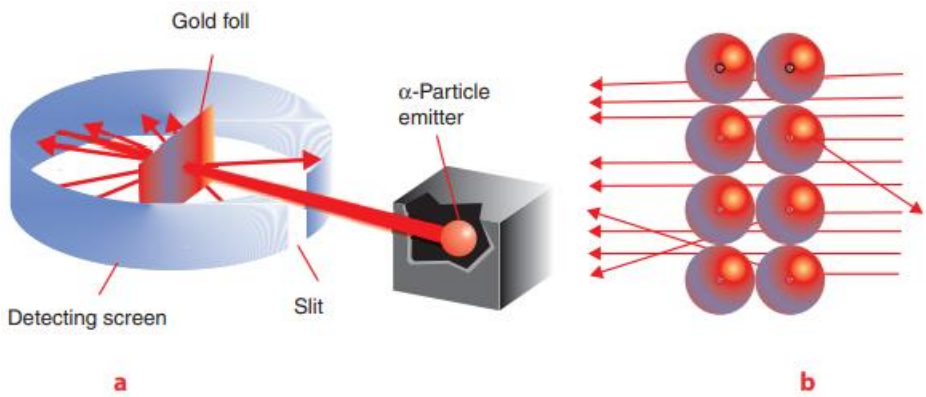


Figure 2. **a.** Rutherford's experimental design for measuring the scattering of α-particles by a piece of gold foil. **b.** Magnified view of α-particles passing through and being deflected by the nucleus.

C. Discovery of Neutron

Except for the lightest hydrogen isotope, protium (1H), atoms have more mass than is indicated by the numbers of their protons (*Before the 1930's, protons were considered as the sole contributors to the mass of an atom*). For example, a helium nucleus, with two protons has a mass four times that of hydrogen. If all the mass came from the protons, a helium atom would have only twice the mass of a hydrogen atom. The reason for this "*excess*" mass puzzled scientist for several years.

In the 1920s and early 1930s, alpha particles were used as projectiles to bombard a variety of materials. Bombardment of beryllium atoms produced a strange, highly

penetrating form of radiation. In 1932, James Chadwick (1891-1972) showed that this radiation was best explained as a beam of neutral particles. These particles, called *neutrons*, were found to have about the same mass as protons but no electric charge.

This discovery finally provided an explanation for the mysterious excess mass. A helium atom has two protons and two neutrons. Because protons and neutrons have roughly the same mass (and *electrons have almost no mass*) the helium atom should have about four times the mass of the hydrogen atom. The mass of a neutron, $mn = 1.67493 \times 10^{-27}$ kg, is about 1840 times the mass of electron.

1.4. Atomic Mass and Isotopes

The number of protons in the nucleus of an atom is its atomic number (Z). This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

$$\boldsymbol{atomic\ number(Z) = number\ of\ protons}$$

$$\boldsymbol{mass\ number(A) = number\ of\ protons + number\ of\ neutrons}$$

$$\boldsymbol{A - Z = number\ of\ neutrons}$$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are not equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

Atomic charge = number of protons − number of electrons

Atomic charge = number of protons − number of electrons

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms called cations are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+).

A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2- charge (8 − 10 = 2-).

Element	Symbol	Atomic No.	No of Protons	No of Neutrons	Mass (amu)	% Natural Abundance
Lithium	$^{6}_{3}Li$	3	3	3	6.0151	7.59
	$^{7}_{3}Li$	3	3	4	7.0160	92.41
Berylliu m	$^{9}_{4}Be$	4	4	5	9.0122	100
Boron	$^{10}_{5}B$	5	5	5	10.0129	19.9
	$^{11}_{5}B$	5	5	6	11.0093	80.1
Carbon	$^{12}_{6}C$	6	6	6	12.0000	98.89
	$^{13}_{6}C$	6	6	7	13.0034	1.11
	$^{14}_{6}C$	6	6	8	14.0032	— (trace)

Nitrogen	$^{14}_{7}N$	7	7	7	14.0031	99.63
	$^{15}_{7}N$	7	7	8	15.0001	0.37
Oxygen	$^{16}_{8}O$	8	8	8	15.9949	99.757
	$^{17}_{8}O$	8	8	9	16.9991	0.038
	$^{18}_{8}O$	8	8	10	17.9992	0.205
Fluorine	$^{19}_{9}F$	9	9	10	18.9984	100
Neon	$^{20}_{10}Ne$	10	10	10	19.9924	90.48
	$^{21}_{10}Ne$	10	10	11	20.9938	0.27
	$^{22}_{10}Ne$	10	10	12	21.9914	9.25

Atomic mass unit and average atomic mass because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are 10B with a mass of 10.0129 amu, and the remaining 80.1% are 11B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned} boron\ average\ mass &= (0.199 \times 10.0129\ amu) + (0.801 \times 11.0093\ amu) \\ &= 1.99\ amu + 8.82\ amu = 10.81\ amu \end{aligned}$$

Calculation of Average Atomic Mass: A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% 20Ne (mass 19.9924 amu), 0.47% 21Ne (mass 20.9940 amu), and 7.69% 22Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Exercise 2. There are two isotopes of lithium found on earth. Isotope ^{6}Li (6.01512 mu) accounts for 7.42% of the total, and isotope ^{7}Li (7.01600 mu) accounts for the remaining 92.58%. What is the average atomic mass of lithium?

Solution:

$$\frac{7.42}{100} \times 6.01512\ m_u + \frac{92.58}{100} \times 7.01600\ m_u = 6.942\ m_u$$

2. What is the mass number of an isotope of tin that has 66 neutrons and 50 protons?

3. Calculate the number of protons and neutrons for 24 12Mg and 88 38Sr.

4. Why do isotopes of an element have similar chemical properties?

5. Element X is toxic to humans in high concentration but essential to life at low concentrations. Identify element X whose atoms contain 24 protons and write the symbol for the isotope with 28 neutrons

6. Copper (Cu: atomic mass 63.546 m_u) contains the isotopes ^{63}Cu (mass = 62.9298 m_u) and ^{65}Cu (mass = 64.9278 m_u). What percent of a Cu atom is ^{65}Cu?

7. The element chlorine contains two isotopes: ^{35}Cl, which has a mass of 34.97 mu, and ^{37}Cl, which has a mass of 36.97 m_u. Calculate the percentage of each chlorine isotope. The average atomic mass of chlorine is 35.5 m_u.

8. Carbon exists as the isotopes carbon-12, with a fractional abundance of 0.9890 and a mass of exactly 12 m_u, and carbon-13, with a fractional abundance of 0.0110 and a mass of 13.00335 m_u. Calculate the average atomic mass of carbon

1.5. The Bohr Theory of the hydrogen atom

In 1913, Niels Bohr, a Danish physicist, who had worked with Rutherford, combined ideas from classical physics and the new quantum theory to explain the structure of the hydrogen atom. He suggested a model for the hydrogen atom that predicted the existence

of line spectra. In doing so, he was able to explain the spectrum of radiation emitted by hydrogen atoms in gas-discharge tubes.

Based on the work of Planck and Einstein, Bohr made the revolutionary assumption that certain properties of the electron in a hydrogen atom – including energy, can have only certain specific values. That is to say, these properties are quantized. Bohr proposed the following three postulates for his model.

1. The hydrogen atom has only certain allowable energy levels, called stationary states. Each of these states is associated with a fixed circular orbit of the electron around the nucleus.
2. The atom does not radiate energy while in one of its stationary states. That is, even though it violates the ideas of classical physics, the atom does not change energy while the electron moves within an orbit.
The electron moves to another stationary state (*orbit*) only by absorbing or emitting a photon whose energy equals the difference in the energy between the two states.

$$E_{ph} = E_f - E_i = h\nu$$

The subscripts f and i represent the final and the initial states, respectively. The Bohr radius, denoted by a_o (a_o = 0.0529 nm) can be calculated using the formula

$$a_o = \frac{r}{n^2}$$

where n is a positive integer which is called quantum number. r is the radius of the orbit and is given by:

$$r = \frac{n^2 \varepsilon_o h^2}{\pi m_e e^2 z}$$

where $\boldsymbol{\varepsilon_o}$ is the vacuum dielectric constant ($\boldsymbol{\varepsilon_o} = 8.854 \times 10^{-12}$ C V^{-1} m^{-1}).

A spectral line results from the emission of a photon of specific energy (*and therefore, of specific frequency*), when the electron moves from a higher energy state to a lower one.

An atomic spectrum appears as lines rather than as a continuum because the atom's energy has only certain discrete energy levels or states.

In Bohr's model, the quantum number n (n = 1, 2, 3 ...) is associated with the radius of the electron's orbit, which is directly related to the atom's energy. The lower the quantum number, the smaller is the radius of the orbit and the lower is the energy level of the atom. When the electron is in the orbit closest to the nucleus (n = 1), the atom is in its lowest (first) energy level, which is called the ground state. By absorbing a photon whose energy equals the difference between the first and second energy levels, the electron can move to the next orbit. This second energy level (second stationary state) and all higher levels are called excited states. The hydrogen atom in the second energy level (first excited state) can return to the ground state by emitting a photon of a particular frequency:

$$\Delta E = E_e - E_g$$

Where E_g and E_e represent the ground and the excited energy states, respectively. When a sample of atomic hydrogen absorbs energy, different hydrogen atoms absorb different amounts. Even though each atom has only one electron, so many atoms are presented that all the allowable energy levels (orbits) are populated by electrons. When an electron drops from orbits with $n > 3$ (*second excited state*), the infrared series of spectral lines is produced *i.e*, Paschen Series. The visible series arises from the photons emitted when an electron drops to the n = 2 orbit *i.e*, Balmer Series (*first excited state*), and the ultraviolet series arises when these higher energy electrons drop to the n = 1 orbit (*ground state*).

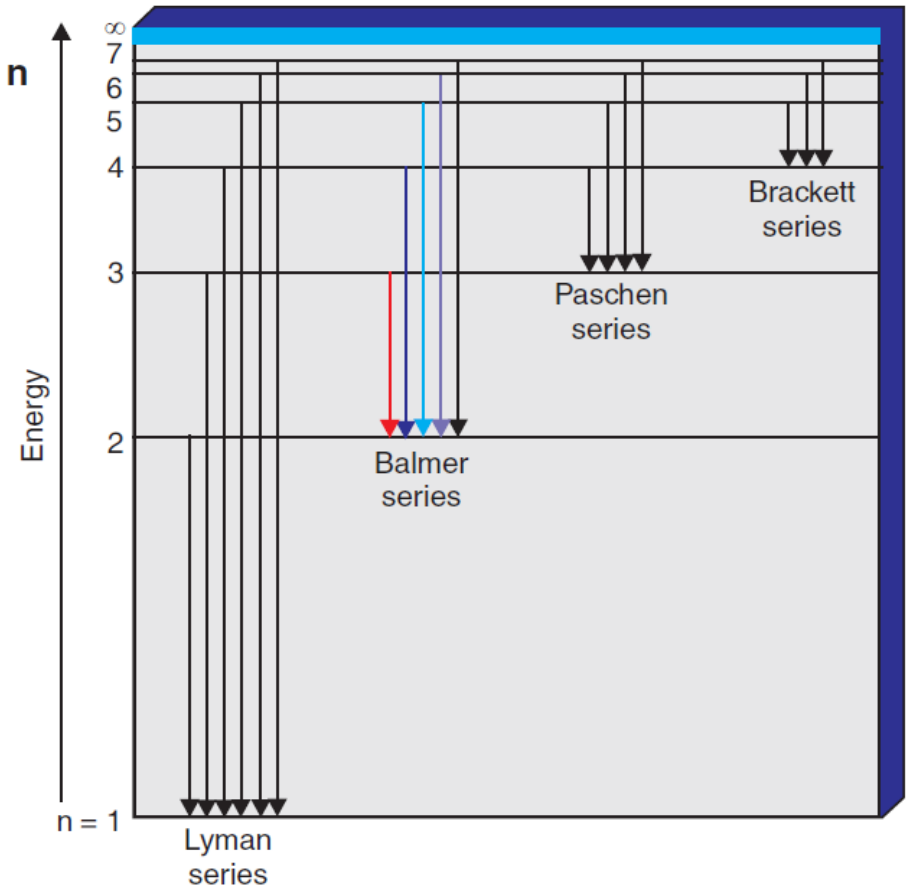


Figure 3. Representation of the observed spectral lines of the hydrogen atom.

Since a larger orbit radius means a higher atomic energy level, the farther the electron drops, the greater is the energy (higher v, shorter λ) of the emitted photon. The spectral lines of hydrogen become closer and closer together in the short wavelength (*high energy*) region of each series because the difference in energy associated with the jump from initial state (n_i) to the final state (n_f) becomes smaller and smaller as the distance from the nucleus increases.

Having made this basic assumption, Bohr was then able to use classical physics to calculate properties of the hydrogen atom. In particular, he derived an equation for the electron energy (En). Each specified energy value (E_1, E_2, E_3...) is called an energy level of the atom. A very useful result from Bohr's work is an equation for calculating the energy levels of an atom,

$$E_n = -A \times \frac{Z^2}{n^2}$$

Where A is the constant, has a value of, $A = 2.18 \times 10^{-18}$ J. The number n is an integer called the principal quantum number (n = 1, 2, 3, ...). Z is the charge of the nucleus. The negative sign in the equation appears because it is defined as zero energy when the electron is completely moved form the nucleus, i.e. $En = 0$ when $n = \infty$, so, En < 0 for any smaller n.

A can be expressed in terms of Rydberg constant as $A = hCR$, where R is Rydberg constant with a value of 1.0967 x$10^7 M^{-1}$. For the H atom, Z = 1, so we have

$$E_n = -2.18 \times 10^{-18}\ \text{J} \times \frac{1}{n^2}$$

Therefore, the energy of the ground state n = 1 is -2.18×10^{-18} J. This equation is easily adapted to find the energy difference between any two levels:

$$\Delta E = h\nu = E_f - E_i = -2.18 \times 10^{-18}\ \text{J} \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- When an electric discharge is passed through a sample of hydrogen, the H_2 molecules dissociate into atoms, and the electron in a particular H atom is excited.
- These states are transient and the electron falls back to a lower energy state by emitting energy as it does so.
- The consequence is the observation of spectral lines in the emission spectrum of hydrogen.
- The spectrum (a small part of which is shown in below Figure consists of groups of discrete lines.
- In1885, Balmer pointed out that the wave number of the spectral lines observed in the visible region of the atomic spectrum of hydrogen is given by V= R ($1/2^2$- $1/n^2$)

where, R = Rydberg constant for =1.097 x 10^7 m^{-1} = 1.097 x 10^5 cm^{-1}

and n is an integer 3, 4, 5 . . .

- Wave number = reciprocal of wavelength($v=1/\lambda$); convenient (non-SI) units are 'reciprocal centimetres', cm^{-1}

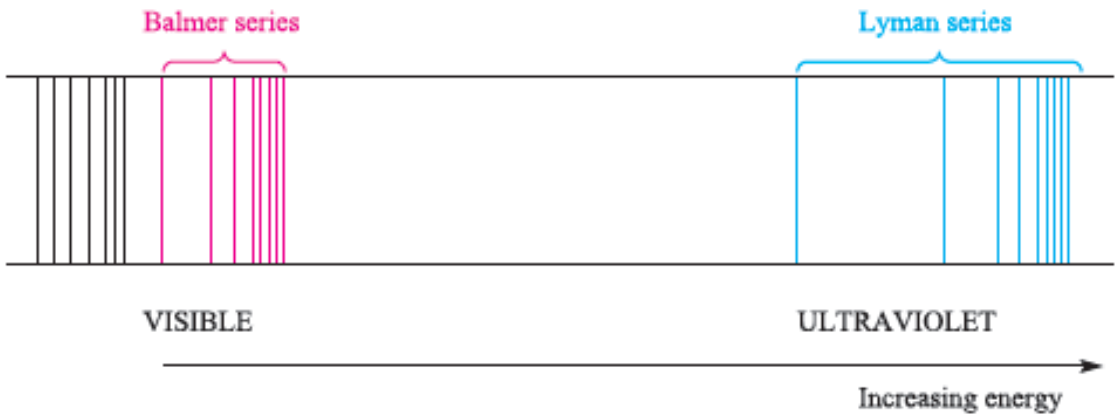


Figure 4. Spectrum of hydrogen

Note that: the line become close together as the wave length decrease until the continuum reached

Similar equation will be developed to hold for the other series in the H- spectrum

Lyman series, $V= R[1/1^2 - 1/n^2]$ n=2,3,4... , Uv region

Balmer series, $V = R[1/2^2 - 1/n^2]$ n= 3,4,5..., Visible region

Paschen series, $V= R[1/3^2 - 1/n^2]$ n= 4,5,6..., Infrared region

Bracket series, $V= R[1/4^2 - 1/n^2]$ n= 5,6,7... Infrared region

Pfund series, $V= R[1/5^2 - 1/n^2]$ n= 6,7,8…Infrared region

Example 2. Calculate the wave number if an electron transit from1st energy level to 5th energy level in Uv, visible and infrared region

Example 3. Calculate wave number for third transition in:

A. Lyman series B. Balmer series C. Paschen series D. Bracket series

Example 4. Calculate wave length for 6th transition in Balmer series

- **Solution:**
- **given:-** $n_i= 1$ $n_f= 5$

i. $V= R(1/1^2-1/n^2)$----------uv region

$= 1.097 \times 10^7\ m^{-1}\ (1/1^2-1/5^2)= \underline{1.05X\ 10^7\ m^{-1}}$

ii. $V= R(1/2^2-1/n^2)$ ---------- visible region

$V=1.097 \times 10^7\ m^{-1}\ (1/4-1/5^2) = 1.05X\ 10^7\ m^{-1}$

$= 0.21\ X1.097 \times 10^7\ m^{-1} = \underline{2.3 \times 10^6\ m^{-1}}$

iii. $V= R(1/3^2-1/n^2)$ ---------- visible region

$V=1.097 \times 10^7\ m^{-1}\ (1/9-1/5^2)= 1.097 \times 10^7\ m^{-1} \times 0.071$

$=0.077887x\ 10^7\ m^{-1} = \underline{7.789x\ 10^5\ m^{-1}}$

1.6. The quantum mechanical model of the atom

Bohr's model was very important because it introduced the idea of quantized energy states for electrons in atoms. This feature is incorporated in our current model of the atom, the quantum mechanical model of the atom.

The sophisticated mathematical description of atomic structure based on the wave properties of subatomic particles is called wave mechanics or quantum mechanics.

Principally, the Austrian physicist Erwin Scrödinger developed a model of the hydrogen atom based on the wave nature of the electron in the late 1920s.

Mathematical equations describing the nature of electron waves in atoms are fundamental to the modern picture of the atom. The wave equations that are acceptable solutions to the Schrödinger equation are called wave functions. To obtain one of these acceptable solutions, we must assign integral values called quantum numbers to three quantities in the wave equation. This requirement is similar to the requirement for an integral value of *n* in the Bohr equation for the hydrogen atom.

In contrast to the precise planetary orbits of the Bohr atom, the wave mechanics picture of the hydrogen atom is less certain. Instead of determining the exact location of the electron, we can only speak of the probability of the electron being found in certain regions of the atom. Or, if we adopt the view that the electron is just a cloud of negative electric charge, we can only speak of the charge densities in various parts of the atom. quantum mechanical model of the atom is called Modern Atomic Theory (Electron Cloud

Mode**)** It states that “electrons are always moving around the nucleus in a "cloud" of energy levels**”.** It also states that the small particle atom is consists of three parts such as, proton, neutron and electron**.**

- The **electrons** are found around the nucleus whereas; **protons and neutrons** are found in the central part of atom which is called **nucleus**.
- Describes that, the mass of one atom is the summation of the number of proton and the number of neutrons. A= p + n
- **NB**: the mass of an atom is occupying by the nucleus whereas the large space of the atom is occupying by electrons.

1.6.1. Quantum Model of Atom

- Bohr's theory worked well for hydrogen atom (one electron).
- Complications such as elliptical rather than circular orbits were introduced in an attempt to fit the data to Bohr’s theory.
- The Bohr Atomic Theory and its modifications that forced the theorists to work hard to explain the spectroscopists’ observations.
- In spite of their efforts, the Bohr Atomic Theory eventually proved unsatisfactory; the **energy levels are valid only for the hydrogen atom.**
- An important characteristic of the electron, its wave nature, still needed to be considered.
- According to the **de Broglie equation**, proposed in the 1920s, all moving particles have wave properties described by the equation

$$\lambda = \frac{h}{mv}$$

- where λ=wavelength of the particle, h = Planck's constant, m = mass of the particle, v = velocity of the particle.
- Particles massive enough to be visible have very short wavelengths, too small to be measured.
- Electrons, on the other hand, have wave properties because of their very small mass.

- Electrons moving in circles around the nucleus (in Bohr's Atomic theory), can be thought of as forming standing waves that can be described by the de Broglie equation.
- However, we no longer believe that it is possible to describe the motion of an electron in an atom so precisely.
- This is a consequence of another fundamental principle of modern physics,

1.6.2. The Heisenberg's Principle

Heisenberg formulated what is known as the Heisenberg uncertainty principle, which states that it is impossible to know simultaneously both the momentum and the position of a particle with certainty. Mathematically,

- **Heisenberg's uncertainty principle**, which states that there is a relationship between uncertainties in the **location** and **momentum** of an electron moving in the x direction:

$$\Delta x \Delta p_x \geq \frac{h}{4\pi}$$

Where:

- Δx= uncertainty in the position of the electron
- Δp= uncertainty in the momentum of the electron.

- Working with Heisenberg's Principle, Schrödinger developed a compromise which calculates both the **energy of an electron** and **the probability of finding** an electron at any point in the molecule.

1.6.3. Quantum Numbers

An atomic orbital is specified first by three quantum numbers that are associated respectively, with the orbital's size (*energy*), shape, orientation and, later, independent of these three quantum numbers, the electron spins. The first three sets of quantum numbers have a hierarchical relationship: the size-related number limits the shape related number, the shape-related number in turn limits the orientation-related number.

Three among the four quantum numbers characterize the orbitals in the atom. That is, they describe the orbital or the space the electron is supposed to occupy. The fourth quantum number is used to describe the spin of the electrons that occupy the orbitals.

- The four quantum numbers are:
- 1. The principal quantum number (n) is a positive integer having values n = 1, 2, 3, ...
- It gives the following information:
- (*i*) Relative size of the orbital or the relative distance of the electron from the nucleus. Size of orbital increases with the increase of principal quantum number n.
- (*ii*) Energy of the orbital. Higher the n value, greater is the energy. For example: when the electron occupies an orbital with n = 1, the hydrogen
- atom is in its ground state and has lower energy than when the electron occupies an orbital with n = 2 (*first excited state*).
- (*iii*) Maximum number of electrons present in any shell (given by the formula $2n^2$).

2. The azimuthal quantum number (l) is also known as angular momentum or subsidiary quantum number. It is an integer having values from 0 to (n – 1). For an orbital with n = 1, l can have a value only of 0. For orbitals with n = 2, l can have a value of 0 or 1; for those with n = 3, l can be 0, 1 or 2; etc. So, the number of possible l values equals the value of n. *For a given value of n, the maximum possible value of l is (n – 1).* The azimuthal quantum number gives the following information: Number of subshell present within any shell.

(*ii*) It describes the shape of the orbital and is sometimes also called the orbital-shape quantum number.

3. The magnetic quantum number (ml) is also known as the orbital-orientation quantum number. It is an integer having values from –l through 0 to +l. The possible values of an orbital's magnetic quantum number are set by its angular momentum quantum number (*that is, l determines ml)*. An orbital with l = 0 can have only ml = 0. However an orbital with l = 1, can have ml value of –1, 0, or + 1; thus there are three possible orbitals with l = 1 each with its own spatial orientation. *The number of possible ml values or orbitals for a given l value is ($2l$ + 1). It prescribes the orientation* of the orbital in the three-dimensional space about the nucleus.

4. The electron spin quantum number (*ms*) has only two possible values, +½ (*represented by the arrow*, ↑) and – ½ (represented by the arrow ↓). The name electron spin quantum suggests that electrons have a spinning motion. However, there is no way to attach a precise physical reality to electron spin. The quantum numbers specify the energy states of the atom.

• The atom's energy levels or shells are given by the *n* value.

• The atom's sublevels or subshells are given by the *n* and *l* values. Each level contains sublevels that designate the shape of the orbital.

• The atom's orbitals are specified by the *n*, *l* and *ml* values. Thus, the three quantum numbers that describe an orbital express its size (energy), shape and spatial orientation. Each sublevel is designated by a letter:

l = 0, is an *s* sublevel

l = 1, is a *p* sublevel

l = 2, is a *d* sublevel

l = 3, is a *f* sublevel

The letters *s*, *p*, *d*, and *f* are derived from the names of spectroscopic lines: *s*, sharp; *p*, principal; *d*, diffuse; and *f*, fundamental. Sublevels are named by joining the *n* value and the letter designation. For example, the sublevel (subshell) with *n* = 2, *l* = 0 is called the 2*s* sublevel; the only orbital in this sublevel has *n* = 2, *l* = 0 and *ml* = 0. A sublevel with *n* = 3, *l* = 1, is a 3*p* sublevel. It has three possible orbitals: one with *n* = 3, *l* = 1 and *ml* = –1 ; another with *n* = 3, *l* = 1 and *ml* = 0 and the third *n* = 3, *l* = 1, and *ml* = +1.

For a given principal quantum number, *n*, the total number of orbitals is determined as:

Number of orbitals = n^2 in a shell.

Similarly, the number of orbitals in each subshell is determined as:

➢ Number of orbitals in a subshell = 2*l*+1.

Example 5

1. What values of the angular momentum quantum number (*l*) and magnetic quantum number (*ml*) are allowed for a principal quantum number (*n*) of 3? How many orbitals are allowed for *n* = 3?

2. Give the name, magnetic quantum numbers, and numbers of orbitals for each sublevel with the following quantum numbers:

a. $n = 3, l = 2$ c. $n = 5, l = 1$

b. $n = 2, l = 0$ d. $n = 4, l = 3$

3. What is wrong with each of the following quantum number designations and/or sublevel names?

	n	l	m_l	Name
a	1	2	0	1*p*
b	4	3	+1	4*d*
c	3	1	-2	3*p*

Exercise 2

1. Give the sublevel notation for each of the following sets of quantum numbers.

a. $n = 3, l = 2$ c. $n = 4, l = 1$

b. $n = 2, l = 0$ d. $n = 4, l = 3$

2. Indicate whether each of the following is a permissible set of quantum numbers. If the set is not permissible, state why it is not.

a. $n = 3, l = 1, ml = +2$ b. $n = 4, l = 3, ml = –3$ c. $n = 3, l = 2, ml = –2$

d. $n = 0, l = 0, ml = 0$ e. $n = 3, l = 3, ml = –3$

3. Consider the electronic configuration of an atom:

a. What are the *n*, *l* and *ml* quantum numbers corresponding to the 3*s* orbital?

b. List all the possible quantum number values for an orbital in the 5*f* sub shell.

c. In which specific subshell will an electron be present if the quantum numbers $n = 3$, $l = 1$, and $ml = –1$?

4. Which of the quantum numbers relates to the electron only? Which relate (*s*) to the orbital?

1.7. The electromagnetic radiation and atomic spectra

1.7.1. Electromagnetic radiation

In 1873, James Clerk Maxwell proposed that light consists of electromagnetic waves. According to his theory, an electromagnetic wave has an electric field component and a magnetic field component. Further, his theory accurately describes how energy, in the

form of radiation, propagates through space as electric and magnetic fields. Electromagnetic radiation is the emission and transmission of energy in the form of electromagnetic waves. The wave properties of electromagnetic radiation are described by two interdependent variables, frequency and wavelength. Wavelength (λ, *Greek lambda*) is the distance between any point on a wave and the corresponding point on the next wave; that is, the distance the wave travels during one cycle.

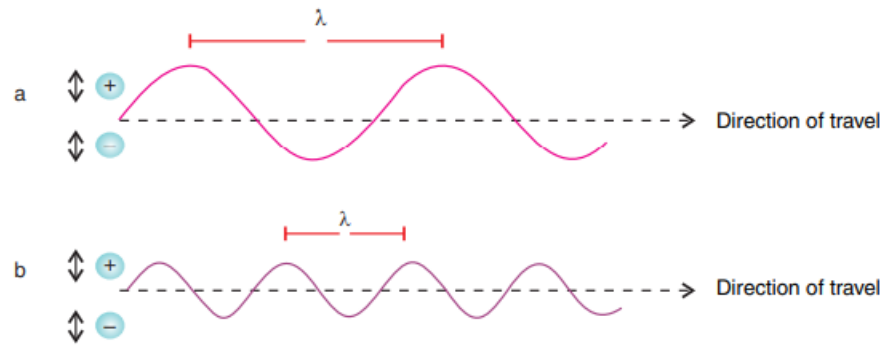


Figure 5. Electromagnetic wave

In Figure 5, two waves with different wave lengths (λ) and thus different frequencies (ν) are shown. Wavelength is commonly expressed in meters, but since chemists often deal with very short wavelengths the nanometre, picometer and the angstrom are also used. Frequency (ν Greek nu) is the number of cycles that pass a given point in space per second, expressed in units of s^{-1} or hertz (Hz). The speed of the electromagnetic wave (light), *c* (distance travelled per unit time, in meters per second), is the product of its frequency (*cycles per second*) and itswavelength (*metres per cycle*),

$$c_0 = \nu \times \lambda$$

In vacuum, light travels at a speed of 2.99792458×10^8 m s^{-1} (3.00×10^8 m s^{-1} to three significant figures).

The speed of an electromagnetic wave depends on the nature of the medium through which the wave is travelling. The speed of an electromagnetic wave in medium (*c*) is the product of its wavelength and its frequency.

$$c = \lambda \times \nu$$

Another characteristic of a wave is its amplitude, the height of the crest (or depth of the trough) of the wave. The amplitude of an electromagnetic wave is a measure of the

strength of its electric and magnetic fields. Thus, amplitude is related to the intensity of the radiation, which we perceive as brightness in the case of visible light.

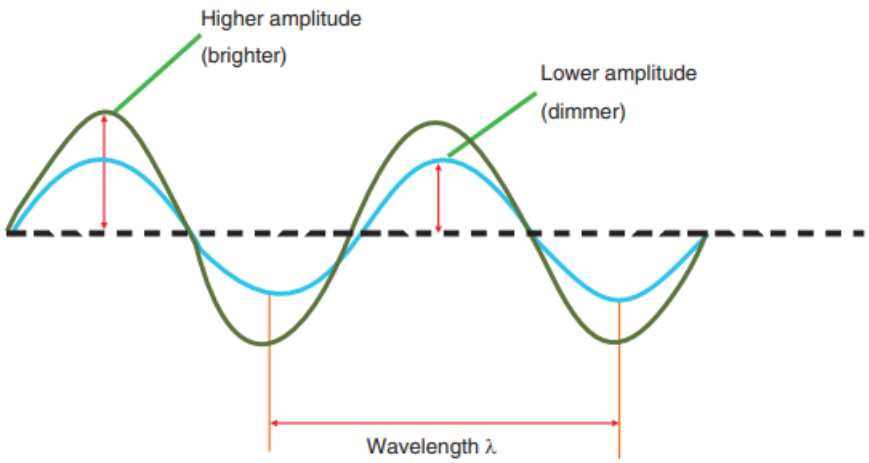


Figure 6. Amplitude (intensity) of waves.

Light of a particular shade of red, for instance, always has the same frequency and wavelength, but it can be dim (*low amplitude*) or bright (*high amplitude*) Figure 6. Visible light occupies a small portion of the continuum of radiant energy which is known as the electromagnetic spectrum (Figure 7). The electromagnetic waves in the different spectral region travel at the same speed but differ in frequency and wavelength.

The long wavelength, low-frequency portion of the spectrum comprises the microwave and radio wave regions. The infrared (IR) region overlaps the microwave region on one end and the visible region on the other.

We perceive different wave lengths (*or frequencies*) of visible light as different colours, from red (λ= 750 nm) to violet (λ= 400 nm). Light of a single wavelength is called monochromatic (*Greek* "*one colour*"), whereas light of many wavelengths is polychromatic (*Greek* "*many colours*"). White light is polychromatic.

The region adjacent to visible light on the short-wavelength end consists of ultraviolet (UV) radiation. Still shorter wavelengths (*higher frequencies*) make up the X-ray and gamma ray (γ-ray) regions.

Thus, a TV signal, Infrared (IR) light, and a gamma ray emitted by a radioactive element differ principally in frequency and wavelength.

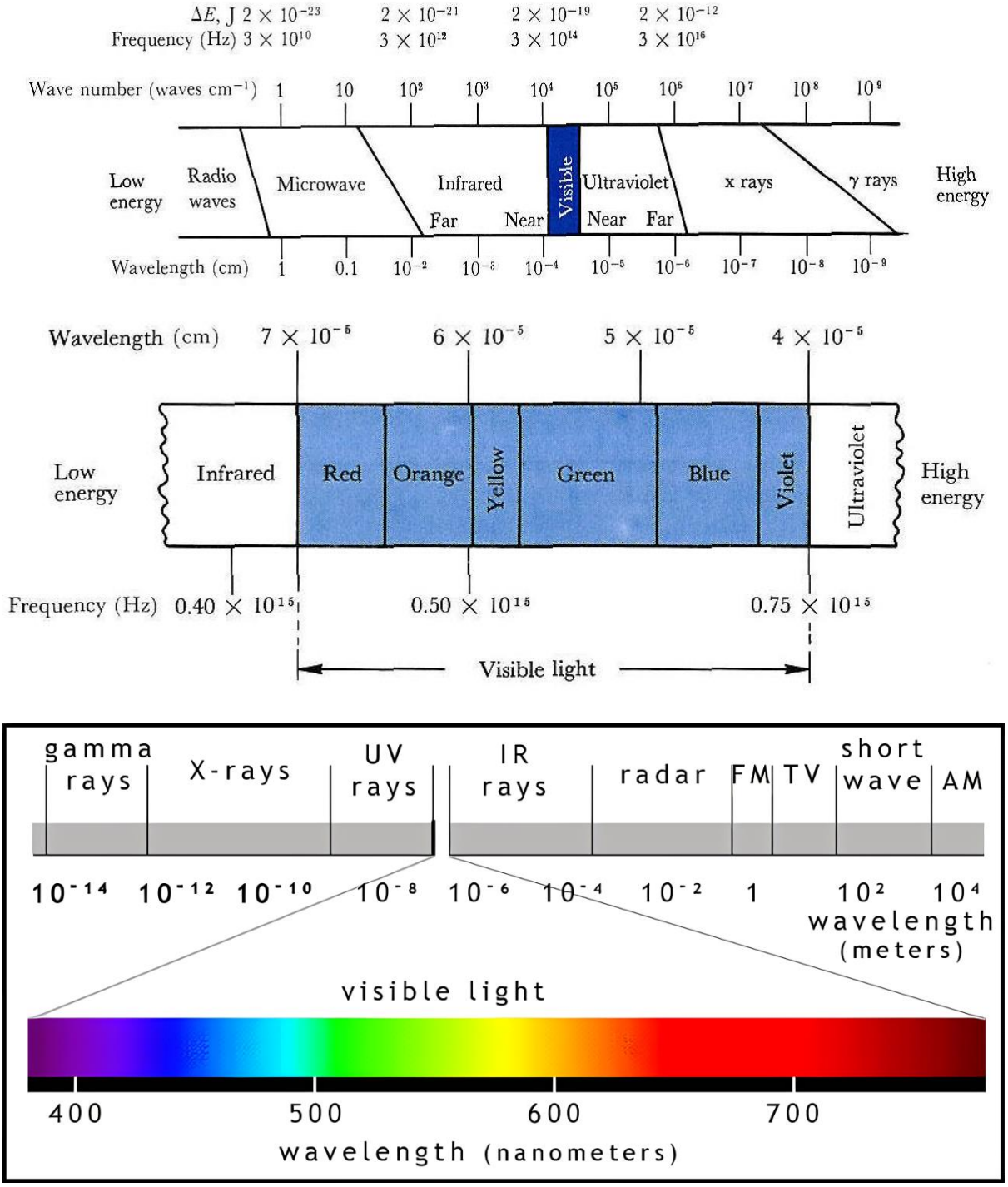


Figure 7. Regions of the electromagnetic spectrum.

These wave and particle nature of light is linked by energy since both particle and wave have energy.

- **E=hv** , the relationship between energy and frequency
- **E= hc/λ,** the relationship between energy and wavelength

- **E= hvc,** the relationship between energy and wave number

The wavelength(λ): is the distance between any two adjacent identical points of the wave.

The frequency (v) is the number of wave crests passing a given point per unit time; and is usually expressed in cycles per second or, more commonly, simply as 1/s with "cycles" understood. It is the number of cycles or oscillations per time.

Wave number: is the reciprocal of wavelength.

Period (T): the time required to complete one complete cycle.

Black body: is a body which absorbs all radiate energy from the sun.

Photon: is a packet of light energy which carries hv amount of quantized energy.

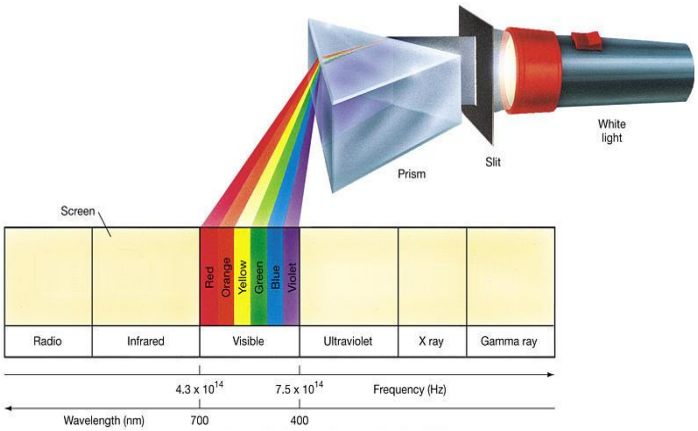
Quantized energy: the motion of the electron is not free. The electron is bound to the atom by the attractive force of the nucleus and consequently quantum mechanics predicts that the total energy of the electron is quantized. White light is a combination of light of many different wavelengths.

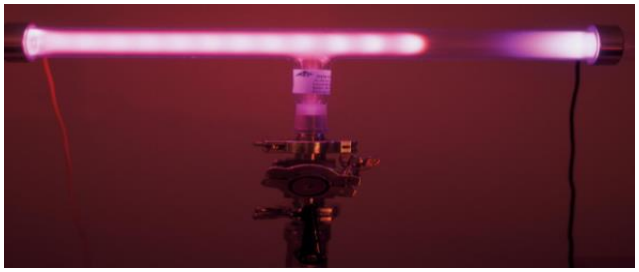
When passed through a prism, it is spread into its constituent wavelengths, resulting in a **band spectrum**.

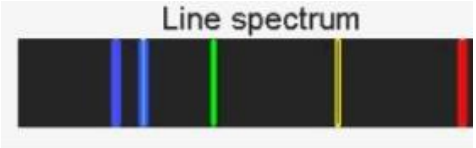
A band spectrum resembles a rainbow and contains many different wavelengths of light.

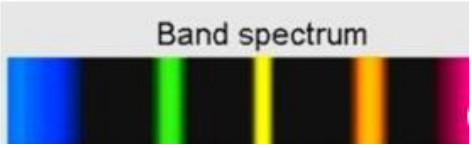
When light from a gas discharge tube is passed through a prism, the result is a **line spectrum**.

In contrast to a band spectrum, a line spectrum contains only certain discreet wavelengths of light.









Example 7. The yellow light given off by a sodium lamp has a wavelength of 589 nm. What is the frequency of this radiation? 2. A dental hygienist uses X-ray (λ = 1.00 Å) to take a series of dental radiographs while the patient listens to an FM radio station (λ = 325 cm) and looks out the window at the blue sky (λ = 473 nm). What is the frequency (in s–1) of the electromagnetic radiation for each source?

Solution:

1. Rearranging Equation 2.1, and ν = co/λ. We insert the value for c and ? and then convert nm to m. This gives us

$$\nu = \frac{3.00\times10^{8}\,\text{m/s}}{589\,\text{nm}}\times\frac{10^{9}\,\text{nm}}{1\,\text{m}} = 5.09\times10^{14}\,\text{s}^{-1}$$

2. Because we are provided with the wavelengths, we can find the frequencies from Equation 2.1. Since co has units of m s–1, we first convert the entire wavelength to metres.

For X-ray

$$\lambda = 1.00\ \cancel{\text{Å}} \times \frac{10^{-10}\,\text{m}}{1\ \cancel{\text{Å}}} = 1.00 \times 10^{-10}\ \text{m}$$

$$\lambda = c_o/\lambda = \frac{3.00 \times 10^{8}\,\text{m/s}}{1.00 \times 10^{-10}\,\text{m}} = 3.00 \times 10^{18}\ \text{s}^{-1}$$

For the radio station, $\lambda = 325\ \text{cm} \times \frac{1\ \text{m}}{100\ \text{cm}} = 3.25\ \text{m}$

$$\nu = \frac{3.00 \times 10^{8}\,\text{m/s}}{3.25\,\text{m}} = 9.23 \times 10^{7}\ \text{s}^{-1}$$

For the blue sky, $\lambda = 473\ \text{nm} \times \frac{10^{-9}\,\text{m}}{1\ \text{nm}} = 4.37 \times 10^{-7}\ \text{m}$

$$\nu = \frac{3.00 \times 10^{8}\ \text{m/s}}{4.73 \times 10^{-7}\,\text{m}} = 6.34 \times 10^{14}\ \text{s}^{-1}$$

Exercise 4. Some diamonds appear yellow because they contain nitrogenous compounds that absorb purple light of frequency 7.23×1014 s^{-1}. Calculate the wavelength (in nm) of the absorbed light. 2. The FM station broadcasts traditional music at 102 MHz on your radio. Units for FM frequencies are given in megahertz (MHz). Find the wavelength of these radio waves in meters (m), nanometers (nm), and angstrom (Å).

1.8. Electronic Configuration and Periodic Table

Electron configuration is the way of filling\distribution of electrons among the given orbitals. In writing electronic configurations or electron filling of orbitals, we follow the **Aufbau's principle, Hund's rule, and the Pauli Exclusion Principle.** These are:

A.The Aufbau's Principle (building up principle): explains the order of filling electrons in various orbitals of an atom. Filling begins with the orbitals in the lowest energy, or most stable, shells and Thus, the 1s orbital fills first, then the 2s, followed by the 2p and the 3s orbitals.

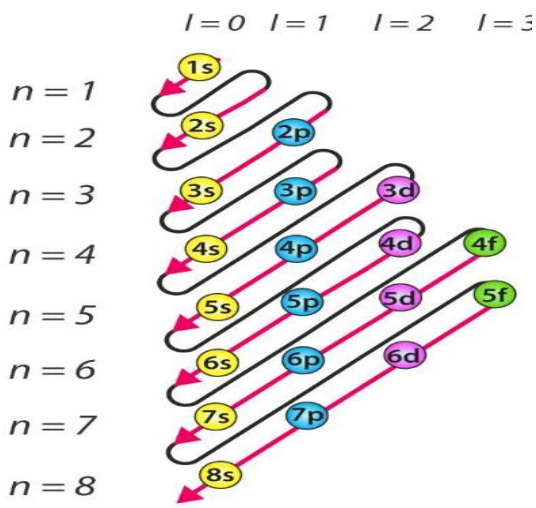
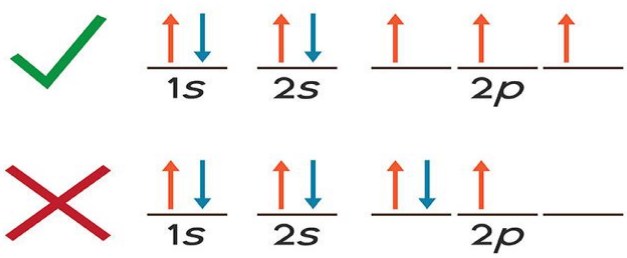


Figure 8. Increasing order of filling orbitals.

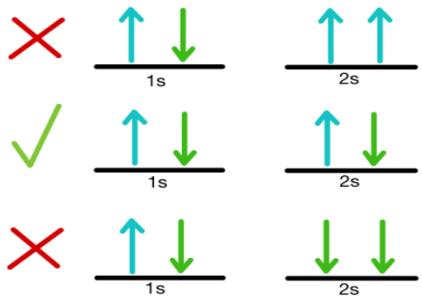
B. Hund's rule: It's Principle: Equal energy orbitals (degenerate orbitals) are each occupied by a single electron before the second electrons of opposite spin enters the orbital. In other words, each of the three 2*p* orbitals (2*px*, 2*py* and 2*pz*) will hold a single electron before any of them receives a second electron. It states that each degenerate orbital, (e.g.$2p_x$, $2p_y$, and $2p_z$) must first receive one electron before any of the orbitals can receive a second electron.



C. Pauli Exclusion Principle: It's Principle. No two electrons can have the same four quantum numbers. *i.e*. they must differ in at least one of the four quantum numbers.

- each orbital contains a maximum of two electrons.

- These two electrons must have opposite values for the spin, which is generally indicated by showing the electrons as arrows pointing up (↑) or down (↓).



Excise 5. write the ground electron configuration of based on example given

Atomic Number	Element	Orbital diagram	Full electron configuration	Condensed electron configuration
11	Na	3s ↑ 3p	$[1s^2\ 2s^2\ 2p^6\ 3s^1]$	$[Ne]\ 3s^1$
12	Mg	↑↓	$[1s^2\ 2s^2\ 2p^6\ 3s^2]$	$[Ne]\ 3s^2$
13	Al			
14	Si			
15	P			
16	S			

Atomic Number	Element	Orbital Diagram	Electron configuration (ground state)	Condensed Electron configuration
21	Sc			
22	Ti			
23	V			
24	Cr			
25	Mn			
26	Fe			
27	Co			
28	Ni			
29	Cu			

n	1	2	3	4
l	0	0, 1	0, 1, 2	0, 1, 2, 3
Subshell designation	*s*	*s*, *p*	*s*, *p*, *d*	*s*, *p*, *d*, *f*
Orbital in subshell	1	1, 3	1, 3, 5	1, 3, 5, 7
Subshell capacity	2	2, 6	2, 6, 10	2, 6, 10, 14
Principal shell capacity	2	8	18	32

	Expected	**Observed**
Cr ($Z = 24$)	[Ar] $4s^2 3d^4$	[Ar] $4s^1 3d^5$
Cu ($Z = 29$)	[Ar] $4s^2 3d^9$	[Ar] $4s^1 3d^{10}$

The reason for these exceptions to the aufbau principle is not completely understood, but it seems that the half-filled 3*d* subshell of chromium ($3d^5$) and the fully filled 3d subshell of copper ($3d^{10}$) lends a special stability to the electron configurations. Apparently, having a half-filled 4s subshell and a half-filled 3*d* subshell gives a lower energy state for a Cr atom than having a filled 4s subshell.

Exercise 6

1. Write the electron configuration for the Co^{3+}, Cl^- , Al^+, Cr, As^-, and Cu.
2. Write the electron configuration and the orbital diagram of the first excited state of sodium. (Hint: The outermost electron is excited).
3. What is the electron capacity of the *n*th energy level? What is the capacity of the fourth energy level?

1.9. Periodic table and Periodic Properties of Elements

The periodic law (**Modern periodic table)** tells us that if we arrange the elements in order of increasing atomic number, we periodically encounter elements that have similar chemical and physical properties. Elements in a group have similar chemical and physical properties, and those within a period have properties that change progressively across the table.

1.9.1. Classification of the Elements

Representative or main group elements: These consist of all *s*- and *p*-block elements.

The chemical properties of the representative elements are determined by the number of valence electrons in their atoms.

Transition elements: These are *d*-block elements. There are four series of transitional elements, 3*d*, 4*d*, 5*d* and 6*d* depending on the energy levels of *d*-orbitals.

Inner transition elements: These are the *f*-block elements. There are two series of *f*-block elements, 4*f* and 5*f* series called lanthanides and actinides, respectively. The periodic table is unable to include the inner transition elements in its main frame. They have been allotted the same single place in the periodic table though their electronic configurations are not identical. Besides, the variation in their properties is not much.

The general properties of metals and nonmetals are distinct. Physical and chemical properties that distinguish metals from nonmetals are summarized in Table:

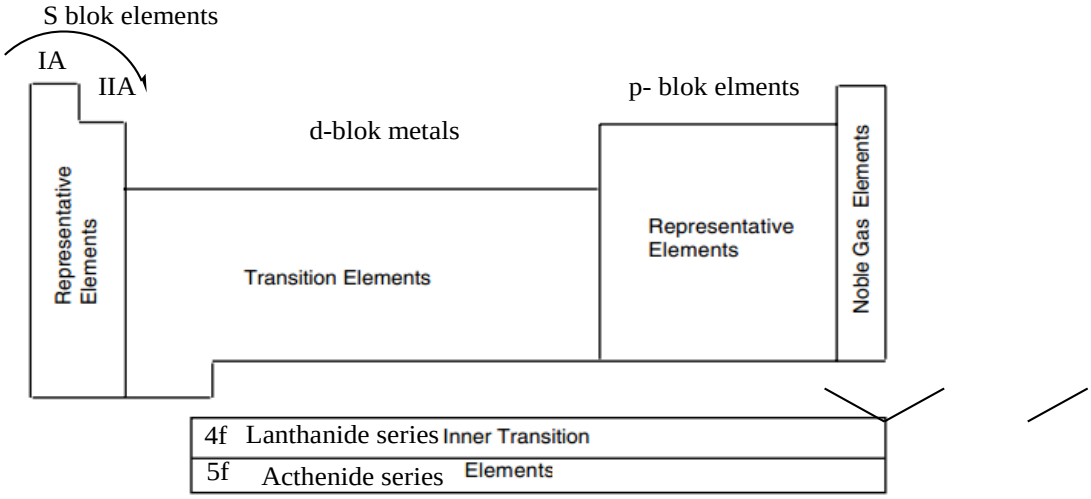


Figure 9. the general periodic presentation

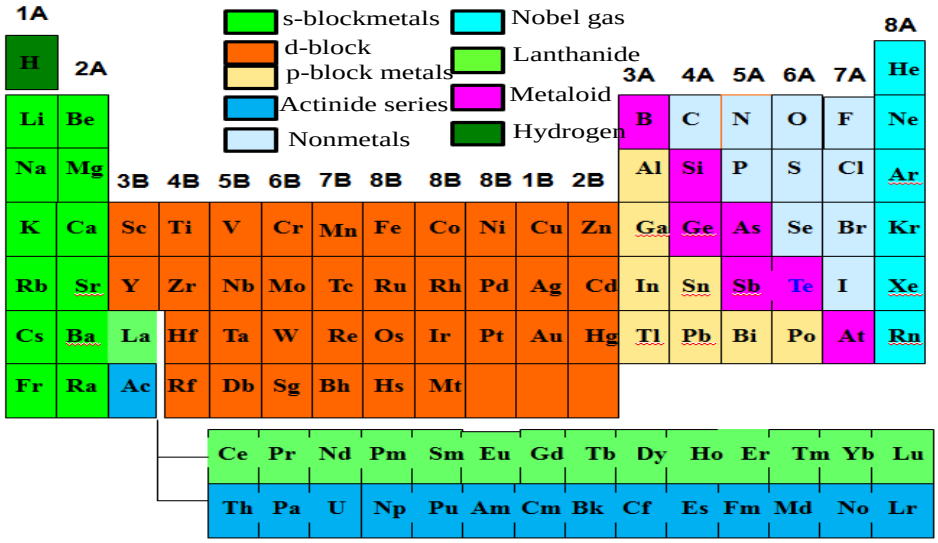


Figure 10. the modern periodic table

The vertical columns are referred to as **groups** or **families**, and the horizontal rows are called **periods**. Elements in a group have similar chemical and physical properties, and those within a period have properties that change progressively across the table. Several groups of elements have common names that are used so frequently they should be learned. The Group IA elements, except H, are referred to as **alkali metals**, and the Group IIA elements are called the **alkaline earth metals**. The Group VIIA elements are called **halogens**, which means "**salt formers**," and the Group VIIIA elements are called **noble(or rare) gases**.

1.9.2. Periodic Variation in Physical Properties

a) **Atomic Radii**

As we move across the periodic table, atoms become smaller due to increasing effective nuclear charges. As we move from left to right across a period in the periodic table, atomic radii of representative elements decrease as a proton is added to the nucleus and an electron is added to a particular shell.

The effective nuclear charge, Z_{eff} experienced by an electron in an outer shell is less than the actual nuclear charge, Z. This is because the attraction of outer-shell electrons by the nucleus is partly counterbalanced by the repulsion of these outer-shell electrons by electrons in inner shells. This concept of a screening, or shielding, effect helps us understand many periodic trends in atomic properties. Consider an atom of lithium; it has two electrons in a filled shell, $1s^2$, and one electron in the 2s orbital, $2s^{1.}$ The electron in the 2s orbital is fairly effectively screened from the nucleus by the two electrons in the filled 1s orbital, so the 2s electron does not "feel" the full 3 charge of the nucleus. The effective nuclear charge, Z_{eff}, experienced by the electron in the 2s orbital:

$$Z_{eff} = Z - \sigma.$$

Example;11Na, Z_{eff} =11-10 = +**1,** 12Mg, Z_{eff} =12-10**= +2,** 13Al, Z_{eff} =13-10**= +3**

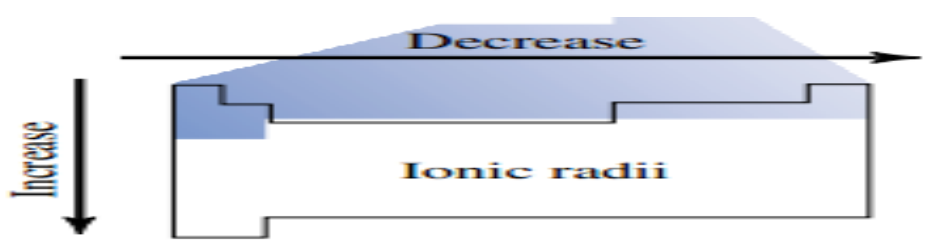
b) **Ionic Radii**

Ionic Radii of metals always greater than the corresponding cations because they lost electrons from shells which reduced electron-electron repulsions. Example;Mg (1.6 Å) > Mg^{2+}(0.85 Å). Simple negatively charged ions (anions) are always larger than the neutral atoms from which they are formed because there is addition of extra electron to the shell which increased electron. Example: Cl^- (1.67 Å) > Cl (1.1 Å). Both sizes of cations and anions decrease from left to right across a period whereas both cation and anion sizes increase going down a group. Within an **isoelectronic series**, radii decrease with increasing atomic number because of increasing nuclear charge.

Isoelectronic ions: ions with the same number of core electrons. Na^+, Mg^{+2}, Al^{+3}, F^-, O^{-2}, N^{-3} all contain 10 electrons; all have the same electron configuration as Ne but, in terms of size,

$N^{-3}>O^{-2}>F^->Na^+>Mg^{+2}>Al^{+3}$; the ion with the greater number of protons in an isoelectronic series will be the smallest due to the greater nuclear charge pulling the electrons in closer.

In general,



Arrange the following ions in order of increasing ionic radii: (a) Ca^{2+}, K^+, Al^{3+} **+**, (b) Se^{2-}, Br^-, Te^{2-} **Answers: a) Al^{3+}< Ca^{2+} <K , b)Br^-< Se^{2-} < Te^{2-}**

c) **Ionization Energy**

Ionization (potential) Energy: the minimum amount of energy required to remove an electron from ground state (loosely bounded) atom in gaseous state. It measures how outermost electrons held by the nucleus.

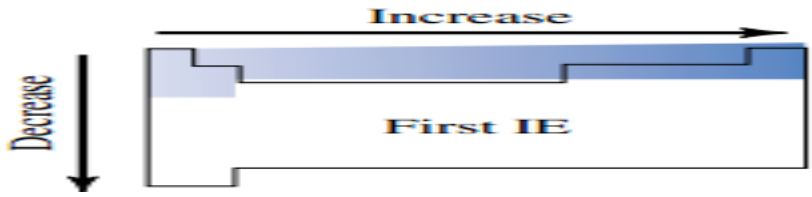
$$X\,(g) + IE \rightarrow X^+\,(g) + e^-$$

The first ionization energy (IE_1), also called first ionization potential, is the minimum amount of energy required to remove the most loosely bound electron from an isolated

gaseous atom to form an ion with a 1^+charge. Elements with low ionization energies (IE) lose electrons easily to form cations.

General trends in first ionization energies of A group elements with position in the periodic table. Exceptions occur at Groups IIIA and VIA. The first ionization energies for the Group IIIA elements (B, Al, Ga, In, Tl) are exceptions to the general horizontal trends. They are lower than those of the IIA elements in the same periods because the IIIA elements have only a single electron in their outermost p orbitals. Less energy is required to remove the first p electron than the second s electron from the outermost shell, because the p orbital is at a higher energy (less stable) than an s orbital within the same shell (n value) Effective nuclear charge, Z_{eff}, increases going from left to right across a period. The increase in effective nuclear charge causes the outermost electrons to be held more tightly, making them harder to remove. The first ionization energies of the Group IIA elements (Be, Mg, Ca, Sr, Ba) are significantly higher than those of the Group IA elements in the same periods. This is because the Group IIA elements have higher Z_{eff} values and smaller atomic radii. Thus, their outermost electrons are held more tightly than those of the neighboring IA metals. It is harder to remove an electron from a pair in the filled outermost s orbitals of the Group IIA elements than to remove the single electron from the half-filled outermost s orbitals of the Group IA elements. The general left-to-right increase in IE1for each period is interrupted by a dip between Groups VA (N, P, As, Sb, Bi) and VIA elements (O, S, Se, Te, Po). Presumably, this behavior is because the fourth np electron in the Group VIA elements is paired with another electron in the same orbital, so it experiences greater repulsion than it would in an orbital by itself. This increased repulsion apparently outweighs the increase in Z_{eff}, so the fourth np electron in an outer shell (Group VIA elements) is somewhat easier to remove (lower ionization energy) than is the third np electron in an outer shell (Group VA elements). The first ionization energies therefore generally increase from left to right across the periodic table. The order of ionization energies decreased as 3rd > 2nd >1st because it is too difficult to remove an electron from cation specie.

In general ionization energy increase across the period since Z_{eff} increase by one; the size of atoms decrease which results the outermost electrons bound tightly with the nucleus.



d) **Electron Affinity (EA):**

The electron affinity (EA) of an element may be defined as the amount of energy released when an electron is added to an isolated gaseous atom to form a negative charge.

$$X\,(g) + e^- \rightarrow X^-(g) + EA$$

This process can be either endothermic or exothermic, depending on the element. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive.

Electron Affinity (EA): Energy is always required to bring a negative charge (electron) closer to another negative charge (anion). So the addition of a second electron to anion to form an ion with a -2 charge is always endothermic. Thus, electron affinities of anions are always positive.

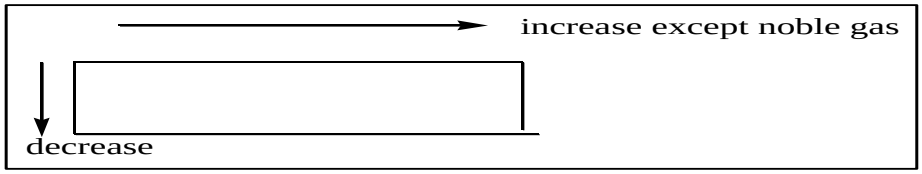
$$X^-(g) + e^- \rightarrow X^{2-}(g) + EA$$

Most elements have no affinity for an additional electron and thus have an electron affinity (EA) equal to zero. We can represent the electron affinities of helium and chlorine as

$$He(g) + e^- \not\longrightarrow He^-(g) \qquad EA = 0\ kJ/mol$$

$$Cl(g) + e^- \longrightarrow Cl^-(g) + 349\ kJ \qquad EA = -349\ kJ/mol$$

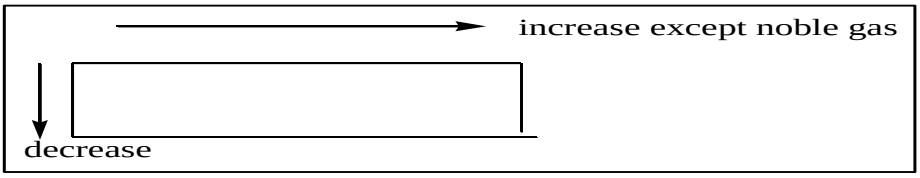
Halogens have ns^2-np^5 electron cofiguration which are most electron affinities to form noble gas cofiguration.



e) **Electro-negativity (EN):**

The electro-negativity (EN) of an element is a measure of the relative tendency of an atom to attract electrons towards it when it is chemically combined with another atom. Elements with high electro-negativities (nonmetals) often gain electrons to form anions. Example; F (4.0) > O (3.5) > Cl=N (3.0). Elements with low electro-negativities (metals) often lose electron to form cations.

For the representative elements, electro-negativities usually increase from left to right across periods **except noble gas** and decrease from top to bottom within groups



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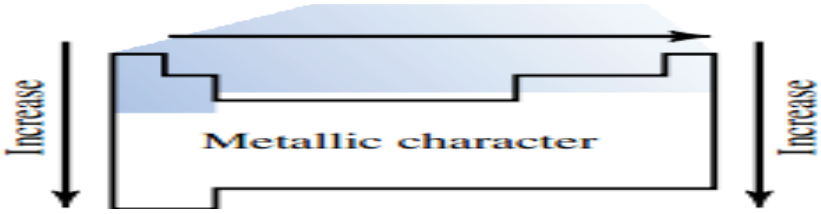
Arrange the following elements in order of increasing electro-negativity? B, Na, F, O

<u>answer,</u> **Na< B< O< F**

f) **Metallic character**:

Metallic character increases from top to bottom and decreases from left to right with respect to position in the periodic table. Nonmetallic character decreases from top to bottom and increases from left to right in the periodic table.



General trends in metallic character of A group elements with position in the periodic table.

In modern periodic table, elements are arranged as the function of their atomic number. Main group elements are elements contain s-block metals and p-block metal, metalloid and nonmetals. This periodic table constructed with the columns (family) and the horizontal row (periods). Periodicity is the variation of physical properties in periodic table such as atomic size, electronegativity, ionization energy, metallic character and others as summarized below.

Advantages of Periodic Classification of the Elements

Some of the advantages of periodic classification of elements are: 1. The classification of elements is based on the atomic number, which is a fundamental property of an element. 2. The reason for placing isotopes at one place is justified as the classification is on the basis of atomic number. 3. It explains the periodicity of the properties of the elements and relates them to their electronic configurations. 4. The position of the elements that were misfits on the basis of mass number (anomalous pairs like argon and potassium) could be justified on the basis of atomic number. 5. The lanthanides and actinides are placed separately at the bottom of the periodic table. 6. The table is simple, systematic and easy way for remembering the properties of various elements as it is based on the electronic configuration.

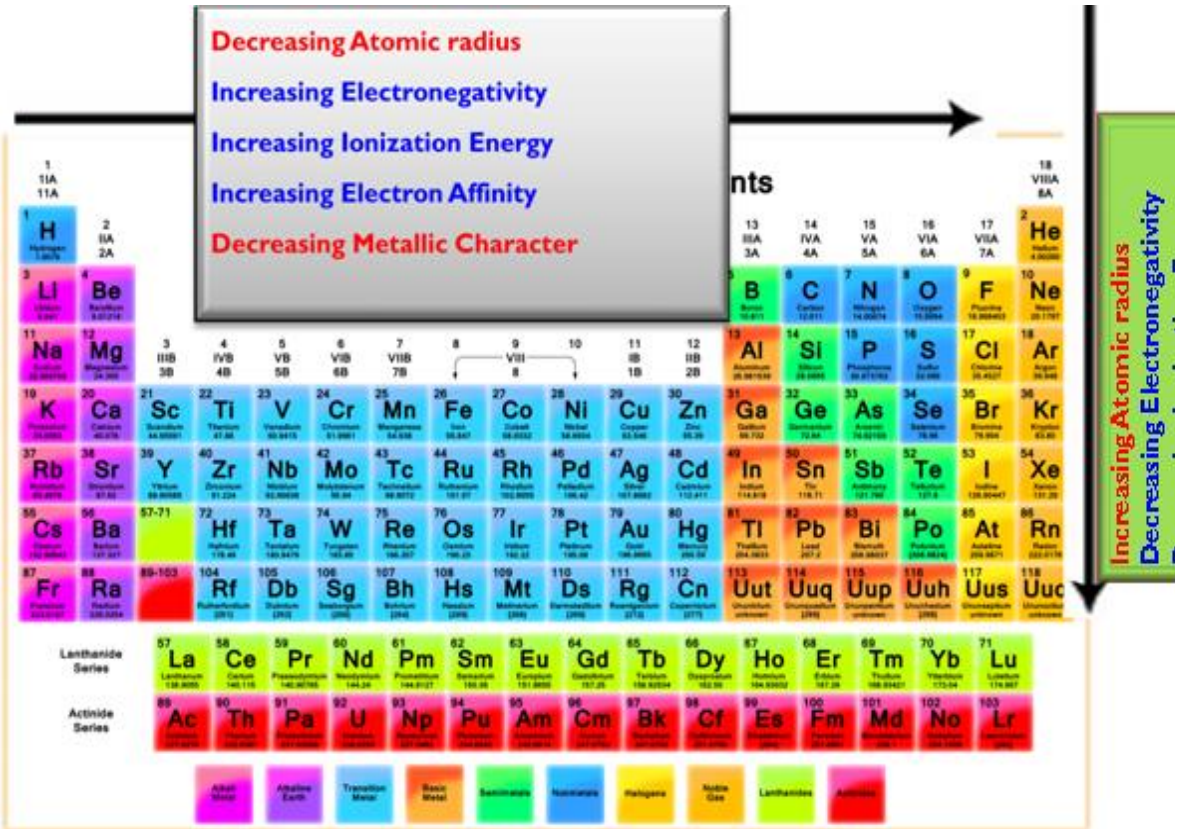
Unit summary

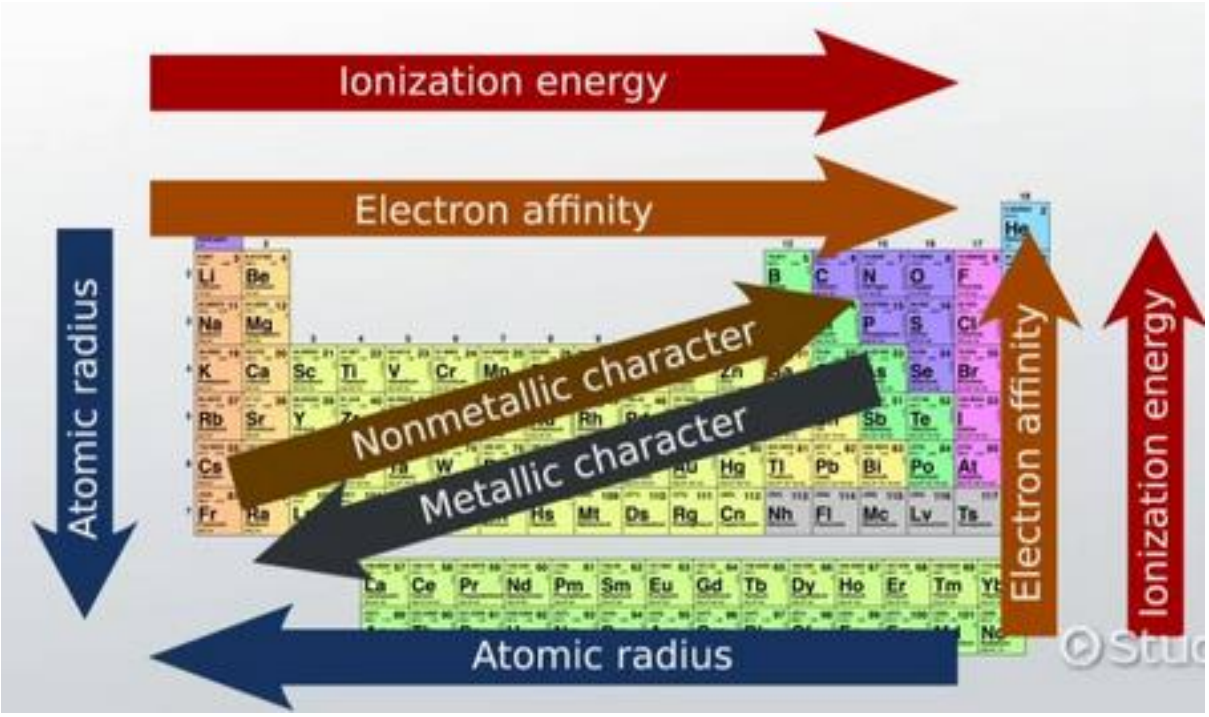
- Cathode rays (electrons) are produced when electricity passes through evacuated tubes. X-rays form when cathode rays strike matter.
- Radioactivity is the emission of radiation by unstable nuclei, and the most common types of radiations are alpha (α) particles, beta (β) particles and gamma (γ) rays. Alpha particles are helium nuclei; beta particles are electrons; and gamma rays are high frequency electromagnetic radiation similar to X-rays.
- Rutherford's atomic model is that of a very small positively charged nucleus and extra-nuclear electrons. The nucleus consists of protons and neutrons and contains practically all the mass of an atom. Atomic masses and relative abundances of the isotopes of an element can be established by mass spectrometry. The atomic mass of the element is the average of these mass numbers based on their percentage abundances Electromagnetic radiation is the transmission of electric and magnetic

fields as a wave motion. The waves are characterized by their velocity in a medium: $c = \nu\lambda$. A light source that emits an essentially unbroken series of wavelength components has a continuous spectrum. Only a discrete set of wavelength components is present in the emission spectrum of an atom.

- Einstein's explanation of the photoelectric effect views light as packets of energy called photons. The energy of the photon (Eph) is given by the expression $E = h\nu$ where h is Planck's constant.
- Bohr's theory requires the electron in a hydrogen atom to be in one of a discrete set of energy levels. The fall of an electron from a higher to a lower energy level releases a discrete amount of energy as a photon of light with a characteristic frequency.
- Bohr's theory accounts for the observed atomic spectrum of hydrogen atom.
- The electron in a hydrogen atom can be viewed as a matter-wave enveloping the nucleus. The matter-wave is represented by a wave equation, and solutions of the wave equation are wave functions. Each wavefunction is characterized by the value of four quantum numbers: the principal quantum number, n; the angular momentum quantum number l; the magnetic quantum number, ml; and the spin quantum number, ms. Wave functions with acceptable values of the three are called atomic orbitals. An orbital describes a region in an atom that has a high probability of containing an electron or a high electron change density. Orbitals with the same value of n are in the same principal energy level or principal shell. Those with the same value of n and of l are in the same sublevel or subshell. The shapes associated with orbitals depend on the value of l. Thus, the s orbital ($l = 0$) is spherical and the p orbital ($l = 1$) is dumbbell-shaped.
- The n, l and ml quantum numbers define an orbital, but a fourth quantum number is also required to characterize an electron in an orbital - the spin quantum number, ms. This quantum number may have either of two values: +½ or –½.
- The wave mechanical treatment of the hydrogen atom can be extended to multi-electron atoms, but with this essential difference: principal energy levels are (i) lower than those of the hydrogen atom and (ii) split, that is, having different energies for the different subshells.

- Electron configuration refers to the distribution of electrons among orbitals in an atom. Introduced here are the subshell notations (or "s,p,d, f") and the orbital diagram. Key ideas required to write a probable electron configuration are: (i) electrons tend to occupy the lowest energy orbitals available; (ii) no two electrons in an atom can have all four quantum numbers alike; and (iii) where ever possible, electrons occupy orbitals singly rather than in pairs.
- The Aufbau principle describes a hypothetical process of building up one atom from the atom of preceding atomic number. With this principle and the idea cited above, it is possible to predict probable electron configurations for many of the elements. In the Aufbau process, electrons are added to the s or p subshell of highest principal quantum number in the representative or main group elements. In transition elements, electrons go into the d subshell of the second last shell, and in the inner transition elements, into the f subshell of the third last shell.
- Elements with similar valence-shell electron configurations fall in the same group of the periodic table. For A-group elements, the group number corresponds to the number of electrons in the principal shell of highest quantum number. The period number is the same as the highest number of principal shell containing electrons (the outer shell). The division of the periodic table into s, p, d and f blocks greatly assists in the assignment of probable electron configurations.
- Certain atomic properties vary periodically, when atoms are considered in terms of increasing atomic number. The properties and trends considered in this unit are those of atomic radius, ionic radius, ionization energy and electron affinity. Values of these atomic properties strongly influence physical and chemical properties of the elements.





Review questions

Part I: Multiple Choice Type Questions

1. The number of neutrons in an atom of $^{226}_{88}Ra$ is:

   a. 88 b. 82 c. 138 d. 314

2. Which of the following are usually found in the nucleus of an atom?

   a. Protons and neutrons only b. Protons, neutrons and electrons

   c. Neutrons only d. Electrons and neutrons only

3. An atom has an atomic number of 31 and a mass numbers of 70. How many electrons will it have in its valence shell?

   a. 5 b. 4 c. 3 d. 2

4. Which of the following would produce a line spectrum rather than a continuous spectrum?

   a. Sunlight b. Excited hydrogen atom

   c. A normal filament light bulb d. A yellow (*sodium*) street light

5. Among the following, which colour corresponds to light of the highest frequency?

   a. Green b. Red c. Yellow d. Blue

6. Which one of the following is not a valid electronic configuration?

   a. 2, 8, 8, 2 b. 2, 8, 9, 1 c. 2, 6 d. 2, 8, 4

7. Which of the given elements will have the electronic configuration?

   $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$.

   a. Neon atoms b. Chlorine atoms c. Magnesium ion d. Calcium atoms

8. Which of the following elements has the lowest first ionization energy?

   a. Potassium b. Sodium c. Calcium d. Argon

9. How many 3*d* electrons are present in the ground state of chromium atom?

   a. 9 b. 4 c. 6 d. 5

10. The first ionization energy of aluminium is slightly lower than that of magnesium because:

    a. magnesium has a higher nuclear charge

    b. the outer electron in aluminium is in a *p*-orbital not an *s*-orbital

    c. in aluminium the electron is being lost from a doubly filled orbital

    d. the radius of the aluminium atom is greater than that of the magnesium atom

11. Which of the following atoms would have the highest fourth ionization energy?

a. P b. Si c. N d. C

12. How many unpaired electrons are there in the Cr3+ ion?

a. 6 b. 3 c. 1 d. 0

13. Which of the following species would require the highest energy for the removal of one electron?

a. Mg^{2+} b. Na^{+} c. Ne d. F^{-}

14. Which of the following has the lowest electronegativity?

a. Carbon b. Magnesium c. Beryllium d. Boron

15. Which of the following has the smallest radius?

a. Na b. Na^{+} c. Mg d. Mg^{2+}

Part II: Answer the following questions:

16. Identify the following subatomic particles:

17. The number of these in the nucleus is equal to the atomic number.

18. The particle that is gained or lost when ions are formed.

19. The particle that is not found in the nucleus.

20. The particle that has no electrical charge.

21. The particle that has a much lower mass than the others.

22. Calculate the number of protons, neutrons and electrons in the following:

Element	Mass Number	Protons	Neutrons	Electrons
Neon (Z = 10)	20			
Nitrogen (Z = 7)	14			
Gallium (Z = 31)	70			
Nickel (Z = 28)	59			
Iron (Z = 26)	56			

23. Carbon has atomic number 6. It comprises three isotopes, the first with 6 neutrons, the second with 7 neutrons, the third with 8 neutrons.

24. Calculate the mass numbers of the three isotopes and represent them in the form of *x*C*y*

25. Explain what is meant by “isotope”
26. In naturally occurring copper isotopes, $^{63}_{29}Cu$ contributes 69.09% and $^{65}_{29}Cu$, 30.91%. Calculate the relative atomic mass of copper. (Accurate mass determined; $^{63}_{29}Cu$ = 62.9298 m_u, $^{65}_{29}Cu$ = 64.9278 m_u)
27. Two particles X and Y have the following composition: X: 17 protons, 18 neutrons, 17 electrons Y: 17protons, 18 neutrons, 18 electrons
28. What is the relationship between these particles?
29. Will these two particles have similar chemical properties? Explain why?
30. Arrange the following in order of increasing ionization energy: Li, Na, Ne, N, O
31. Explain the following:
32. The first ionization energy of beryllium is greater than that of boron.
33. The first ionization energy of oxygen is less than that of nitrogen.
34. The first ionization energy of lithium is greater than that of sodium.
35. The electron configuration of a particular metal cation M^{3+} is [Ar] $3d^{2}$.
36. Identify the corresponding metal.
37. Write the electron configuration of the metal atom.
38. Arrange the following in order of increasing atomic radius Mg, Cs, Ca, Al, Ba.
39. Explain briefly, why potassium always occurs as a +1 ion in its compounds and calcium as a +2 ion.
40. Arrange the atoms (ions) in each of the following groups in order of increasing size based on their location in the periodic table.

    a. Mg^{2+}, O^{2-}, Na^{+}, F^{-}, Al^{3+}

    b. Ne, N^{3-}, F^{-}, Na^{+}, C^{4-}

    c. F, Be, C, B, Li

    d. K^{+}, S^{2-}, As^{3-}, Cl^{-}, Ca^{2+}
41. Excited sodium atoms emit light with a wavelength of 589 nm. Calculate the:

    a. frequency of the light, and

    b. energy of one of these photons in joules
42. A hydrogen atom is excited to the n = 8 energy level. It emits a photon of light as it falls to the n = 2 energy level. Calculate the:

    a. wavelength of light emitted, and

    b. frequency of the light emitted
43. The electron of a hydrogen atom is in the n = 3 level. What is its energy?

44. Calculate the wavelength of the light emitted when an electron falls from $n = 3$ to the $n = 1$ state in hydrogen atom.

45. The photon emitted by a cyclotron has a velocity of 1.50×10^{3} m s^{-1}. What is the wavelength of this photon? Given that the mass of photon = 1.676×10^{-27} kg and Planck's constant = 6.62×10^{-34} J.s.

46. Write the number and the letter for the orbital that corresponds to the following pairs of n and l quantum numbers:

a. $n = 3$, $l = 1$ b. $n = 4$, $l = 0$ c. $n = 3$, $l = 2$ d. $n = 5$, $l = 3$

47. Write the electron configurations for the following atoms and ions:

a. Fe^{3+} b. V c. Cr^{3+} d. Al^{3+}

48. Identify the transition element (s) from the following:

a. $_{40}Zr$ b. $_{88}Ra$ c. $_{56}Fe$ d. $_{36}Kr$

2. Chemical Bonding and Structure (10 hours)

2.1. Introduction

Octet Rule

You have studied in your earlier classes that noble gases have very stable electron arrangements such as 2; 2, 8; 2, 8, 8 and their outer shells are fully saturated. The first three are shown in Figure 1 and explains why noble gases are so reluctant to form compounds with other elements.

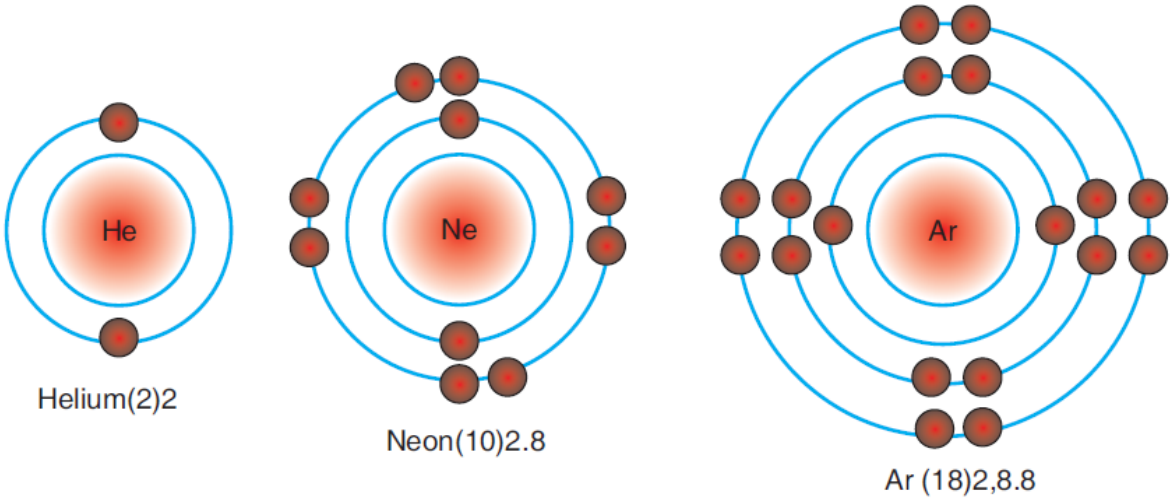


Figure 1. First three noble gases.

The noble gases have very stable electron configuration, as reflected by their high ionization energies, low electron affinity and general lack of reactivity. Because all noble gases (except He) have eight valence electrons, many atoms undergoing reaction also attain eight valence electrons. The ns^2np^6 electron configuration of the valence shell of all noble gas (except Helium) atoms, is commonly called an octet of electrons. The octet rule, a useful generalization that applies to all types of bonding which states that when atoms bond, they lose, gain or share electrons to attain the electronic configuration *ns*2*np*6 of the nearest noble gas. Nearly every main-group monoatomic ion has a filled outer level of electrons (*either two or eight*), the same number as in the nearest noble gas.

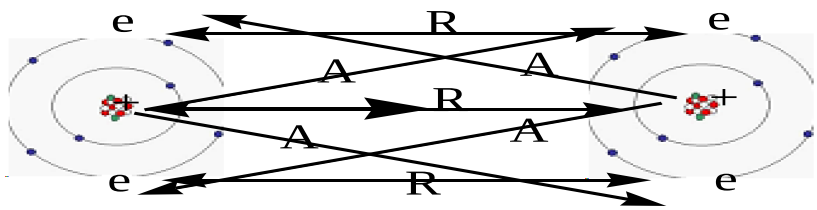
Note! Octet rule states that during the formation of a chemical compound, each atom has an octet (8) electrons in its highest occupied energy level by gaining, losing, or sharing electrons.

Bonding: Bonding is the joining of at least two atoms to form a molecule or compound. The electrons in the valence shell are the active portion of an atom during bonding.

A **chemical bond** is a mutual electrical attraction between the nuclei and valence electrons of different atoms that binds the atoms together.

Why atoms combined to form compounds, clusters, molecules/ polyatomic ions?

- ✓ to attain octet (eight) rules
- ✓ to have lower energy (to be stable)
- ✓ to have net attractive force



Where, A= attraction force, R= repulsion force

Chemical bond is formed when A>R:

Example: H + H→ H_2 (g) but, He + He → no reaction since R>A.

Most atoms are chemically bonded to each other? As independent particles, they are at relatively high potential energy. However, nature favors arrangements in which potential energy is minimized. This means that most atoms are less stable existing by themselves than when they are combined. By bonding with each other, atoms decrease in potential energy, thereby creating more stable arrangements of matter.

HOW DO ATOMS COMBINED TO FORM COMPOUNDS/ POLYATOMIC IONS?

In chemical bonds, atoms are combined to form compounds, clusters, molecules/ polyatomic ions by:

- Transferring /losing of their valence electrons.
- Gaining of extra valence electrons
- Sharing of valence electrons
- Coordinating valence electrons

2.2. TYPES OF CHEMICAL BONDING

When atoms bond, their valence electrons are redistributed in ways that make the atoms more stable. The way in which the electrons are redistributed determines the type of

bonding. There are different types of chemical bonds that results by transfer or sharing of electrons. These are:

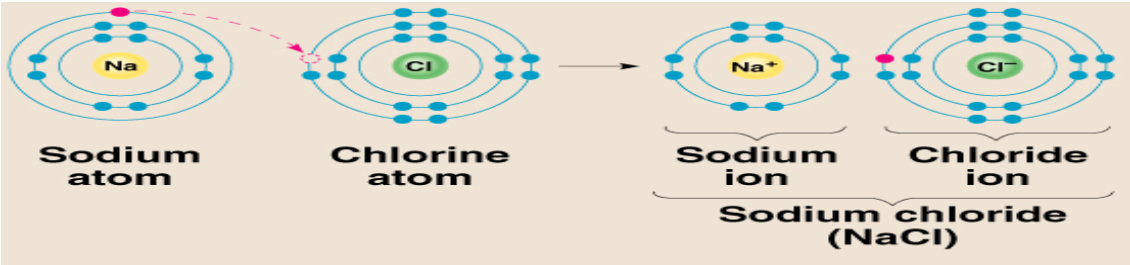
There are three fundamental categories of bonds

- ✓ **Ionic bond =** Electropositive element + electronegative elements
- ✓ Na+Cl → NaCl
- ✓ **Covalent bond =** Electronegative element + electronegative elements
- ✓ F+F → F_2
- ✓ **Metallic bond =** Electropositive element + Electropositive element
- ✓ Li+Li →Li_2
  - Elements can be classified as:
  - Electropositive elements, whose atoms give up one or more electrons
    - Electronegative element which take up electrons

Elements which neither tends to lose or gain electrons

2.2.1. Ionic Bond/Electrovalence bond

Ionic bond is a type of chemical bond that results from the electrostatic force of attraction between two oppositely charged ions. It is formed due to transfer of electrons from one atom (mostly metals) to another (mostly nonmetals) by losing and gaining of electrons. The atom that loses electrons will form a cation and the atom that gains electrons will form an anion. These oppositely charged ions come closer to each other due to electrostatic force of attraction and thus form an ionic bond. In general, an ionic bond is formed between two atoms that contain greater electronegativity difference and it is between a metal atom and a nonmetal atom. Example: NaCl, LiF, $MgCl_2$.



A. **Favorable condition for ionic bond formation**

- Low ionization energy of the metals

- High electro-affinity of the nonmetals
- High lattice energy
- High electro-negativity difference between a metal and a nonmetal atom

Note! Ionic compounds are usually formed when metal cations bond with non-metal anions. The only common exception is ammonium ion which is not a metal, but it forms ionic compounds

2.2.2. Covalent bond:

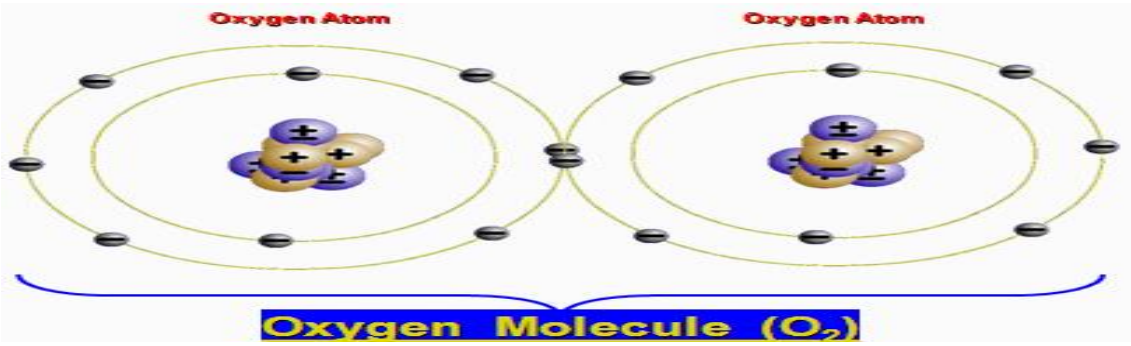
Covalent bond is formed between two atoms due to the sharing of electron pair(s). It is formed between two atoms that contain the same or small difference in electronegativity. Bonding between two atoms of the same element is completely covalent. In covalent bond, single, double, triple and quadruple bonds are formed. There are different types of covalent bonds like **polar** and **non-polar** and **coordinate** covalent bonds.

1. **A polar-covalent bond** is a covalent bond in which the bonded atoms have an unequal attraction for the shared electrons.

Example: hydrogen-chlorine bond ($H^{\delta+}$-$Cl^{\delta-}$).

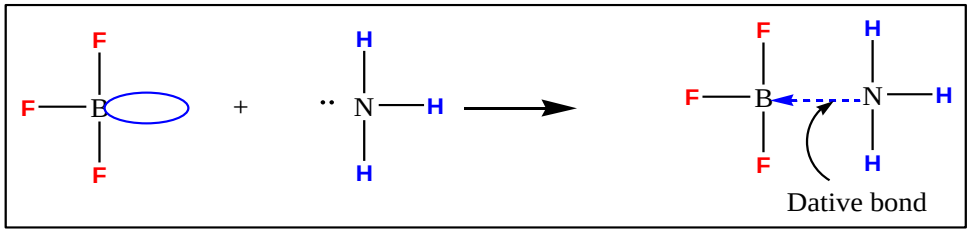
- ✓ Polar covalent bonding occurs because one atom has a stronger affinity for electrons than the other.
- ✓ When electrons are shared but shared unequally.

2. **Non-polar covalent bond** is a covalent bond in which the bonding electrons are shared equally by the bonded atoms, resulting in a balanced distribution of electrical charge. Example; hydrogen-hydrogen bond (H: H), Cl_2. The electrons are shared equally.



3. Coordinate Covalent bond: A coordinate covalent bond (also called a dative bond) is formed when one atom donates both of the electrons to form a single covalent bond. These electrons originate from the donor atom as an unshared pair.

Example:



2.2.2.1. Lewis structures

- The Lewis theory was the first explanation of a covalent bond in terms of electrons that was generally accepted.
- He uses dot (.) to represent valance electron. Atoms continue to form bonds until they have made up on octet of electrons. This is called the **octet rule'**.
- In forming compounds, atoms gain, lose, or share electrons to give a stable electron configuration characterized by **8 valence electrons**.

Hints on Lewis Dot Structures

- Octet rule‖ is the most useful guideline.
- Carbon forms 4 bonds.
- Hydrogen typically forms one bond to other atoms.
- When multiple bonds are formed, they are usually between C, N, O / S.
- Nonmetals can form single, double, and triple bonds, but not quadruple bonds.
- Always account for single bonds and lone pairs before forming multiple bonds.
- Look for resonance structures.

Steps in writing Lewis structure

1) Calculate the total number of valance electrons for molecules by adding the number of valance electrons for each species that participate in the formation of molecules/compounds.
2) Determine the number of electron pairs by dividing the total number of valance electrons by two to get number of paired electrons.
3) Predict the central atoms: Place the least electronegative element at the centre, except for H which is always an outer atom.
4) Distribute the remaining electrons to the attached atoms till they acquired octet rules.
5) If there are still remaining electrons distribute them as lone pairs to the central atom.
6) If octet rules not obeyed for the central atom, it forms multiple bonds.

Let us determine the Lewis structures of CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

For a molecule, we add the number of valence electrons on each atom in the molecule: SiH_4

Si: 4 valences electrons/atom×1 atom = 4

+H: 1 valence electron/atom×4atoms = 4

= 8 valence electrons

For a negative ion, such as SiH_4, CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge): CHO_2^-

C: 4 valences electrons/atom×1 atom=4

H: 1 valence electron/atom×1 atom=1

O: 6 valence electrons/atom×2 atoms=12

+1 additional electron

=18 valence electrons

For a positive ion, such as NO+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

NO^+

N: 5 valences electrons/atom×1 atom=5

O: 6 valences electron/atom×1 atom=6

+ −1 electron (positive charge = -1

=10 valence electrons

Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

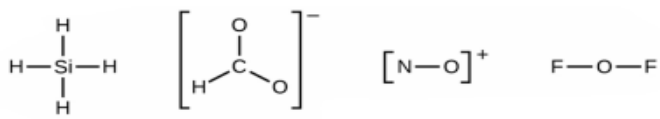
OF_2

O: 6 valences electrons/atom×1 atom=6

F: 7 valence electrons/atom×2 atoms = 14

= 20 valence electrons

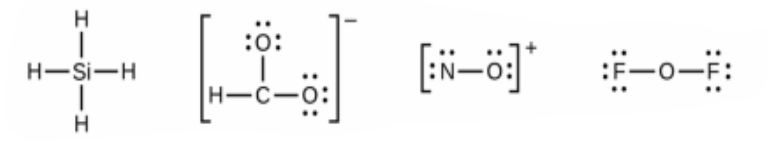
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it.

Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

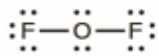
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons. There are no remaining electrons on SiH_4, so it is unchanged:



4. Place all remaining electrons on the central atom.

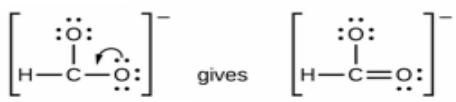
1. For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.

2. For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

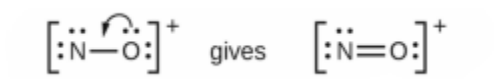


5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

- SiH_4: Si already has an octet, so nothing needs to be done.
- CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



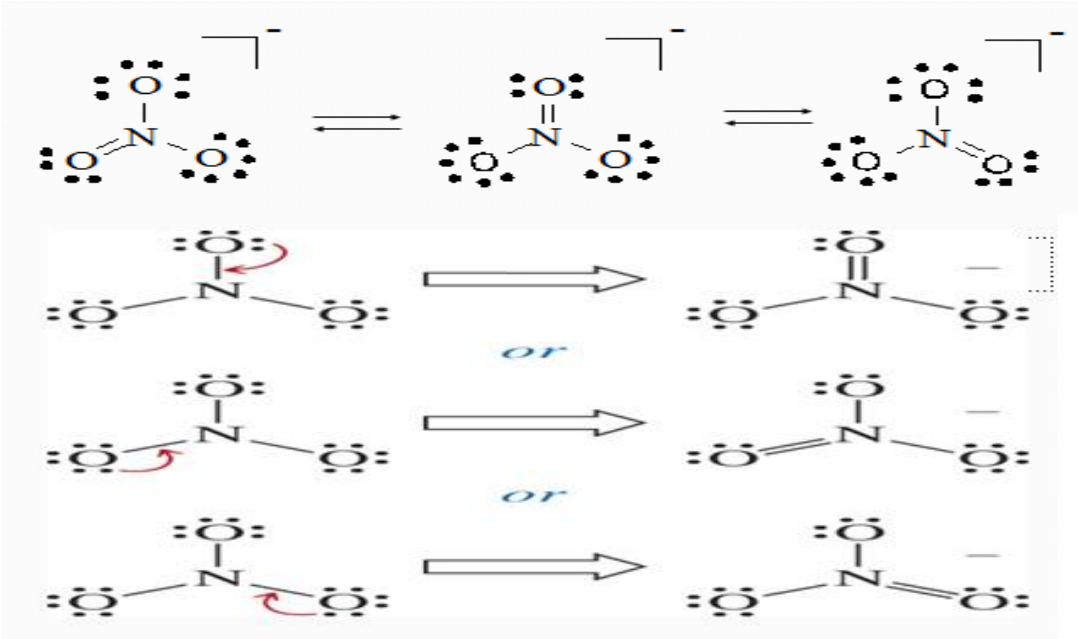
This still does not produce an octet, so we must move another pair, forming a triple bond:

In OF_2, each atom has an octet as drawn, so nothing changes

2.2.2.2. Resonance Structures

We have assumed up to this point that there is one correct Lewis structure. Now we turn our attention to **Resonance structures**: the structure of the same relative placement of

atoms but different locations of bonding and non-bonding electron pairs. Systems which have more than one Lewis structure are Resonance Structures. **Resonance** is delocalization of electrons through double bond. NO_3^- is a classic example of resonance:



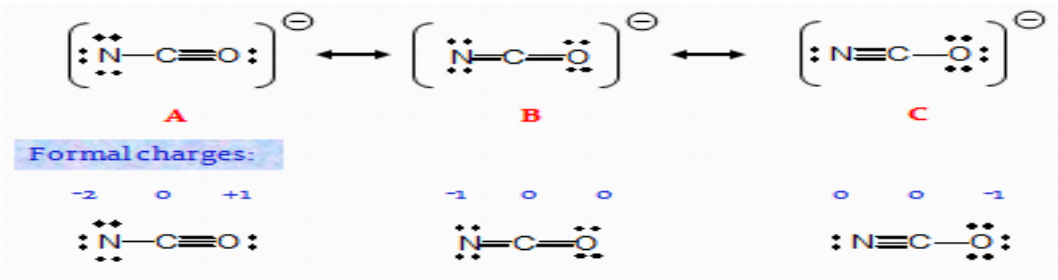
2.2.2.3. Formal Charge: The hypothetical charge on an atom in the molecules. It helps to check whether the Lewis structure is stable or not. The smallest formal charge is the more stable in Lewis structure regardless numerical sign. A more negative formal charge should reside on an atom with a larger EN value.

$$FC = \#Ve. - \left[\frac{1}{2}\#BE + \#LPE\right]$$

FC = formal charge; #Ve. = Number of valence electrons

#BE = bonding electrons; #LPE = lone pair electrons

Example: NCO^- has three possible resonance forms.



Forms B and C have negative formal charges on N and O. These forms are more important than Form A. Form C has a negative charge on O which is more electronegative than N. Therefore, Form C contributes the most to the resonance hybrid and stable.

Limitations: Lewis theory was good for s-block and p-block elements but not for d-block elements. Except in simple cases, Lewis structure can predict neither the 3D shape of the species (bond angles) nor the relative internuclear distances (bond lengths). Lewis theory cannot write one correct structure for many molecules where resonance is important. Lewis theory often does not predict the correct magnetic behavior of molecules. Oxygen, O_2, is paramagnetic, though the Lewis structure predicts it is diamagnetic.

2.2.2.4. Exceptions to the Octet Rule:

- Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:
  - ✓ Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
  - ✓ Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
  - ✓ Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

a) **Electron-Deficient Molecules**: gaseous molecules containing either Be or B as the central atom; have fewer than 8 electrons around the Be or B (4 e^- around Be and 6 e^- around B) (BF_3).

b) **Odd-Electron Molecules**: have an odd number of valence electrons; examples include **<u>free radicals</u>**, which contain a lone (unpaired) electron and are paramagnetic (use formal charges to locate the lone electron) (NO_2). Example: CH_3, OH, H, NO_2 etc.

c) **Expanded Valence Shells**: for molecules that have more than 8 electrons around the central atom; use empty outer *d* orbitals; occurs only with a central atom from Period 3 or higher (SF_6, PCl_5). E.g: PCl_5, SF_6, H_2SO_4, H_3PO_4

2.3 Valence Shell Electron Pair Repulsion Theory and Molecular Geometry

2.2.2.5. Molecular structure and polarity

VSEPR Theory

- Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure.
- The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them.
- The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs.
- The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.
- VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule.
- We should understand, however, that the theory only considers electron-pair repulsions.
- Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

2.2.2.6. Electron-pair Geometry versus Molecular Structure

- It is important to note that electron-pair geometry around a central atom is not the same thing as its molecular structure.
- Molecular structure describes the location of the atoms, not the electrons.
- We differentiate between these two situations by naming the geometry that includes all electron pairs the electron-pair geometry.
- The structure that includes only the placement of the atoms in the molecule is called the molecular structure.

- The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.
- For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure
- On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has tetrahedral electron-pair geometry.

- VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs.
- The order of electron-pair repulsions from greatest to least repulsion is:

Lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

- This order of repulsions determines the amount of space occupied by different regions of electrons.
- A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on.
- The order of sizes from largest to smallest is:

Lone pair>triple bond>double bond>single bond

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1) Write the Lewis structure of the molecule or polyatomic ion.
2) Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3) Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral.
4) Use the number of lone pairs to determine the molecular structure. If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that

will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

- The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

Example 1: Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

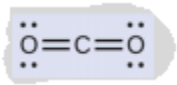
Predict the electron-pair geometry and molecular structure for each of the following:

(a) Carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels

(b) Boron trichloride, BCl_3, an important industrial chemical

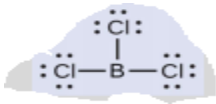
Solution

(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom-each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

2.4 Bonding Theories

2.2.2.7. Molecular structure and dipole moment

- Polar covalent bonds connect two atoms with differing electronegativity, leaving one atom with a partial positive charge (δ^+) and the other atom with a partial

negative charge (δ^-), as the electrons are pulled toward the more electronegative atom.

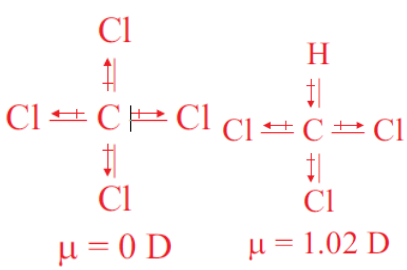
- This separation of charge gives rise to a bond dipole moment.
- The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

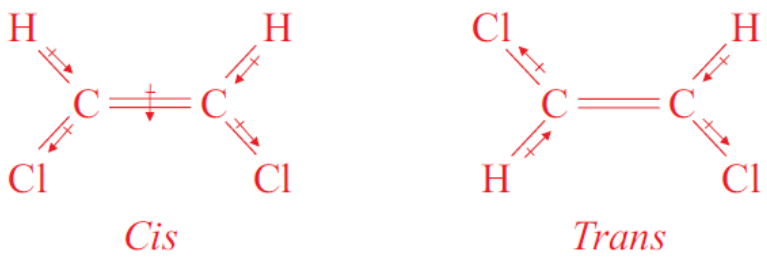
- This bond moment can be represented as a vector, a quantity having both direction and magnitude
- Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom.
- A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond.
- The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

To summarize, to be polar a molecule must:

- ✓ Contain at least one polar covalent bond.
- ✓ Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.



The trans isomer has no dipole moment (μ= 0 D) because the C – Cl bond polarities balance each other. In contrast, the cis-isomer is polar (μ = 1.90 D) because the bond dipoles partially reinforce each other, with the molecular dipole pointing between the Cl atoms.



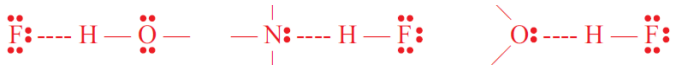
2.2.2.8. Intermolecular Forces in Covalent Compounds

Dipole-Dipole forces: When polar molecules are brought near one another, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces; the partially positive end of one molecule attracts the partially negative end of another For compounds of approximately the same mass and size, greater is the dipole moment, greater is the dipole-dipole forces between their molecules, so greater is the energy required to separate their particles.

For instance, both methyl chloride (CH_3Cl) and ethanol (CH_3CHO) have comparable mass and size, but CH_3Cl has a smaller dipole moment than CH_3CHO; therefore, less energy is needed to overcome the dipole-dipole forces between its molecules and it boils at a lower temperature. Dipole-dipole forces give polar cis-1,2-dichloroethene a higher boiling point than nonpolar trans-1, 2- dichloroethene.

Hydrogen Bonding: Hydrogen bonding is a special type of dipole-dipole forces that arise between molecules that have a hydrogen atom bound to a smaller sized, most electronegative atoms. These atoms are: Fluorine, Oxygen and Nitrogen

The partially positive (δ+) H of one molecule is attracted to the partially negative (δ –) lone pair on the F, O or N of the same or another molecule. As a result, hydrogen bonds result.



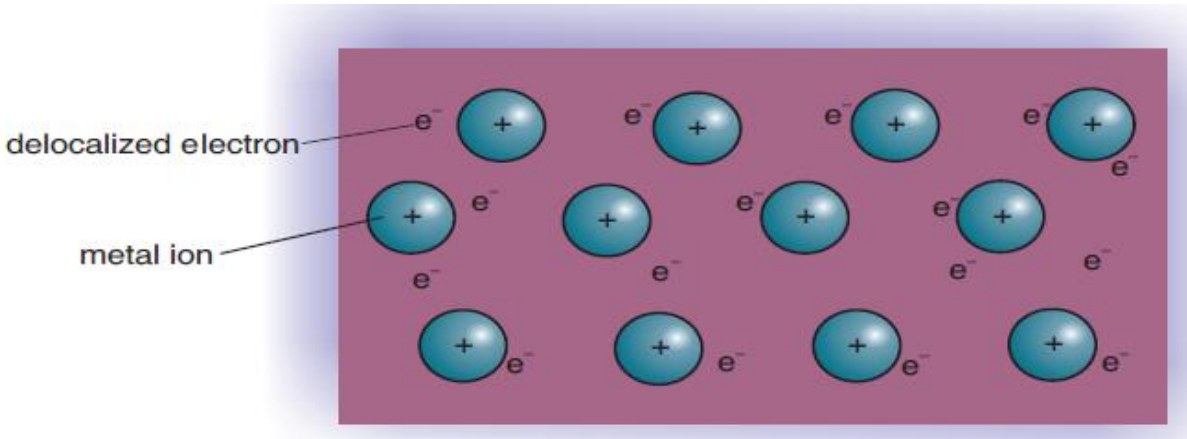
Dispersion or London Forces: Intermolecular forces in which non-polar atoms or molecules interact by inducing dipoles in each other are known as dispersion or London Forces. These classes of intermolecular forces cause substances like CO_2, Cl_2, noble gases, etc., to condense and solidify.

An attractive force must be acting between these non-polar molecules and atoms, or they would remain gaseous under any conditions. In fact, bond dipoles exert some weak attraction but the intermolecular forces are mainly responsible for the condensed state of non-polar substance. These forces are known as London forces or dispersion forces, named after Fritz London, the physicist who explained the quantum mechanical basis of the attractive forces. Dispersion forces are very weak and are caused by a sudden shift of electron density to one side of the nucleus than the other

Intermolecular force	Strength	Polarity
Hydrogen Bonding	The Strongest	Polar
Dipole-dipole Forces	Moderate	Polar
London Dispersion Forces	The Weakest	Non-polar

2.2.3. Metallic Bond

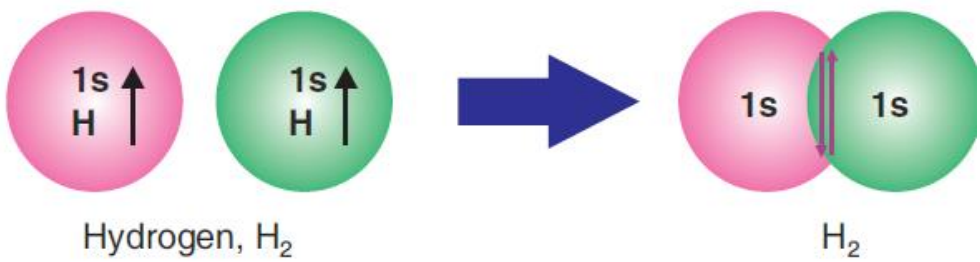
It is the attraction between metal atoms in a metallic crystal. It is formed between electropositive metal atoms of same or different elements. The valence electrons of pure metals are not strongly associated with particular atoms. This is a function of their low ionization energy. Electrons in metals are said to be delocalized (not found in one specific region, such as between two particular atoms). Since they are not confined to a specific area, electrons act like a flowing “sea”, moving about the positively charged cores of the metal atoms. Delocalization can be used to explain conductivity, malleability, and ductility. In general, the greater the number of electrons per atom that participate in metallic bond the stronger the metallic bond. E.g. the metal atoms Na, Cu, Ag, and Fe etc. are bound to each other in their crystals by metallic bonds.

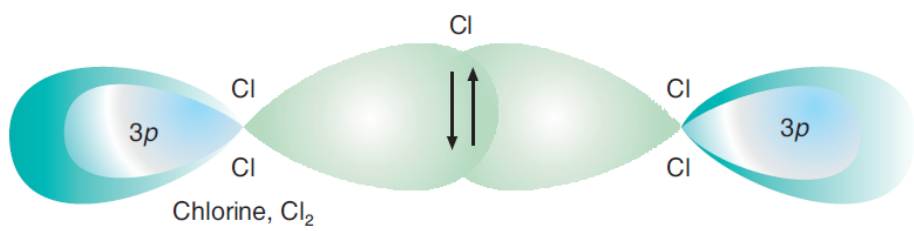


2.3. CHEMICAL BONDING THEORIES

2.3.1 Valence Bond Theory (VBT)

The basic principle of valence bond theory is that a covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons





✓

In the HCl bond, for example, the 1*s* orbital of hydrogen overlaps the half-filled 3*p* orbital of Cl along the axis of that orbital.

Similarly, in the Cl–Cl bond of Cl_2, the two 3*p* orbitals interact end-to-end, that is along the orbital axes, to attain maximum overlap

Overlap of Atomic Orbitals (Sigma and Pi Bonds): Various type of atomic orbital overlap leads to covalent bond formation. Three simple basic ones are *s-s*, *s-p* and *p-p*

1. *s-s* overlap in which half-filled *s* orbitals overlap,

2. *s-p* overlap where half-filled *s* orbital of one atom overlaps with one of the *p* orbital having one electron only and

3. *p-p* overlap in which two half-filled *p* orbitals overlap.

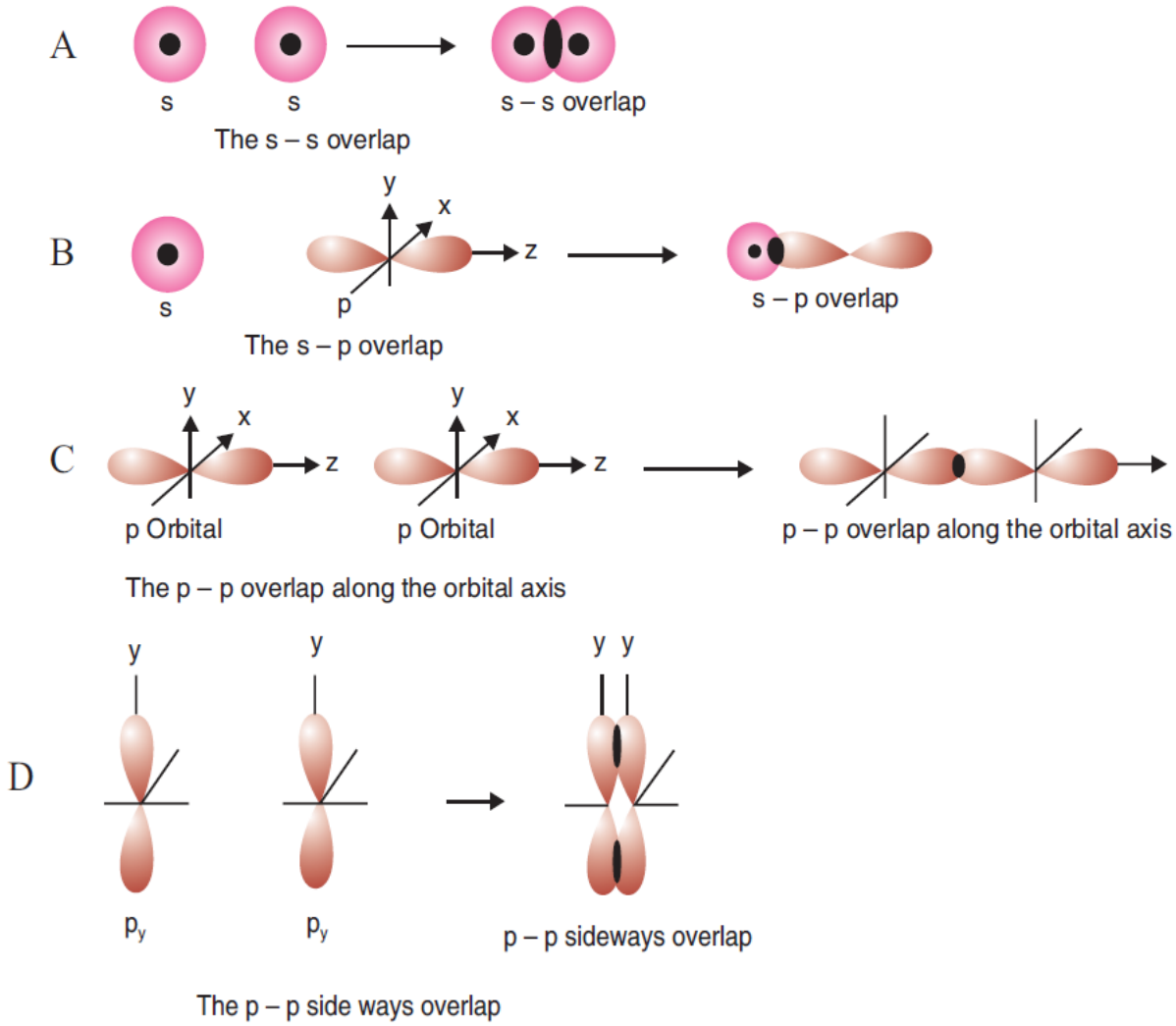


Figure 2. Atomic orbital overlap.

(*A*) s-s overlap, (B) s-p overlap, (C) p-p overlap along the orbital axis and

(D) p-p sideways overlap.

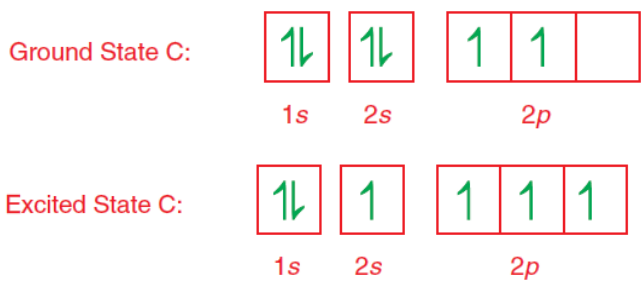
Because of the directional nature of *p* orbital, the overlap may take place in two ways: (i) the half-filled p orbitals along the line joining the two nuclei. This is called as head on, end-to-end, end on or linear overlap and (ii) the half-filled *p* orbitals overlap along the line perpendicular to the nuclear axis. This overlapping of p orbitals is parallel to each other, hence is called lateral or sideways overlapping. These two modes give rise to the two types of covalent bonds, namely, sigma (σ) and pi (π) bond respectively. Valence

bond theory is used to describe the two types here, but they are essential features of molecular orbital theory as well. *s* - *s* and *s* - *p* will always overlap along the nuclear axis, hence results only in sigma bonds. A side - to - side or parallel overlap forms another type of covalent bond called a pi (π) bond. It has two regions of electron density. One above and one below the sigma bond axis. One π -bond holds two electrons that occupy both regions of the bond. A double-bond always consists of one σand one πbond. The extent of overlap influences bond strength, however, many factors, such as lone - pair repulsions, bond polarities, and other electrostatic contributions affect overlap and the relative strength of σ and π bonds between other pairs of atoms.

Hybridization of Orbitals

Hybridization

- The combination of atomic orbital is called hybridisation
- The word 'hybridization' means 'mixing
- Hybrid orbitals may be formed by mixing the characters of atomic orbitals that are close in energy
- The number of bond formed by an atom is the same as the number of unpaired electron that combined in ground state.

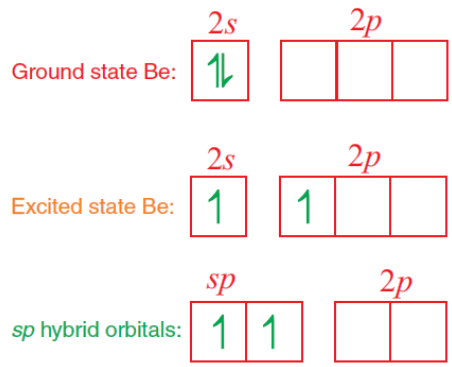


sp hybrid orbitals

Combination (mixing) of one s and one p orbital is called *sp* hybridization and the resultant orbitals are called *sp* hybrid orbitals.

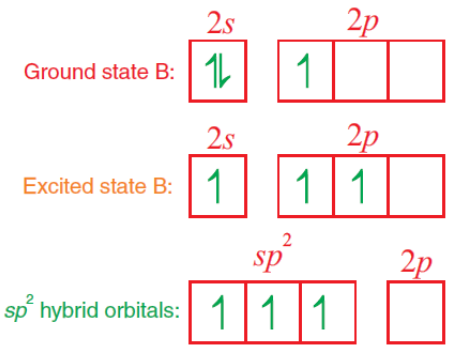
VB theory explains this by proposing that mixing two non-equivalent orbitals of a central atom one s and one *p*, gives rise to two equivalent sp hybrid orbitals that lie 180° apart.

Example: In the triatomic molecule $BeCl_2$ the 2*s* and one of the 2*p* orbitals of the Be atom are hybridized into *sp* hybrid orbitals. The remaining two 2*p* orbitals are left hybridized and unoccupied in the orbital diagram.



sp2 hybrid orbitals

example in BCl_3, the boron atom has four orbitals but only three electrons in its valence shell. In most boron compounds the hybridization scheme combines one 2*s* and two 2*p* orbitals into three sp^2 hybrid orbitals.

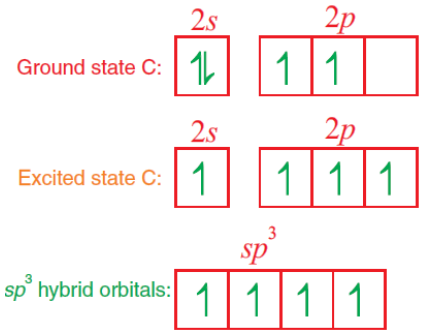


The valence bond method predicts that BCl_3 is a trigonal planar

molecule with 120° Cl–B–Cl bond angle

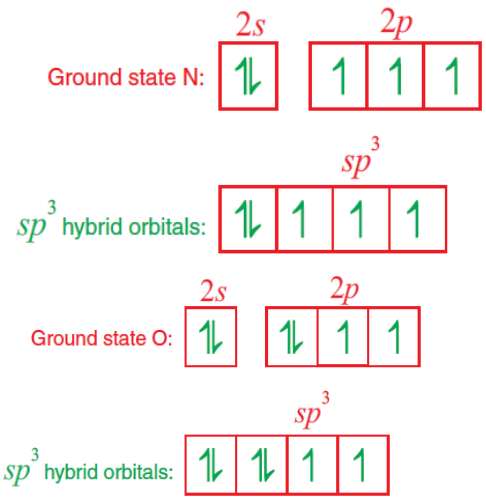
sp^3 hybridization

Carbon, the central atom in a molecule of methane CH_4 has only two unpaired electrons in the ground state. rule. Carbon in its excited state can form four bonds. The one 2*s* and three 2*p*-orbitals of carbon are mixed to produce four new orbitals that are equivalent to each other in energy and in shape, but pointing in different directions,



The four sp^3 hybrid orbitals point to the corners of a regular tetrahedron, and make a bond angle of 109.50° in CH_4

We might also expect to use sp^3 hybridization not only for structures of the type AX_4 type (as in CH_4), but also for AX_3E type (as in NH_3) and AX_2E_2 type (as in H_2O).

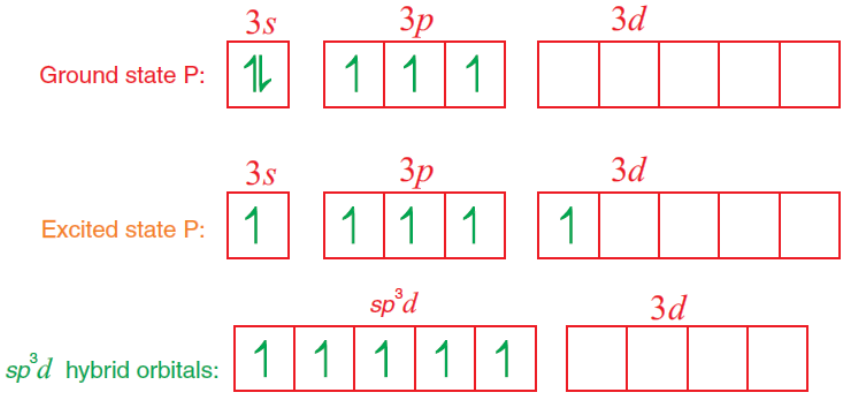


sp^3d hybridization

PCl_5, the central atom phosphorus has only

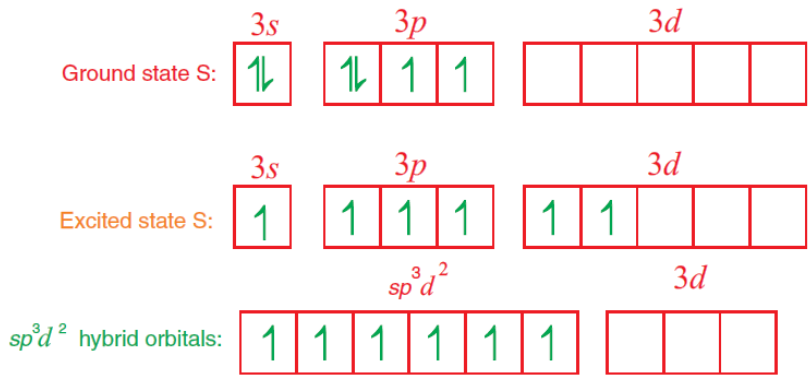
three unpaired electrons in its ground state. Electrons must be unpaired to provide the

correct number of unpaired electrons for bond formation



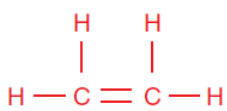
sp^3d^2 Hybridization

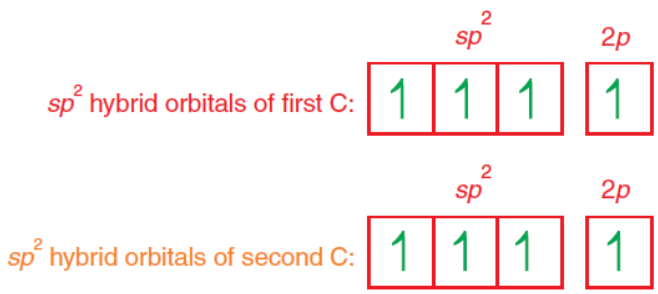
Another structure featuring an expanded octet is SF6. Here, six hybrid orbitals are required in order to describe bonding.



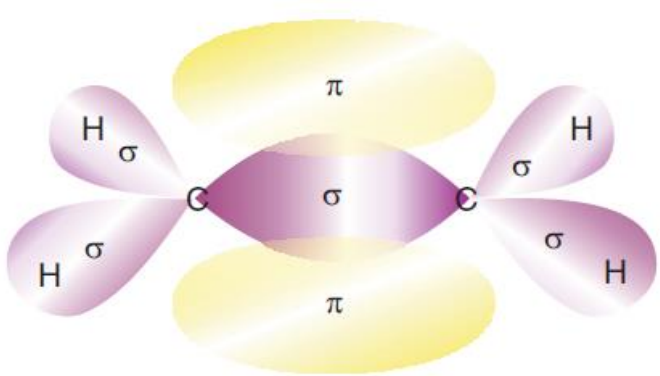
In hybridization schemes, one hybrid orbital is produced for every single atomic orbital involved. In a molecule, each of the hybrid orbitals of the central atom acquires an electron pair, either a bond-pair or a lone-pair. And the hybrid orbitals have the same orientation as the electron-set arrangement predicted by VSEPR theory.

Lewis structure of ethene (*ethylene*) is depicted as





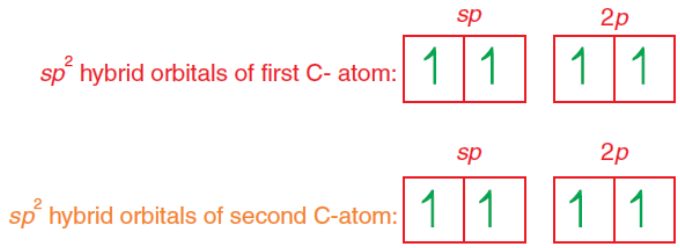
All the C–H bonds in C_2H_4 are formed by the overlap of sp^2 hybrid orbitals of the C atoms with 1*s* orbitals of the H atom, A double covalent bond consists of one σ and one π bond.



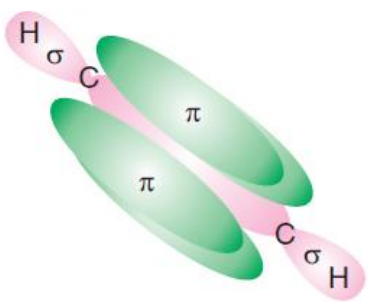
Consider the Ethyne (acetylene) molecule, C_2H_2.

$$H - C \equiv C - H$$

The molecule is linear, with 180° H–C–C bond angles



in C_2H_2, as in all triple bonds, one bond is a σ-bond and two are π- bonds.



2.3.2. Molecular Orbital Theory (MOT)

- Deals with combination of atomic orbitals
- Combination will be; - s—s, s—p, p—p, p—d, d—d combination

Bonding and Anti-Bonding Molecular Orbitals

In place of atomic orbitals of the separated atoms, the molecular orbitals for the united atoms are obtained, and these are of two types. One type, a bonding molecular orbital, places a high electron charge density in between the two nuclei and the other type, an anti-bonding molecular orbital, places a high electron charge density away from the region between the two nuclei. Electrons in bonding orbitals contribute to bond formation and electrons in anti-bonding orbitals detract from bond formation.

In place of atomic orbitals of the separated atoms, the molecular orbitals for the united atoms are obtained, and these are of two types. One type, a bonding molecular orbital, places a high electron charge density in between the two nuclei and the other type, an anti-bonding molecular orbital, places a high electron charge density away from the region between the two nuclei. Electrons in bonding orbitals contribute to bond formation and electrons in anti-bonding orbitals detract from bond formation.

When two atomic orbitals overlap end-to-end, they form two sigma-molecular orbitals (MOs). Consider the H2 molecule, which has two H atoms and therefore two 1*s* AOs. The two 1*s* atomic orbitals combine (see Figure 3) to produce two σMOs, which differ in energy and location. One of the σMOs is a bonding orbital, denoted σ1*s*, the other is an anti-bonding orbital denoted $\sigma^{*}1s$.

The relative energy levels of these two MOs are different. The σ1*s* MO has a lower energy than the original 1*s* AOs, while the σ*1s MO has a higher energy.

Electron Configuration of Diatomic Molecules

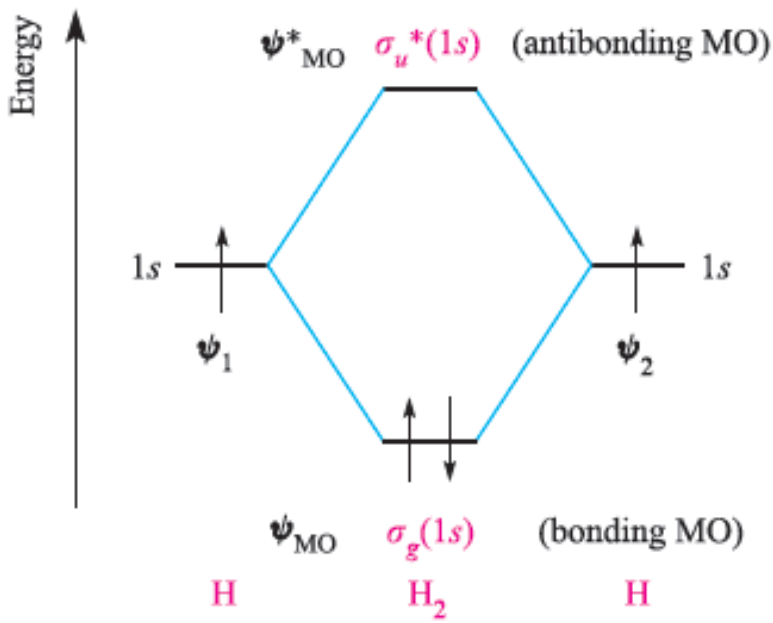


Figure 3 ***Electron Configuration of Hydrogen Molecules***

- Electron configuration in MO is given by:

б1s, б*1s, б2s, б*2s, б2p_x , ∏2p_y ∏*2p_y б*2p_x

∏2p_z ∏*2p_z

- This order show exception for lighter elements such as B, C & N (14 electron and less) as:

б1s, б*1s, б2s, б*2s, ∏2p_y, б2p_x, ∏*2p_y б*2p_x

$\Pi 2p_z$ $\Pi^* 2p_z$

Eg. He_2 molecule consists 4 electron $\sigma 1s^2$, $\sigma^* 1s^2$

Li_2 molecule consists 6 electron $\sigma 1s^2$, $\sigma^* 1s^2$ $\sigma 2s^2$

O_2 molecule consists 16 es. $\sigma 1s^2$, $\sigma^* 1s^2$, $\sigma 2s^2$, $\sigma^* 2s^2$, $\sigma 2p_x^2$, $\Pi 2p_y^2$, $\Pi^* 2p_y^1$, $\sigma^* 2p_x$

$\Pi 2p_z^2$, $\Pi^* 2p_z^1$

O_2 is paramagnetic in nature

Bond Order

The term bond order is used to indicate whether a covalent bond is single (bond order = 1), double (bond order = 2) or triple (bond order = 3).

- The existence of molecules determined by **bond order** which is given by: $BO = \frac{BMO - ABMO}{2}$

Eg. In O_2, $\frac{10-6}{2} = 2$, the molecule can exist

- ❖ A molecule exists only if the bond order is **positive**.
- ❖ If bond order is **zero or negative**, the molecule does not exist.

Magnetic Properties

A species with unpaired electrons exhibits paramagnetic property. The species is attracted by an external magnetic field. A species in which all the electrons are paired, exhibits diamagnetism. Such species are not attracted (and, in fact, are slightly repelled) by a magnetic field.

Exercise 1

1. Use the molecular orbital theory and derive the electron configuration of the following molecules. Identify those which exist and do not exist. a He_2 b Be_2 c B_2 d C_2 e N_2
2. Draw a molecular orbital energy diagrams for: a. C_2^- b. .C_2 c. C_2^+

2.4. TYPES OF CRYSTALS

A crystal is a piece of a solid substance that has plane surface, sharp edges, and a regular geometric shape A structural unit of a crystalline solid has a characteristic repetitive pattern. The crystal types and their basic units are (i) ionic (electrostatic attraction of ions), (ii) Molecular (electrostatic attraction of dipoles in molecules) (a) Polar (dipole-dipole and Hbonding) and (b) Non-polar (London forces) (iii) Network (covalently bonded atoms); and (iv) metallic (positive nuclei in electron sea).There are four important classes of crystalline solids.

A. Ionic Crystals

The fundamental units of an ionic solids are positive and negative ions. As a result, the inter-particle forces (ionic bonds) are much stronger than the van der Waals forces in molecular solids. Ionic solids are table salt (NaCl), saltpeter (KNO_3), washing soda ($Na_2CO_3.10H_2O$), and black board chalk ($CaCO_3$).

B. Molecular Crystals

Various combinations of dipole-dipole, dispersion and hydrogen-bonding forces are operative in molecular solids, which accounts for their wide range of physical properties. Dispersion forces are the principal forces acting in non-polar substances, so melting points generally increase with molar mass. Among polar molecules, dipole dipole forces and where ever possible, hydrogen-bonding dominate. Nevertheless, intermolecular forces are still relatively weak, so the melting points are much lower than ionic, metallic and network covalent solids. The fundamental unit of a molecular solid is the molecule. Such solids are common among organic compounds and simple inorganic compounds. Molecular crystals are usually transparent, brittle, and break easily when stressed. They are usually non-conductors of heat and electricity and usually have low melting points molecular crystalline solids include sugar, dry ice (solid carbon dioxide), glucose and aspirin.

C. Covalent Network Crystals

Character	Ionic solids	Covalent solids	Molecular solids	Metallic solids
Constituent particles	Positive and negative ions	Atoms	molecules	Positive metal ions and free electrons
Bonding forces	Electrostatic attraction	covalent	Van der Waals dipole-dipole	Electrostatic attraction between positive and negative species
Melting point	High melting point	Very high melting oint	Low melting point	Moderate to high melting point
Hard/Soft	Hard and brittle	very hard	Very soft	Hard and soft
Conductance	Conductor in aqueous solution or in molten state	Non-conductor	Insulator Conductor	Good conductor
Examples	NaCl, CaF_2	Diamond, Silica	H_2O, CO_2	Cu, Fe

Type of Solid	Interaction	Properties	Examples
Ionic	Ionic	High melting point, brittle, hard	NaCl, MgO
Molecular	Hydrogen bonding, Dipole-Dipole, London dispersion	Low melting point, non-conducting	H_2, CO_2
Network	Covalent bonding	High melting point, hard, non-conducting	C (diamond), SiO_2 (quartz)
Metallic	Metallic bonding	Variable hardness and melting point (depending upon strength of metallic bonding), conducting	Fe, Mg

Exercise 2

Match the substances from list A with the best suited characteristics given in list B and justify your answer

List A Substances		List B Characteristics
a Fe	a	Forces of attractions are between positive ions and 'sea of electrons'
b I_2	b	High boiling point due to strong covalent bonds
c H_2O	c	High boiling point due to hydrogen bond
d SiO_2	d	Weak van der Waal's forces
e Na	e	Giant metallic lattice, ions packed together very closely leading to high density
	f	Non-polar solvent

Unit summary

- Ionic compounds are crystalline solids at room temperature. The fundamental units of ionic solid are positive and negative ions. Crystalline ionic solids are usually brittle and non-conductors of electricity, although molten crystals may be good conductors. They usually have high melting and boiling points.
- Ionic compounds are nonvolatile.
- Ionic compounds are usually soluble in inorganic solvents (water is the most common solvent for ionic compounds) but insoluble in organic solvents like benzene, ethanol and carbon tetrachloride.
- Lewis symbols of representative elements are related to their location in the periodic table. The lattice energy and enthalpy of formation of an ionic compound, together with other atomic and molecular properties, can be related in a thermochemcial cycle called Born-Haber cycle.
- A covalent bond is created by the sharing of an electron-pair between atoms.

- In a Lewis structure representing covalent bonds, electron-pairs are either bonding-pairs or lone-pairs.
- In a covalent bond between atoms of different electronegativity, electrons are displaced toward the atom with the higher electronegativity. In terms of electronegativity differences chemical bonds vary over the range: non polar to polar covalent to ionic.
- In some cases of covalent bonding, one atom appears to provide both electrons in the bonding pair; the bond is known as coordinate-covalent bond.
- Bonded atoms may share more than one pair of electrons between them, giving rise to multiple covalent bonding.
- In the phenomenon of resonance, two or more Lewis structures have the same skeletal structure but different bonding arrangements. The best description of the resonance structure (resonance hybrid) is obtained by combining plausible structures (contributing structures).
- Exceptions to the octet rule are found in odd-electron molecules and molecular fragments called free radicals. A few structures appear to have too few electrons to complete all the octets. Some structures appear to have too many. In the latter case, a central atom may employ an "expanded" octet with five or six electron-pairs.
- Valance shell electron pair repulsion theory (VSEPR) predicts the geometrical structures of molecules and polyatomic ions based on mutual repulsions among valance shell electron groups.
- Multiple bonds, whether they consist of four electrons (double bond) or six electrons (triple bond), are treated as one electron set.
- The separation of the centers of positive and negative charge in a polar covalent bond creates a bond moment. Whether a molecule as a whole is polar, that is, whether there is a resultant dipole moment, is established by bond moments and molecular geometry.
- A symmetrical distribution of identical bond moments about a central atom results in a cancellation of all bond moments, with the result that the molecule is nonpolar, as in the case of CCl_4.

- In the valence bond method (VB) a covalent bond is viewed as the overlap of atomic orbitals of the bonded atoms in a region between the atomic nuclei.
- Molecular geometry is determined by the spatial orientations of the atomic orbitals involved in bonding.
- The VB method often requires that bonding atomic orbitals be hybridized in order to rationalize known structures of molecules. A hybridized orbital is some combination of s, p and d orbitals, such as sp, sp^2, sp^3, sp^3d and sp^3d^2. The geometric distribution of hybridized orbitals in the valence bond method is the same as the electron set geometry proposed by VSEPR theory.
- Hybrid orbitals overlap in the usual way (end-to-end) and form σ bonds. Unhybridized p orbitals overlap in a side-by-side manner and give rise to π bonds. A double bond consists of one σ bond and one σ bond; a triple bond, one σ bond and two π bonds.
- Acceptable solutions to wave equations written for the electrons in a molecule are called molecular orbitals (MO). The two main types of MOs are bonding molecular orbitals, which concentrate electron charge density between atoms or just above and below the imaginary line joining the two nuclei and antibonding molecular orbitals, which concentrate electron charge densities away from the intermolecular bonding region.
- Electrons can be assigned to molecular orbitals by the scheme similar to the aufbau process. MO theory provides more satisfactory descriptions for certain structures than does the VB method, for example, some odd - electrons species and the O_2 molecule.

Review questions

1. Explain the formation of bonds in the following pairs of elements:

   a. potassium and chlorine b. magnesium and oxygen and c. sodium and oxygen.
2. Which of the following elements will form an ionic bond with chlorine and why?

   Calcium, Carbon, Oxygen and Silicon
3. Why ionic bond is also known as electrovalent bond?
4. How many types of chemical bonding you are familiar with?

5. State and explain the formation of ionic, covalent and metallic bonds. Use diagrams wherever required.
6. List four important characteristics of ionic compounds.
7. What observable properties can you use to distinguish one kind of bond from another?
8. Write the formulas and names of the compounds formed from the following ionic interactions: (use periodic table)
    a. The 2+ ion and 1– ion is both isoelectronic with the atoms of a chemically unreactive period 4 element.
    b. The 2+ ion and the 2– ion are both isoelectronic with the period 3 noble gas.
    c. The ions formed are the largest and smallest ionisable atoms in period 2.
9. In each of the following ionic compounds identify the main group to which X belongs:

    a. XF_2 b. MgX c. X_2O_3 d. Na_2X

10. For lithium, the enthalpy of sublimation is +161 kJ mol^{-1}, and the first ionization energy is +520 kJ mol^{-1}. The dissociation energy of fluorine is +154 kJ mol^{-1}, and the electron affinity of fluorine is –328 kJ mol^{-1}. The lattice energy of LiF is –1047 kJ mol^{-1}. Calculate the overall enthalpy change for the reaction?
11. $Li(s) + ½F_2(g) \rightarrow LiF(s)$ $\Delta H°$ =?
12. The enthalpy of formation of caesium chloride is

    $Cs(s) + ½Cl_2(g) \rightarrow CsCl(s)$ $\Delta H° = – 44.28$ kJ mol^{-1}

    The enthalpy of sublimation of caesium is

    $Cs(s) \rightarrow Cs(g)$ $\Delta H° = + 77.6$ kJ mol–1

    Use these data, with other data from other sources, to calculate the lattice energy of CsCl(s)
13. Using the following data:

    Enthalpy of sublimation of Ca = +178.2 kJ mol^{-1}

    Enthalpy of dissociation of Cl_2 = +243.4 kJ mol^{-1}

    Enthalpy of formation of $CaCl_2$ = –795.8 kJ mol^{-1}

First and second Ionization energies for Ca are +590 kJ mol^{-1} and +1145 kJ mol^{-1} respectively.

The electron affinity of Cl = –348.7 kJ mol^{-1}

Determine the lattice energy of $CaCl_2$

14. Determine the total number of valence electrons for the following species:

    a. CO_2 b. SO_2^{4-} c. NH_4^+ d. N_2O_4

15. Write a plausible Lewis structure of:

16. a. nitrogen trichloride, NCl_3 b. chlorate ion, ClO_3^-

17. c. phosphonium ion, PH_4^+ d. phosgene, $COCl_2$

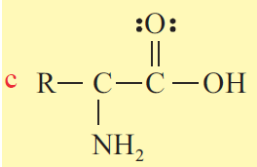
18. Draw a Lewis structure for CO_3^{2-}, SF_4 and HCOOH (formic acid).

19. Which of the following atoms cannot serve as a central atom in a Lewis structure O, He, F, H, P? Explain.

20. Write a plausible Lewis structure for carbonyl sulphide, COS.

21. In which of the following substances do hydrogen bonds occur? Explain with the help of diagrams.

    a. CH_4 b. CH_3CH_2OH

    c 

22. Identify the dominant intermolecular force that is present in each of the following substance and select the substance with the higher boiling point in each pair:

    a. CH_3OH or CH_3CH_2OH c. $MgCl_2$ or PCl_3

    b. Hexane or cyclohexane d. CH_3NH_2 or CH_3F

23. Which type of intermolecular force is dominant in the following substances?

    a. ICl b. H_2O

    c. F_2 d. HBr

24. Compare intermolecular forces with that of intramolecular bonding.

25. How do carbon and silicon differ with regard to the types of orbitals available for hybridization? Explain

26. Are these statements true or false? Correct any that is false.

    a. Two σ bonds comprise a double bond.

b. A triple-bond consists of one π bond and two σ bonds.

c. Bonds formed from atomic *s* orbitals are always σ bonds.

d. A π -bond consists of two pairs of electrons

e. End-to-end overlap results in a bond with electron density above and below the bond axis.

27. Name the three types of hybrid orbitals that may be formed by an atom with only *s* and *p* orbitals in its valence shell. Draw the shapes of the hybrid orbitals so produced.

28. Describe a hybridization scheme for the central atom and molecular geometry of the triiodide ion, I_3^-.

29. Describe a hybridization scheme for the central atom S and the molecule geometry of

a SO_3 and b SO_2

30. Describe a hybridization scheme for the central atom and the molecular geometry of CO_2.

31. Discuss the bonding in nitrate ion, predict the ideal bond angles, bond length, shape of the ion, the number of sigma and pi bonds.

32. Use the MOT to explain bond order and magnetic properties of: A. O_2^{2-} B. O_2 C. O_2^+ D. NO E. CO F. C_2

33. What is the bond order for CN^-, CN and CN^+?

34. Which homonuclear diatomic molecules of the second period elements,

35. besides O_2, should be paramagnetic?

Multiple Choice Questions

1. "Two atoms each provide two electrons that are shared by the two atoms" This is a description of a: a. triple covalent bond c. double covalent bond b. coordinate covalent bond d. single covalent bond

2. A non-metal usually forms two covalent bonds in its compounds. How many electrons will it have in its valence shell? a. 2 b. 6 c. 4 d. 8

3. The noble gases do not usually form chemical compounds because:

(a) they have very stable nuclei.

(b) the bonds between their atoms are very strong.

(c) they already have paired valence shell electrons.

(d) they are not polar.

4. Which of the following compounds contain both ionic and covalent bonds?

   a. CO_2 b. Cl_2O c. Na_2CO_3 d. $BaCl_2$

5. Which of the following molecules would you expect to be non-planar?

   a. CH_4 b. BCl_3 c. XeF_4 d. HCHO

6. If a molecule has a trigonal pyramidal shape, how many non-bonding pairs of electrons are present in the valence shell of the central atom?

   a. 1 b. 2 c. 3 d. 4

7. Of the following, the most polar bond is: a. P – Cl b. Si – F c. S – O d. C – N

8. Carbon and chlorine form a series of compounds: CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4. Which of these will be polar?

   a. CCl_4 only b. CH_3Cl and $CHCl_3$ only

   c. CH_3Cl, CH_2Cl_2 and $CHCl_3$ only d.CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4

9. The carbon atoms in ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2) provide, respectively, examples of the three common types of hybridization corresponding to:

   a. *sp*, *sp*2, *sp*3 b. *sp*3, *sp*2, *sp* c. *sp*, *sp*3, *sp*2 d. *sp*3, *sp*, *sp*2

10. Which of the following correctly describes a π bond?

    a. It is formed by the end-to-end interaction of *p*-orbitals and has a low electron density on the internuclear axis.

    b. It is formed by the parallel interaction of *p*-orbitals and has a high electron density just above and below the internuclear axis.

    c. It is formed by the interaction of *s*-orbitals and has a low electron density on the internuclear axis.

    d. It is formed by the interaction of *s*-orbitals and has a high electron density on the internuclear axis.

11. Which of the following species cannot be adequately described by a single Lewis structure?

    a. OH^- b. C2H2 c. $NH4^+$ d. HCO_3^-

12. In which of the following compounds would inter-molecular hydrogen-bonding occur?

    a. HCHO b. PH_3 c. CH_3OH d. $COCl_2$

13. Which of the following molecules would you expect to have the highest boiling point?

    a. $CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$
    b. $CH_3–CH(CH_3)–CH_2–CH_2–CH_3$
    c. $CH_3–CH_2–CH(CH_3)–CH_2–CH_3$
    d. $CH_3–C(CH_3)_2–CH_2–CH_3$

14. Which of the following molecules possesses the strongest forces between the molecules?

    a. N_2 b. $CH_3–CH_3$ c. H_2CO d. CH_4

15. Which one of the following usually produces the weakest interaction between particles of similar molar mass?

    a. Van der Waals forces …… …. c. Covalent bonds
    b. Dipole-dipole forces ……. d. Hydrogen-bonding

16. The hydrogen bonding is not significant in:

    a. DNA b. protein c. ice d. poleythene

17. A gas is likely to:

    a. have its atoms held together by metallic bonds
    b. have a giant covalent structure.
    c. be a compound of a metal.
    d. have a molecular covalent structure.

18. If an element in group IIA of the periodic table formed a compound with an element in group VIIA of the periodic table, the compound formed is likely to:

    a. be a crystalline solid c. have a low boiling point
    b. dissolve in non-polar solvents d. conduct electricity in the solid state

19. Which of the following substances would you expect to have the lowest boiling point? a. CsCl b. $SrSO_4$ c. Sc_2O_3 d. $AsCl_3$

20. Which of the following would not conduct an electric current?

    a. solid mercury b. Aqueous sodium chloride
    c. liquid sodium chloride d. solid sodium chloride

Part II: Answer the following questions:

21. Name the following compounds:

a. KBr b. Al I3 c. Li3N d. BeO e. BaS

22. Predict the shape for the following molecules:

a. SiF_4 b. PCl_3 c. H_2S d. NF_3 e. CCl_4 f. PCl_5

23. Draw Lewis structures and predict the shapes, giving approximate bond angles for: CH_3^+, CH_3^-, **.**CH_3 (methyl radical), HCN, ICl_2, NH_2^-, NO_2, ClO_2.

24. Classify the given molecules as polar or non-polar:

a. SiF_4 b. NF_3 c. PCl_3 d. H_2S e. CCl_4 f. CO_2

25. Which atom (if any), in each of the following bonds would you expect to carry a partial negative charge?

a. H–N b. S–S c. O–P d. C–F e. B–O f. I–F

26. Draw the Lewis structure for the given molecules and state whether the molecule is polar or non-polar:

a. PF_4^- b. ICl_4^- c. N_2F_2 (*2 forms possible*)

27. Boron trifluoride can react with a fluoride ion to give the tetrahedral BF_4^-ion.

What type of hybridization would you expect the boron to have in BF_4^-?

28. Carbon and oxygen can bond either by a single bond (as in CH_3–OH), a double bond (as in O=C=O), or a triple bond (as in HC≡CH).

a. Describe these three types of bonds in terms of σ-bonds and π-bonds.

b. How would you expect the length of the carbon-oxygen bond to vary in the three given examples?

29. Explain the following in terms of the intermolecular forces that exist in them:

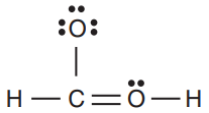
a. Water is a liquid at room temperature and atmospheric pressure, but hydrogen sulphide is a gas.

b. At room temperature and atmospheric pressure chlorine is a gas, bromine is a liquid and iodine is a solid.

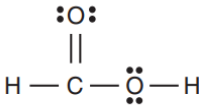
c. Pentan-1-ol boils at 137°C, whereas pentan-3-ol boils at 116°C.

d. The boiling point of sulphur dioxide is 24°C higher than that of chlorine.

30. Of the two possible valence-bond formulas for formic acid (HCO_2H), which one is the more reasonable structure?



(a)



(b)

31. Draw the correct valence-bond formula for hydrazine (N_2H_4).
32. Draw the resonance hybrid of SO_2^-.
33. Based on the VB approach, predict the shape of a ClO_3^- ion.
34. The molecular orbital description of NO is similar to that of O_2 except that the energies of the oxygen atomic orbitals are slightly lower than those of nitrogen atomic orbitals and NO molecule contains different number electrons than O_2.
35. Draw an energy diagram to show how the atomic orbitals of N and O combine to form molecular orbitals of NO.
36. How many unpaired electrons are present in the NO molecule?
37. What is the bond order in NO molecule?
38. Is NO paramagnetic or diamagnetic?
39. List the following in order of increasing O – O bond length: O_2, O_2^+, O_2^-
40. Show the direction of the bond moment (dipole moment) in each of the following bonds: N – F, N – H, N – Si, N – O

Chapter 3

Physical states of matter

3.1 Introduction

Matter is defined as anything that occupies space and has mass. It can exist in the form of gas, liquid and solid. The simplest example is the water we use in our daily life. The three physical states of water are:

- Steam, water in the form of gas.
- Water, in the form of liquid.
- Ice, water in the form of solid.

The physical state of a given sample of matter depends on the temperature and pressure. Changing these conditions or variables may change the behaviour of the substances as solids, liquids, gases or plasma

- ✓ A solid is rigid and possesses a definite shape.
- ✓ A liquid flows and takes the shape of its container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. Both liquid and solid samples have volumes that are very nearly independent of pressure.
- ✓ A gas takes both the shape and volume of its container. ¬ A fourth state of matter, plasma occurs naturally in the interiors of stars.
- ✓ Plasma is a gaseous state of matter that contains appreciable numbers of electrically charged particles. Example of plasma state: Lightning, Comet tail, Solar wind, Stars (including the Sun), Interstellar gas clouds, Welding arcs, fluorescent lights, Static electricity, Rocket exhaust etc.

3.2 The kinetic theory of matter

- ✓ The states of matter in which substances are chemically the same but physically different are explained by the kinetic theory of matter
- ✓ gives an explanation of the nature of the motion and the heat energy

- ✓ according to the theory, every substance consists of a very large number of very small particles called ions, atoms and molecules
- ✓ The motion of the particles increases with a rise in temperature
- ✓ kinetic theory of matter is based on:
  - All matter is composed of particles which are in constant motion.
  - The particles possess kinetic energy and potential energy.
  - The difference between the three states of matter is due to their energy contents and the motion of the particles.

3.3 Properties of Matter

properties of gases can be summarized.

- Gases have no definite shape and definite volume.
- Gases can be easily compressed.
- Gases have low densities compared with liquids and solids.
- Gases exert pressure in all directions.
- Gases easily flow and diffuse through one another.

Properties of Liquids

- Have a definite volume, but have no definite shape.
- Have higher densities than gases.
- Are slightly compressible.
- Are fluids.

Properties of Solids

- Solids have a definite shape and a definite volume.
- Solids generally have higher densities than gases and liquids.
- Solids are extremely difficult to compress.
- Solids are not fluids.

3.4 The gaseous state

3.4.1 The kinetic molecular theory of gases

- ✓ The particles in an ideal gas are very widely spaced and constant random motion.

- ✓ The pressure of a gas is the result of continuous collisions between the particles and the walls of their container

Assumptions of the kinetic molecular theory of gases

1. The particles are in a state of constant, continuous, rapid, random motion and, therefore, possess kinetic energy. The motion is constantly interrupted by collisions with molecules or with the container. The pressure of a gas is the effect of these molecular impacts.
2. The volume of the particles is negligible compared to the total volume of the gas. Gases are composed of separate, tiny invisible particles called molecules. Since these molecules are so far apart, the total volume of the molecules is extremely small compared with the total volume of the gas. Therefore, under ordinary conditions, the gas consists chiefly of empty space. This assumption explains why gases are so easily compressed and why they can mix so readily.
3. The attractive forces between the particles are negligible. There are no forces of attraction or repulsion between gas particles.
4. The average kinetic energy of gas particles depends on the temperature of the gas. At any particular moment, the molecules in a gas have different velocities. The mathematical formula for kinetic energy is K.E. = ½ mv^2, where m is mass and v is velocity of gas molecules. Because the molecules have different velocities, they have different kinetic energies. However, it is assumed that the average kinetic energy of the molecules is directly proportional to the absolute (Kelvin) temperature of the gas.

3.4.2 The Gas Laws

Express mathematical relationships between the volume, temperature, pressure, and quantity of a gas.

Pressure: it is the force applied per unit area.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

- ✓ Can be expressed in atmosphere, Pascal, torr, millimetre of mercury. Its SI unit is Pascal (Pa), and defined as one Newton per square metre. 1 Pa = 1 N/m^2 and

1 atm = 760 mmHg = 76 cmHg = 760 torr = 101325 Pa = 101.325 kPa

Volume: space taken up by a body. ItsSI unit is the cubic metre (m^3) and also expressed in cubic centimetre (cm^3) and cubic decimetre (dm^3). Other common units of volume are millilitre (mL) and litre (L).

$1\ cm^3 = (1\times10^{-2}\ m)^3 = 1\times10^{-6}\ m^3$

$$1\ dm^3 = (1\times10^{-1}\ m)^3 = 1\times10^{-3}\ m^3 = 1\ L$$

Temperature: degree of hotness or coldness of a body. Degree Fahrenheit (°F), degree Celsius (°C) and Kelvin (K) are temperature scales commonly used. Necessary inter-conversions are:

$$K = °C + 273$$

$$°F = \frac{5}{9} C° + 32$$

1. Boyle's Law

- ✓ analyze the relationship between the volume and pressure of a fixed amount of a gas at constant temperature.
- ✓ law states that *the volume of a fixed mass of gas is inversely proportional to the pressure at a constant temperature.* mathematically given as

$$V \ \alpha \ \frac{1}{p} \text{(at constant } T \text{ and } n\text{)}$$

From which follows,

$V = k/p$ or $PV = k$ where k — is a constant at a specific temperature for a given sample of gas.

If P_1 and V_1 represent the initial conditions; and P_2 and V_2 represent the new or final conditions, Boyle's law can be written as:

$P_1V_1 = P_2V_2$;

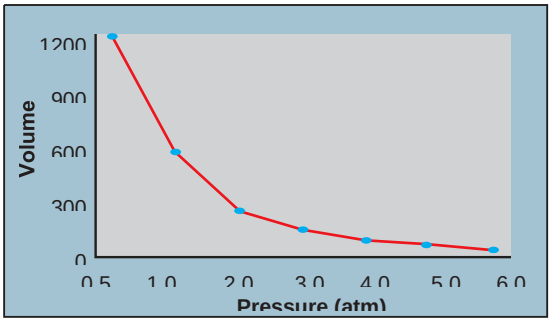


Figure 3.1 Volume versus pressure graph for a gas at constant temperature and mass.

2. Charles' law

States that the volume of a fixed mass of gas at constant pressure varies directly with the Kelvin temperature. Mathematically,

$V \alpha T$ *at constant* P *and* n:

$$V = kT,$$

The value of T is the Kelvin temperature, and k is a constant. The value of k depends only on the quantity of gas and the pressure. The ratio V/T for any set of volumetemperature values always equals the same k. Charles' law can be applied directly to volume-temperature problems using the relationship:

$$T_2\underline{V_1} = T_1\underline{V_2}$$

where V_1 and T_1 represent the initial condition; V_2 and T_2 represent the new condition.

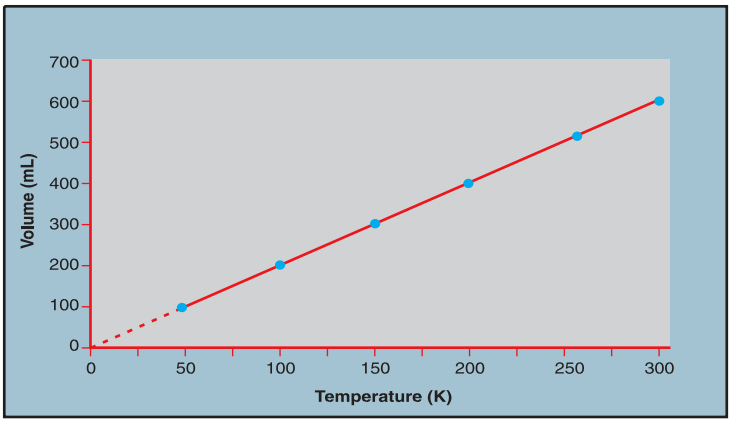


Figure 3.2 A plot of volume versus the Kelvin temperature.

Note that the ratio V/T is constant for every plot of the curve.

3. The Combined Gas Law

Expresses the relationship between pressure, volume, and temperature of a fixed amount of gas.

A sample of a gas often undergoes changes in temperature, pressure, and volume. When this happens, the three variables must be dealt with at the same time.

Derivation of the combined gas law:

Boyle's law: $V \alpha 1/P$

Charles' law: $V \alpha T$ Then, V □

T/P (*combined*)

$V = kT/P$ (where k *is a constant*)

It follows,

$$\frac{P1V1}{T1} = k \text{ and } \frac{P2V2}{T2} = k$$

Since in each case k is constant, the combined gas law equation is given as follows:

$$\frac{P1V1}{T1} = \frac{P2V2}{T2} = k$$

Where P_1, V_1 and T_1 are the initial pressure, volume and temperature; P_2, V_2 and T_2 are the final pressure, volume and temperature of the gas respectively.

Example

If a 50 cm^3 sample of gas exerts a pressure of 60.0 kPa at 35°C, what volume will it occupy at STP?

Solution:

Given V_1=50cm3, P_1 = 60kpa, T_1 =35°C=308K V_2 =?

at STP, P_2 =1atm = 101325pa = 101.325kpa, T_2 = 0°c=273K

$$\frac{P1V1}{T1} = \frac{P2V2}{T2} = \frac{60kpax50cm3}{308k} = \frac{Vx101.325kpa}{273k},$$

$$V_2 = \frac{60kpa*50cm3*273k}{T308k*101.325kp} \quad V2= 26.243cm3$$

4. **Avogadro's *law:*** states that the volume of the gas is directly proportional to the number of mole of gas, when the tempreture and pressure are held constant.

Mathematically, $V \alpha n$; where V is the volume and n is number of moles.

Common example of avogadro's law is the deflation of automobile tires.

5. **The Ideal Gas Equation**

- a hypothetical gas that obeys the gas laws. Real gases only obey the ideal gas laws closely at high temperature and low pressure.
- The ideal gas law is a combination of Boyle's law, Charles' law and Avogadro's law.

  Boyle's law: $V \alpha 1/p$ (*at constant T and n*)

  P

  Charles' law: $V \alpha T$ (*at constant P and n*)

  Avogadro's law: $V \alpha n$ (*at constant P and T*)

  This relationship indicates how the volume of gas depends on pressure, temperature and number of moles.

  $V\alpha \frac{nT}{V}$ or $V= R\frac{nT}{P}$ where R, is a proportionality constant called the gas constant.

  $$\boxed{PV = nRT}$$ the ideal gas equation

  Thus, the ideal gas equation describes the relationship among the four variables P, V, T and n. An ideal gas is a gas whose pressure-volume-temperature behavior can be completely explained by the ideal gas equation. At STP, the values of R can be calculated from the ideal gas equation.

6. *Graham's Law of Diffusion*

States that *at constant temperature and pressure, the rate of diffusion of a gas, r, is inversely proportional to the square root of its density, d, or molar mass, M.*

Mathematically it can be expressed as:

$$r \propto \sqrt{\frac{1}{d}} \quad \text{or} \quad r \propto \sqrt{\frac{1}{M}};$$

where r is the rate of diffusion, d is the density and M is the molecular mass of the gas. For two gases (Gas 1 *and* Gas 2), their rates of diffusion can be given as:

$$r_1 \propto \sqrt{\frac{1}{d_1}} \quad or \quad r_1 \propto \sqrt{\frac{1}{M_1}}$$

$$r_2 \propto \sqrt{\frac{1}{d_2}} \quad or \quad r_2 \propto \sqrt{\frac{1}{M_2}}$$

Rearranging these relationships gives the following expression

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad or \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}};$$

Where r_1, d_1 and M_1 represent the rate of diffusion, density and molecular mass of gas 1. r_2, d_2 and M_2 represent the rate of diffusion, density and molecular mass of gas 2.

The rate at which a gas diffuses is also inversely proportional to the time taken. Mathematically,

$$\mathbf{r \propto \frac{1}{t}}$$

If two different gases (gas 1 and gas 2) under the same conditions of temperature and pressure diffuse through a porous container, then the time required to diffuse for the two gases can be given by the following formula:

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

where t_1 and t_2 are the time taken, r_1 and r_2 are the rates, M_1 and M_2 are the molecular masses of Gas 1 and Gas 2 respectively

3.5 The liquid state

As in a gas, particles in a liquid are in constant motion. However, the particles in a liquid are closer together than those in a gas. The attractive forces between particles in a liquid are more effective than between particles in a gas. This attraction between liquid particles is caused by the intermolecular forces (dipole-dipole forces, London dispersion forces, and hydrogen bonding). Liquids are more ordered than gases because of the stronger intermolecular forces and the lower mobility of liquid particles. Accordingly, liquid particles are not bound together in fixed positions.

Surface tension of liquids

Surface tension is property of a liquid surface displayed by its acting as if it were a stretched elastic membrane. This phenomenon can be observed in the nearly spherical shape of small drops of liquids and of soap bubbles. Because of this property, certain insects can stand on the surface of water. A razor blade also can be supported by the surface tension of water. The razor blade is not floating: if pushed through the surface, it sinks through the water.

$$\Gamma = \frac{1}{2}\frac{x\,F}{L}$$ **Γ-surface tension, F-force, L- length**

Surface tension depends mainly upon the forces of attraction between the particles within the given liquid and also upon the gas, solid, or liquid in contact with it. The molecules in a drop of water, for example, attract each other weakly. Water molecules well inside the drop may be thought of as being attracted equally in all directions by the surrounding molecules. However, if surface molecules could be displaced slightly outward from the surface, they would be attracted back by the nearby molecules. The energy responsible for the phenomenon of surface tension may be thought of as approximately equivalent to the work or energy required to remove the surface layer of molecules in a unit area. Surface tension may be expressed, therefore, in units of energy per unit area. Water has a surface tension of 0.073 joule per square metre at 20 °C. In comparison, organic liquids, such as benzene and alcohols, have lower surface tensions, whereas mercury has a higher surface tension. An increase in temperature lowers the net force of attraction among molecules and hence decreases surface tension

Surface tension is the energy, or work, required to increase the surface area of a liquid due to intermolecular forces. Since these intermolecular forces vary depending on the nature of the liquid (e.g. water vs. gasoline) or solutes in the liquid (e.g. surfactants like detergent), each solution exhibits differing surface tension properties

Molecular Perspective

In a sample of water, there are two types of molecules. Those that are on the outside, exterior, and those that are on the inside, interior. The interior molecules are attracted to all the molecules around them, while the exterior molecules are attracted to only the other surface molecules and to those below the surface. This makes it so that the energy state of the molecules on the interior is much lower than that of the molecules on the exterior. Because of this, the molecules try to maintain a minimum surface area, thus allowing more molecules to have a lower energy state. This is what creates what is referred to as surface tension.

The water molecules attract one another due to the water's polar property. The hydrogen ends, which are positive in comparison to the negative ends of the oxygen cause water to "stick" together. This is why there is surface tension and takes a certain amount of energy to break these intermolecular bonds. Same goes for other liquids, even hydrophobic liquids such as oil. There are forces between the liquid such as Van der Waals forces that are responsible for the intermolecular forces found within the liquid. It will then take a certain amount of energy to break these forces, and the surface tension. Water is one liquid known to have a very high surface tension value and is difficult to overcome.

Cohesive and Adhesive Forces

There are several other important concepts that are related to surface tension. The first of these is the idea of cohesive and adhesive Forces. Cohesive forces are those that hold the body of a liquid together with minimum surface area and adhesive forces are those that try to make a body of a liquid spread out. So if the cohesive forces are stronger than the adhesive forces, the body of water will maintain its shape, but if the opposite is true than

the liquid will be spread out, maximizing its surface area. Any substance that you can add to a liquid that allows a liquid to increase its surface area is called a wetting agent.

Viscosity of liquids

Resistance of a fluid (liquid or gas) to a change in shape, or movement of neighboring portions relative to one another. Viscosity denotes opposition to flow. The reciprocal of the viscosity is called the fluidity, a measure of the ease of flow. Molasses, for example, has a greater viscosity than water. Because part of a fluid that is forced to move carries along to some extent adjacent parts, viscosity may be thought of as internal friction between the molecules; such friction opposes the development of velocity differences within a fluid. Viscosity is a major factor in determining the forces that must be overcome when fluids are used in lubrication and transported in pipelines. It controls the liquid flow in such processes as spraying, injection molding, and surface coating. For many fluids the tangential, or shearing, stress that causes flow is directly proportional to the rate of shear strain, or rate of deformation, those results. In other words, the shear stress divided by the rate of shear strain is constant for a given fluid at a fixed temperature. This constant is called the dynamic, or absolute, viscosity and often simply the viscosity

The unit of viscosity, accordingly, is newton-second per square metre, which is usually expressed as pascal-second in SI units.

The viscosity of liquids decreases rapidly with an increase in temperature. Thus, upon heating, liquids flow more easily. For example, the viscosities of water at 27 °C and at 77 °C are **8.5** $\times 10^{-4}$ and **3.6** $\times 10^{-4}$ pascal-second, respectively.

Inter molecular forces

The forces holding liquids together are called intermolecular forces. It is weaker than intramolecular forces (e.g. ionic, metallic, or covalent bonds)

TABLE 11.2 Melting and Boiling Points of Representative Substances

Force Holding Particles Together	Substance	Melting Point (K)	Boiling Point (K)
Chemical bonds			
Ionic bonds	Lithium fluoride (LiF)	1118	1949
Metallic bonds	Beryllium (Be)	1560	2742
Covalent bonds	Diamond (C)	3800	4300
Intermolecular forces			
Dispersion forces	Nitrogen (N_2)	63	77
Dipole–dipole interactions	Hydrogen chloride (HCl)	158	188
Hydrogen bonding	Hydrogen fluoride (HF)	190	293

The strength of these intermolecular forces is directly related to the melting/boiling points, enthalpy of fusion, enthalpy of vaporization, and solubility of the substances. The strength of these intermolecular forces is directly related to the melting/boiling points, enthalpy of fusion, enthalpy of vaporization, and solubility of the substances.

Factors Affecting Dispersion Forces

1. Number of electrons in an atom (more electrons, more dispersion force)
2. Size of atom or molecule/molecular weight
3. Shape of molecules with similar masses (more compact, less dispersion force). The shape of the molecule affects the dispersion forces: long, thin molecules (like n-pentane tend to have stronger dispersion forces than short, round ones (like neopentane). This is due to the increased surface area in n-pentane.

Types of Attractive Forces

There are several types of attractive intermolecular forces:

Dipole-dipole forces, London dispersion forces, Hydrogen bonding, and Induced-dipole forces. The first three forces are also collectively called van der Waals forces. All molecular and intermolecular attractive forces are electrostatic in nature. That is, they involve attractions between positive and negative species. The strengths of these attractive forces vary widely, though usually the intermolecular forces between small molecules are weak compared to the intramolecular forces that bond atoms together

within a molecule. All of the intermolecular forces that hold a liquid together are called **cohesive** forces.

1. Dipole-Dipole Forces

Polar molecules that have permanent dipoles are attracted to each other via electrostatic attractions. •The partial positive, δ+, end of one is attracted to the partial negative, δ−, end of the other and vice-versa. •These forces are only important when the molecules are close to each other.

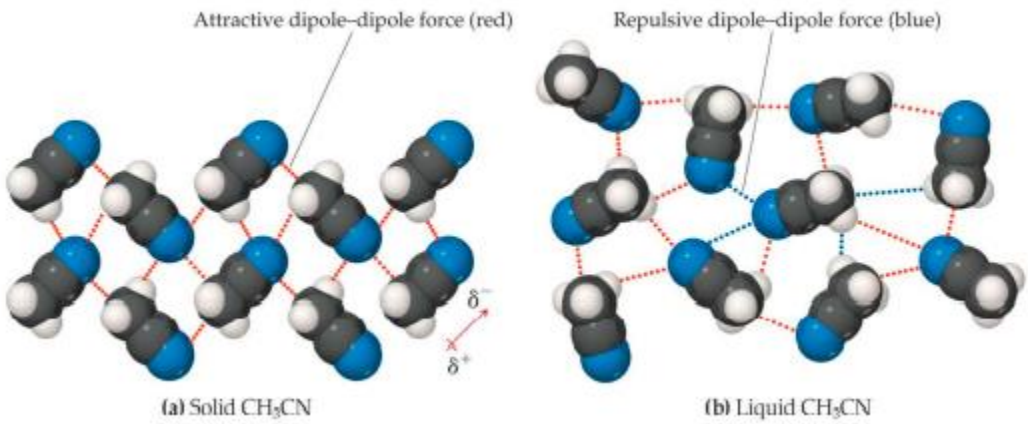


Figure 3.3 dipole forces

2. London Dispersion Forces

All molecules, including those without dipole moments, exert forces on each other. We know this because all substances, even the noble gases, change from liquid to solid state under different conditions. It act between all atoms and molecules. They are the only forces that exist between noble gas atoms and non-polar molecules.

Because dispersion forces result from temporary redistribution of the electrons causing induced dipoledipole interactions, their strength increases with the number of electrons in the interacting atoms or molecules. Hence, dispersion forces increase with atomic number or molar mass. This trend can be seen by

comparing the boiling points of gases (helium, He, and argon, Ar), (hydrogen, H_2, and oxygen, O_2), and (chlorine, Cl_2, and bromine, Br_2).

3. Hydrogen Bonding

A special form of dipole-dipole attraction, which enhances dipole-dipole attraction. It is a particular type of intermolecular force arising when a hydrogen atom is bonded to highly electronegative elements, fluorine, oxygen and nitrogen.

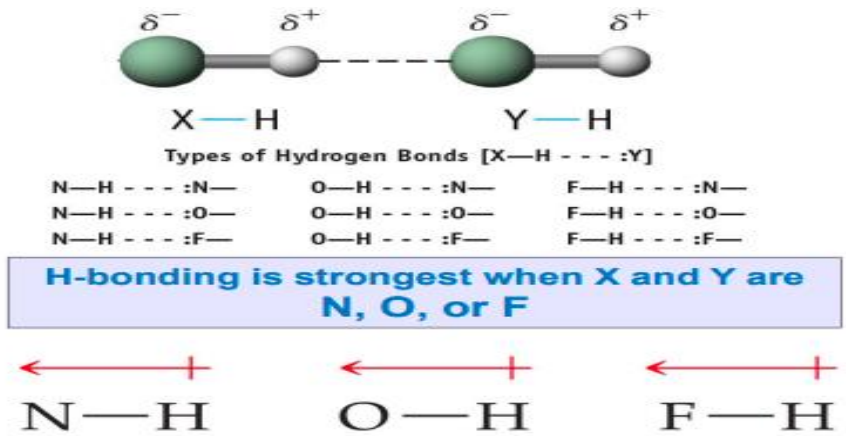


Figure 3.4 hydrogen bonding

Hydrogen bonding in ice results in an ordered, open arrangement. Density of ice at 0 °C is 0.917 g/mL vs liquid water at 0 °C is 1.00 g/mL

3.6 The solid state

3.6.1 classification of solids

Based on their crystal structures, solids can be classified into the following categories:

1. Crystalline solids(true solids)

The solids featuring highly ordered arrangements of their particles (atoms, ions, and molecules) in microscopic structures are called crystalline solids. These ordered microscopic structures make up a crystal lattice that accounts for the structure of the solid at any given point. Examples of crystalline solids include salt (sodium chloride), diamond, and sodium nitrate.

Crystalline solids consist of atoms, ions, and molecules arranged in a strongly ordered microscopic arrangement in consistent and repeated three-dimensional structures, forming a crystal lattice that stretches in any direction. What are the 7 types of crystals? Seven crystal structures are available in total: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic.

Geometry:

Crystalline Solids – Particles are arranged in a repeating pattern. They have a regular and ordered arrangement resulting in a definite shape.

Amorphous Solids – Particles are arranged randomly. They do not have an ordered arrangement resulting in irregular shapes

Melting Points

Crystalline Solids – They have a sharp melting point

Amorphous Solids – They haven't sharp melting points. Tends to soften gradually over a temperature range

Heat of Fusion: (The change in enthalpy when a substance is heated to change its state from solid to liquid.

Crystalline Solids – They have a definite heat of fusion.

Amorphous Solids – They do not have definite heat of fusion

Cleavage Property

Crystalline Solids – When cutting with a sharp edge, the two new halves will have smooth surfaces

Amorphous Solids- When cutting with sharp edge, the two halves will have irregular surfaces

Rigidity:

Crystalline Solids – They are rigid solids and applying mild forces will not distort its

shape.

Amorphous Solids – They are not rigid, so mild effects may change the shape

2. **Amorphous solids (Pseudo – Solids or super-cooled liquids)**

The solids in which the particles are not arranged in any specific order or the solids that lack the overall order of a crystal lattice are called amorphous solids.

The term ‘amorphous’, when broken down into its Greek roots, can be roughly translated to “without form”. Many polymers are amorphous solids. Other examples of such solids include glass, gels, and nanostructured materials.

In compounds like coal and charcoal, carbon also occurs as an amorphous, or “shapeless,” form. Allotropes are called varying variants of the same substance.

However, crystalline solids can be further classified into molecular, ionic, metallic, and covalent solids. A brief introduction to the classification of solids is provided in this article. Classification of Solids – Crystalline and Amorphous Solids

Crystalline solids are made of stone, wood, paper and cloth. Such solids consist of atoms arranged in a particular fashion. The transition to liquid, called melting, is sharp and transparent as crystalline solids are heated. Amorphous solids are made of rubber, glass, and sulphur.

3.7 Phase transition in solids

A phase is any part of a system that has uniform composition and properties. A state of matter represents a phase. Most solid substances undergo two changes of state when heated. A solid change to a liquid at the melting point, and the liquid changes to vapor at the boiling point. To understand this consider the heating curve for a substance given in Figure 3.5. A heating curve is a plot of temperature verses the uniform addition of heat. This can be illustrated for a hypothetical substance, in which the temperature of the substance is on the vertical axis and the passage of time during which heat is added to the substance is on the horizontal axis. Figure 3.5 shows the changes in the temperature and

phases of a pure substance as it is heated, beginning with a solid and continuing to the gaseous state as described.

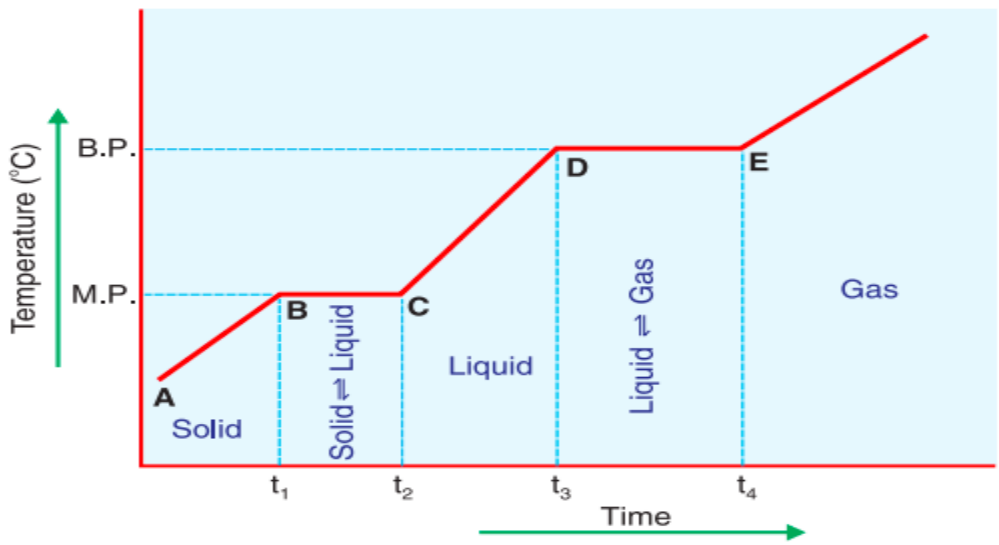


Figure 3.5 Heating curve.

Initially, the substance exists in the solid state, and the addition of heat increases its temperature. When the solid is heated, its temperature rises (A to B) until it reaches the melting point (point B), and the temperature remains constant (B to C) until all the solid is converted to a liquid (point C). The added heat energy is used to break the intermolecular forces, thus disrupting the solid structure. At point C phase change is completed. Once melting is completed, heating of the liquid raises its temperature (C to D) until the boiling point is reached at point D. In region (D to E) the addition of heat is utilized to break the intermolecular forces of the liquid to change it to a gas.

Unit four

4. SOLUTIONS

4.1 Introduction

Solution is a homogeneous mixture in which no settling occurs and in which solute particles are at the molecular or ionic state of subdivision. Solutions have no fixed

composition. However, the components of solution should be distributed uniformly throughout the entire solution A **homogeneous mixture** is a mixture, in which the composition of the mixture is the same throughout, i.e., it has no visible boundaries because the components are mixed as individual atoms, ions and molecules. Example: air, sugar solution, salt solution, alloys, soft drinks (pepsi, coca cola, etc.), gasoline and so on.

There are two components of a solution: solute and solvent. A solute is a component of a solution present in a smaller amount than the solvent. A solvent is either a components of solution that is present in a large amount or the component that determines the physical state of the solution.

4.2 Types of solutions

A typical solution consists of at least two components;

- **solute:** substance being dissolved; present in smaller or lesser amount
- **solvent:** substance doing the dissolving; present in larger amount

Solutes and solvents may be of any form of matter: solid, liquid or gas. Therefore, solutions may exist in any of the three states of matter. In general, the physical state of the solvent determines the physical state of the solution.

Type of solutions	State of solute	State of solvent	State of solution	Examples
Gas in gas	Oxygen (g)	Nitrogen (g)	Gas	Air
			Gas	Natural gas
Liquid in gas	Water (l)	Carbon dioxide(g)	Gas	
Solid in gas			Gas	
Gas in liquid	Carbon dioxide (g)	Water (l)	Liquid	Soda water
Liquid in liquid	Acetic acid (l)	Water (l)	Liquid	Vinegar
			Liquid	Gasoline
Solid in liquid	Salt (s)	Water (l)	Liquid	Seawater
	Sugar (s)	Water (l)	Liquid	Sugar solution
Gas in solid	Hydrogen (g)	Palladium (s)	Solid	H_2 in Pd
	Hydrogen (g)	Platinum (s)		H_2 in Pt
Liquid in solid	Mercury (l)	Silver (s)	Solid	Dental amalgam
Solid in solid	Zinc (s)	Copper (s)	Solid	Brass
	Lead (s)	Tin (s)	Solid	Solder

PROJECT

Do you know how jewellery gold is made?

Your teacher will arrange a visit to the nearby goldsmith. Ask the following questions during your visit to the goldsmith:

a. How is jewellery made from gold?
b. What are the possible components, other than gold present in the jewellery?
c. Which component is present in large quantity?
d. What is the advantage of mixing gold with other materials?
e. Can you separate the components present in the jewellery?
f. How purity of gold assessed and what is the unit of measuring the purity?
g. Write a report about what you have observed during your visit and present it to the class.

Exercise 4.1

Instruction: Choose the correct answer from the alternatives given and circle the letter of your choice.

1. What is the solvent in 70 % alcohol solution? (UEE, 2008)

   A) Water B) Alcohol C) Sugar D) Kerosene

2. Which of the following types of solutions are possible? (UEE, 2002)

   I. solid dissolves in a liquid II. Gas dissolved in a liquid

   III. Gas dissolved in a gas IV. Solid dissolved in a solid

   A) I and II B) I, II, III and IV C) I, II and IV D) I

3. Which of the following is NOT a solution? (UEE, 2004)

   A) Milk B) Brass C) Whisky D) Coca cola drink

4. What percent is gold in 18 karat gold? (UEE, 2003)

   A) 18 B) 09 C) 25 D) 75

5. What kind of solution forms when gasoline evaporates in air? (UEE, 2008)

   A) Gas in gas solution B) Gas in liquid solution

   C) Liquid in liquid solution D) Liquid in gas solution

6. Give two examples of:

   a. gas-gas solution
   b. gas-liquid solution
   c. liquid-liquid solution
   d. solid-liquid solution

4.3 The solution process

4.3.1 Liquid solutions and inter-particle force of attractions

What are the major factors that affect the solubility of substances in liquid solvents?

When a solute dissolve in a solvent, particles of the solute disperse throughout the solvent. The solute particles occupy positions that are normally taken by solvent molecules i.e., particles of the solute mix with particles of the solvent. The tendency to mix is affected by the relative strengths of three types of interaction. These are:

- Solvent-solvent interaction
- Solute-solute interaction
- Solvent-solute interaction

For simplicity, we can imagine the solution process taking place in three distinct steps.

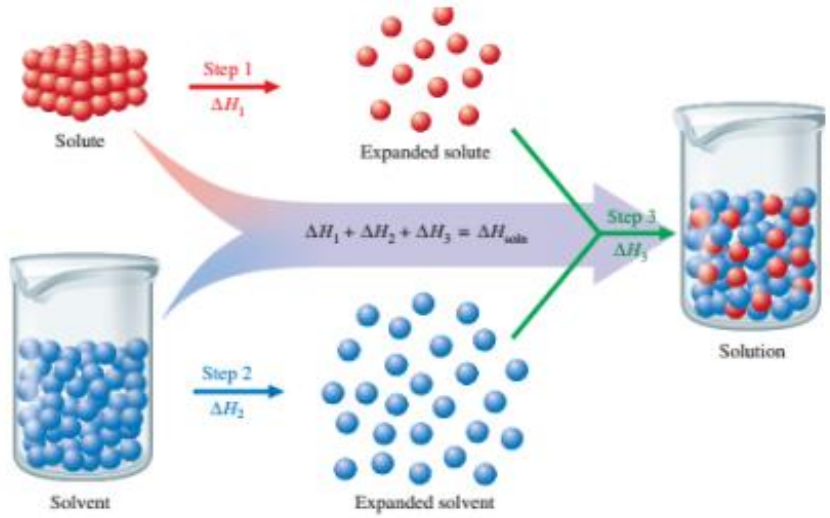


Figure 4.1 A molecular view of the solution process, portrayed as taking place in three steps

Step 1: is the separation of solvent molecules from each other to "make room" for the incoming solute particles and

Step 2: is the separation of solute molecules. These steps require energy input to break attractive intermolecular forces; therefore, they are endothermic.

Step 3: the solvent and solute molecules mix. This process can be exothermic or endothermic.

Strong forces of attraction between solute particles (solute-solute interactions) or between solvent particles (solvent-solvent interactions) tend to keep like particles close together and reduce the solubility of solute in the solvent. On the other hand, strong attraction forces between solute and solvent particles (solute-solvent interactions) makes dissolving easier and helps to keep particles in solution.

Activity: Ethanol mixes with water but oil does not. Why?

The saying "**like dissolves like**" is helpful in predicting the solubility of a substance in a given solvent.

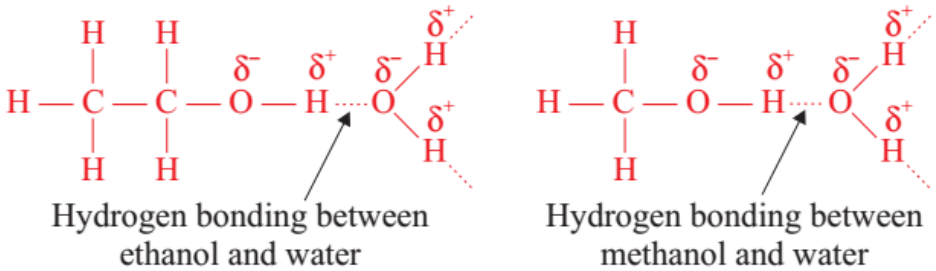
Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature.

"**Like dissolves like**" principle states that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. This is because the

forces between the solute molecules are replaced by the forces between the solute and solvent molecules.

For example: carbon tetrachloride and benzene

Water is the most prominent solvent. This is because it is common and it dissolves a large number of ionic and polar substances. Water molecules are strongly associated with each other through hydrogen bonding. Compounds that form hydrogen bond such as certain alcohols tend to be soluble in water. **Examples**: methanol, ethanol and 1, 2-ethylene glycol



If a compound has both polar and non-polar components, it may dissolve in both polar and non-polar solvents.

For example: Acetic acid, CH_3COOH, is a liquid that forms hydrogen bonds with water. It is fully miscible with water. Acetic acid also dissolves in non-polar solvents, such as benzene and carbon tetrachloride, because the CH_3 component is non-polar.

- Fluids that mix with or dissolve in each other in all proportions are said to be **miscible fluids.**
- If two fluids do not mix but, rather, form two layers, they are said to be **immiscible fluids**.

For example: acetone is miscible in water where as gasoline, which is a mixture of hydrocarbons, is immiscible with water.

Exercise 4.2

Instruction: Choose the correct answer from the alternatives given and circle the letter of your choice.

1. Which of the following is most likely to be miscible in carbon tetrachloride, CCl_4? (UEE 2001)

A) Na_2CO_3 B) CH_3F C) $(CH_2)_4O_2$ D) I_2

2. What would be the solubility of $HOCH_2(CH_2)6CH_2OH$ compared to $CH_3(CH_2)_6CH_2OH$? (UEE, 2005)
   A. A) Less soluble in water
   B. More soluble in water
   C. The same solubility in water
   D. More soluble in a non-polar solvent such as dichloro ethane
3. The dissolution of water in octane (C_8H_{18}) is prevented by (UEE, 2007)
   A) Dipole-dipole attraction between octane molecules

B) Hydrogen bonding between water molecules

   C) London dispersion forces between octane molecules

D) Repulsion between like charged water and octane molecule

4. Gasoline and water do not mix because gasoline is (UEE, 2000)
   A. Less dense than water
   B. Volatile
   C. Less viscous than water
   D. Nonpolar
5. Which of the following compounds is likely to be more soluble in water: C_4H_9OH or C_4H_9SH? Explain.
6. Would boric acid, $B(OH)_3$, be more soluble in ethanol, C_2H_5OH, or in benzene, C_6H_6?
7. Would naphthalene, $C_{10}H_8$, be more soluble in ethanol, C_2H_5OH, or in benzene, C6H6?
8. Arrange the following substances in order of increasing solubility in hexane, C_6H_{14}: CH_2OHCH_2OH, $C_{10}H_{22}$, H_2O.
9. Indicate which of the following is more soluble in ethanol, C_2H_5OH: acetic acid, CH_3COOH, or stearic acid, $C_{17}H_{35}COOH$.

Solutions of Solids in Liquids

Activity 4.1

Take two containers and add water to both. Put table salt in the first container and table sugar inthe second container and stir.

a. What did you observe?

b. Did both solids dissolve in water?

Repeat the same procedure using oil instead of water.

c. What did you observe?

d. Did both solids dissolve in oil?

Solids that are made up of polar molecules or ions are not soluble in non-polar solvents. The interaction between the polar solid and the non-polar liquid is weak compared to the interaction within the solid. Therefore, the solute and solvent particles do not mix. For example sugar which has molecules that are likely bound together by hydrogen bonding is not soluble in solvents like oil. Sugar does dissolve in water though.

Why does sugar dissolve in water, but not in oil?

Sugar dissolves in water because the water molecules attract the sugar molecules in the same way that the sugar molecules attract each other. Both of these substances are polar.

The Sugar does not dissolve in the oil because the sugar is polar but the oil is non-polar. The interaction between these two substances is weaker than the interaction within sugar molecules.

Solids containing crystals held together by London forces can dissolves somewhat in non-polar solvents.

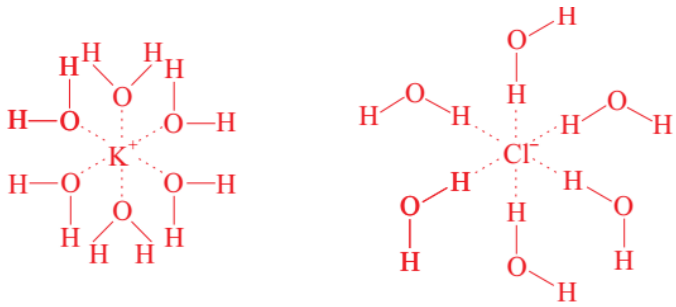
However, they do not dissolve in polar solvents. For the same reason non-polar liquids do not dissolve in polar solvents.

Water as well as other polar molecules is attracted to ions.

The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These are important in the dissolution of ionic compounds in water.

When ionic compounds dissolve in water, the ions in the solid separate because they are surrounded by water molecules. The water molecules penetrate the compounds and surround the individual components.

This reduces the strong inter-ionic forces that bind the ions together. This allows them to move into the solution as hydrated ions. Thus, when a solute particle becomes surrounded by solvent molecules, we say that it is solvated. When the solvent is water we call the process hydration. This image shows a potassium chloride (KCl) molecule being solvated or hydrated.



Solvation is the process of surrounding a solute particle with solvent particles. When the solvent is water the process is called **hydration**.

4.3.2 The Rate of Dissolution

Dissolution is the process of dissolving a solute in a solvent to form a solution.

Solute + solvent ⟶ solution

The rate of dissolution is the speed with which a solute goes into solution. This largely depends upon the inter-particle forces and to a lesser extent, on conditions such as the surface area of the solid solute, the temperature and the pressure of the system.

Inter-particle force is the extent to which solvent molecules interact with particles of the solute. When the solvent-solute interactions are stronger than those between solute-solute and solvent- solvent particles, the dissolution process becomes easier.

Increasing surface area will increase the rate of dissolution because it increases the number of solute particles in contact with the solvent.

4.3.3 Energy Changes in the Solution Process

Heat of Solution

The heat of solution of an ionic compound in water is the sum of the lattice energy of the compound and the heat of hydration. The relative magnitudes of these two quantities determine whether the solution process is endothermic or exothermic.

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{hydration} + \Delta H_{Lattice\ energy}$$

ΔH_{soln} value may be exothermic or endothermic, depending on the substance involved. For instance, the ΔH_{soln} value for: $CaCl_2$ (s) is -81.3 kJ/mol and NH_4NO_3(s) is +25.7 kJ/mol

Hydration of Ionic Solids in Water

Activity 4.2

Discuss the following questions and write a report. Present your report to the class.

1. How do you compare the hydration of the ions of Group I metals with that of Group II metals? Give reasons.
2. Compare the solubility of $Mg(OH)_2$ with $Ba(OH)_2$, $MgSO_4$ with $BaSO_4$. Justify your answers in terms of lattice energy and hydration energy.

Hydration of ions favors the dissolution of an ionic solid in water. The ions in an ionic crystal are very strongly attracted to one another. Therefore, the solubility of an ionic solid depends not only on the energy of the hydration of ions, but also on lattice energy, which are the energy holding ions together in the crystal lattice.

- The energy required to completely separate one mole of a solid ionic compound into gaseous ions is called **lattice energy, $\Delta H_{Lattice\ energy}$**. It is always a positive quantity.

$$\text{energy} + NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$$

- The enthalpy change associated with the hydration process is called the **heat of hydration,**

ΔH_{hydr}. It is always a negative quantity.

$$Na^+(g) + Cl^-(g) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq) + \text{energy}$$

Lattice energy works against the solution process, so an ionic solid with relatively large lattice energy is usually insoluble. Lattice energies depend on the charge on the ions and also the distance between the centers of the neighboring positive and negative ions.

- As the charge of the ions increases, the lattice energy increases. For example, the energy of hydration is greater for Mg^{2+} than for Na^{+}

MgO has greater lattice energy than NaCl

- As the size of the ions increases, the lattice energy decreases

Note: Overall as we go down in a group, ionic radius increases and lattice energy decrease. In a period from left to right as the charge on ion increases, lattice energy increases.

- The magnitude of lattice energies depends predominantly on the ionic charges because ionic radii vary over only a limited range.

The energy of hydration also depends on:

- ionic radius, the energy of hydration is greatest for a small ion
- charge on the ion, the energy of hydration increases with the charge on the ion

Solved problems

1. Arrange the following ionic compounds in order of increasing lattice energy: NaF, CsI, and CaO.

   Solution: CsI < NaF < CaO

   Consider the dissolution of sodium chloride (NaCl) in water.

   $$NaCl(s) \xrightarrow{H_2O} Na^{+}(aq) + Cl^{-}(aq)$$

   Given that: $\Delta H_{LE} = 788$ KJ and $\Delta H_{hydr} = -784$ KJ, what is the heat of solution?

   $$\Delta H_{soln} = \Delta H_{hydration} + \Delta H_{Lattice\ energy} = -784\ KJ + 788\ KJ = 4\ KJ$$

   Therefore, when 1 mole of NaCl dissolves in water 4 kJ of heat will be absorbed from the surroundings.

2. What is the relationship between solvation and hydration?
3. Solvation can be the same as hydration if the solvent used for the solution process is water. If the solvent is not water, we use the term solvation to describe the process in which solvent molecules surround solute particles.
4. Sodium carbonate is soluble in water, while calcium carbonate is insoluble. Why?

   Answer: Because the lattice energy of calcium carbonate $CaCO_3$ is higher than that of Na_2CO_3. Thus, $CaCO_3$ is less soluble than Na_2CO_3.

5. Which ion in each pair has the larger heat of hydration?

Na^+ or Cs^+ b) **O^{2-}** or F^- c) **Na^+** or Cl^-

Exercise 4.3

Instruction: Choose the correct answer from the alternatives given and circle the letter of your choice.

1. What is the most important type of solute-solvent interaction in a solution of CaCl2 in water? (UEE 2003 E.C)

   A) Dipole-dipole B) Dispersion forces

   C) Hydrogen bonding D) Ion-dipole

2. Which of the following is the most important type of solute-solvent interaction in a solution of n-butanol in water? (UEE, 2005)

   A) Dispersion B) Ion-dipole C) Dipole-dipole D) Hydrogen bonding

3. What type of solute-solvent interactions should be the most important in a solution of iodine in carbon tetrachloride? (UEE, 2007)

   A) London forces B) Ionic bonding C) Ion-dipole forces D) Dipole-dipole forces

4. Which of the following ionic compounds has the greatest lattice energy? (UEE, 2007)

   A) LiF B) LiCl C) LiBr D) LiI

5. The exothermic step in the dissolution of a salt in water is (EHEECE, 2003)

   a. Separation of the salt into ions in gaseous state
   b. Separation of the water molecules
   c. Hydration (salvation) of the ions from the salt
   d. Separation of the salt into ions in gaseous state and separation of the water

6. Indicate the type of solute-solvent interaction that should be most important in each of the following solutions:

   a. $AgNO_3$ in water
   b. Ammonia in water
   c. Bromine in CCl_4
   d. KBr in water
   e. NaOH in water

f. Sugar in water

g. Toluene in cyclohexane

7. The rate of dissolution largely depends on inter-particle forces. What other factors influence the rate of dissolution?
8. Which of the following ions would be expected to have the greater energy of hydration?

   a) Mg^{2+} or Al^{3+} b) F^- and Cl^-

4.4. SOLUBILITY

Solubility is defined as the maximum amount of a solute that will dissolve in a given amount of solvent at a specified temperature. Solubility is a characteristic property of a specific solute–solvent combination, and different substances have greatly differing solubility. Usually, it is expressed as the amount of solute in gram that dissolves in 100 ml of water.

Example

a) The solubility of NaCl is 39.12 g /100 mL of water at 100°C

b) The solubility of AgCl is 0.0021 g /100 mL water at 100°C

Factors Affecting Solubility

"The solubility of a solute is the number of grams of the solute necessary to saturate 100gm of the solvent at that particular temperature. There are three main factors that control solubility of the solute.

(1) Temperature

(2) Nature of solute or solvent

(3) Pressure

Effect of Temperature on Solubility

The solubility of most molecular and ionic solids increases with temperature, although some are almost unchanged, and some decrease.

In endothermic process solubility increases with the increase in temperature and vice versa

❖ For a solute with $\Delta H_{soln} > 0$:

solute + solvent + heat → Saturated solution

☞ Solubility increases with temperature. For instance, solubility of potassium nitrate increases with the increase in temperature

In exothermic process solubility decreases with the increase in temperature

- For a solute with ΔHsoln < 0:

Solute + Solvent → Saturated solution + heat

☞ Solubility decreases with temperature.

For example solubility of sodium sulphate decreases with the increase in temperature, fig. 4.2

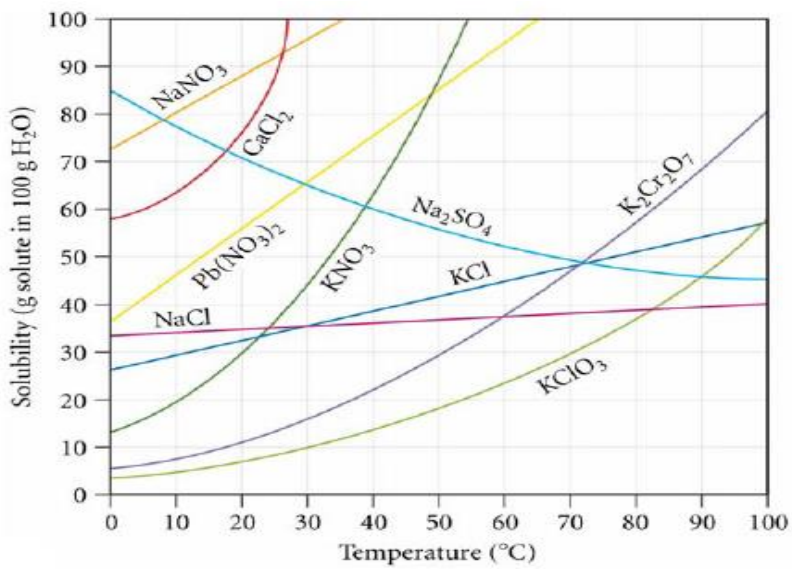


Fig 4.2. Solubility vs temperature of some salts

Solubility of Gases in Water:

Gases are more soluble in cold solvent than in hot solvent (see fig 4.3). Gases become less soluble at higher temperatures.

Example.

- Soft drinks become "flat" as they warm up and lose carbon dioxide.
- Aquatic life is affected by decreasing amounts of dissolved oxygen as a result of thermal pollution.

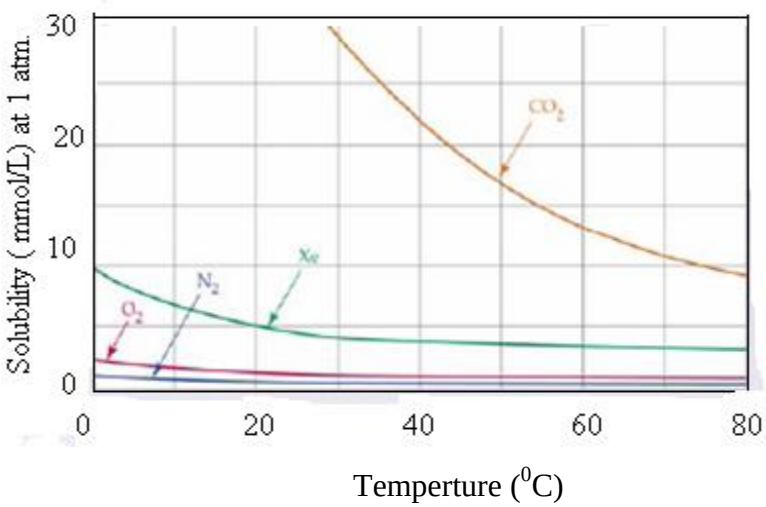


Fig 4.3. Solubility vs temperature of some gas

In general,

- for most exothermic solution processes, solubility decreases with an increase in temperature
- for most endothermic solution processes, solubility increases with an increase in temperature

Nature of Solute and Solvent

Solubility of a solute in a given solvent depends purely on the nature of both the solute and solvent. A polar solute dissolves in a polar solvent whereas a polar solute has low solubility in non-polar solvent.

Liquids that mix with each other in all proportion are said to be completely **miscible** with each other. Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attraction or hydrogen bonding of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence the two kinds of molecules mix easily.

Two liquids that do not mix are called **immiscible**. When two immiscible liquids are poured in to the same container, two layers are formed. Immiscibility occurs when either the solvent or solute is non polar and the other is polar or vice versa.

Gasoline, carbon disulfide, benzene, Carbon tetrachloride, and many other non-polar liquids are immiscible with water (polar liquid).There is no effective attraction between the molecules of such non-polar liquids and polar water molecules.

Non-polar liquids may be miscible with each other because of the absence of appreciable tendency of attraction between molecules of similar kind or molecules of another non polar liquid.

Polar molecules are soluble in polar solvent and non-polar molecules in non-polar solvent (like dissolves like).

There are still partially miscible liquids. Liquids, such as ether and water or bromine and water, are said to be **partially miscible.** The two partially miscible liquids usually form two layers when mixed. The general rule in solubility is that "**like dissolves like".**

Hydrogen bonds- substances with O—H and N—H bonds are often soluble in water because of H-bonding

Dipole-dipole forces -polar solutes interact well with polar solvents through attraction of partial charges.

Ion - induced dipole forces- responsible for the attraction between Fe^{2+} and O_2 molecules in the bloodstream.

Dipole - induced dipole forces are responsible for the solvation of gases (nonpolar) in water (polar).

London (dispersion) forces -the principal attractive force in solutions of nonpolar substances (e.g. petroleum).

Activity: Decide whether the following liquids are miscible, immiscible or partially miscible

Mixture	Conditions
Methanol + Water	
Hexane + water	
Hexane+ Benzene	
Iodine + Carbontetrachloride	
Iodine	

Effect of pressure on solubility

Pressure has little effect on the solubility of solids and liquids, but has a large effect on the solubility of gases. An increase in pressure increases solubility of a gas in a liquid. At a given pressure, there is equilibrium between the gas which is dissolved in the solution and the gas in the vapor phase. If the pressure increases, more gas dissolves to reduce the "extra" pressure; the new equilibrium is established with more gas dissolved. . For example, carbon dioxide is filled in soft drink (such as coca cola, Pepsi, 7up, etc.) under pressure

When you open the bottle of carbonated beverage, the pressure decreases and some gases escape from the solution. This escape of bubbles of a gas from a liquid is known as **effervescence.** It occurs due to decrease in pressure.

All gases become soluble in a liquid at a given temperature when the partial pressure of the gas over the solution is increased. The solubility of gas is governed by Henry's law.

Henry's law states that the solubility of a gas (S_{gas}, in mol/L) is directly proportional to the partial pressure of the gas (P_{gas}, in atm) over the solution.

$$S_{gas} = k_H P_{gas}$$

Where, k_H is Henry's law constant and it is unique to every gas, at a given temperature, with units of **mol L^{-1} atm^{-1}.**

This expression can be rearranged to deal with changing solubility and pressure

$$\frac{S_1}{P_1} = \frac{S_2}{P_2} = k_H$$

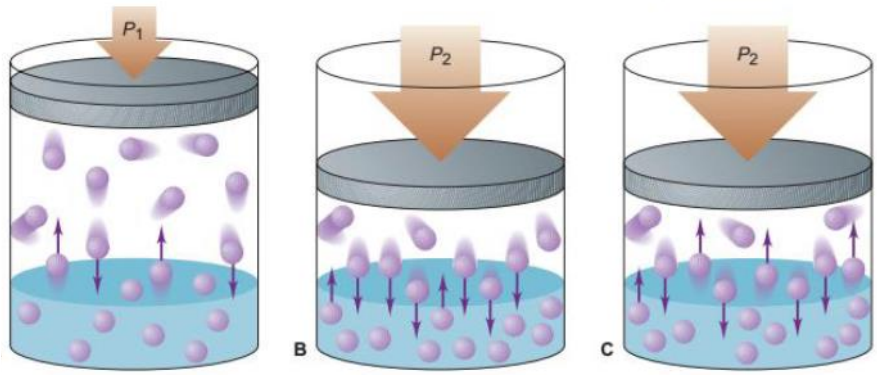


FIGURE 4.4 The effect of pressure on gas solubility

Table 4.1 Henry's law constants for some gases in water at 25^0C

Gas	K_H (M/atm)
O_2	$1.3x10^{-3}$
N_2	$6.1x10^{-4}$
CO_2	$3.4x10^{-2}$
NH_3	$5.8x10^{2}$
He	$3.7x10^{-4}$

Example:

Calculate the solubility of oxygen in water at 25^oC for a partial pressure of 0.22 atm.

Solution: - From table 2.3, the value of solubility constant for oxygen is 1.3x10-3mol//L.atm. Then, the Solubility of oxygen is

$$S_{O_2} = k_H.P_{O2}$$

$$= 1.3x10^{-3}mol/L.atmx0.22\ atm.$$

$$= 2.86x10^{-4}\ mol/L$$

Example:

1. The partial pressure of carbon dioxide gas inside a bottle of mineral water is 4 atm at 25°C. What is the solubility of CO_2? The Henry's law constant for CO_2 dissolved in water is 3.3×10^{-2} mol/Latm at 25°C.

   Solution: C_{CO2}=KH P_{CO2}=3.3×10^{-2}molL atm⁄×4 atm = 0.1molL/L

2. Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm.

   Solution: C_{O2}=KH P_{O2}=1.23×10^{-3} molL atm/ × 0.22 atm = 2.706×10^{-4}molL⁄

Exercise 4.4

Instruction: Choose the correct answer from the alternatives given and circle the letter of your choice.

1. Which law relates the concentration of a dissolved gas, Cg, to its partial pressure? (UEE 2004)

   A) Henry's law B) Raoult's law

   C) Boyle's law D) Ideal gas law

2. Which of the following is **NOT** correct? (UEE, 2003)

   a. Addition of a strongly solvated solute decreases the solubility of a gas in liquid

   b. For solid dissolved in liquid that is exothermic, increase in temperature increases the solubility

   c. The solubility of a substance is its concentration in the saturated solution

   d. For solution to occur solvent-solute attractions must overcome solute-solute and solvent-solvent attractions

3. The solubility of oxygen gas in wter at 25°C and 1.0 atm pressure of oxygen is 0.04 g/L. the solubility of oxygen in water at 3.0 atm and 25°C is _____ g/L. (UEE, 2007)

   A) 0.014 B) 0.31 C) 0.041 D) 0.123

4. Which of the following does NOT affect the solubility of a gas dissolved in a liquid?(2008)

   A. Nature of solute and solvent C. Pressure

   B. Temperature D. Rate at which the gas dissolves

4.5. SOLUBILITY AS AN EQUILIBRIUM PROCESS

Activity 4.3

Form a group and perform the following activity.

i. Pour 50 mL water in a beaker.

ii. Add some crystal of Na_2SO_4 into the water using spatula and stir until it dissolves.

What do you call this type of solution?

iii. Continue adding more and more Na_2SO_4 stirring to dissolve.

What do you observe after addition of large amount of solute?

iv. Filter the undissolved solute. Collect the filtrate or the solution.

Why does the solute remain undissolved?

What is the name of such a solution?

v. Add some more solute to the filtrate and stir.

Does the additional solute dissolve?

Discuss your findings with the rest of the class.

Since solutions are mixtures of two or more substances they are not governed by the law of constant composition. Hence, one can make solutions of different concentrations from the same solute and solvent. So, solutions can be unsaturated, saturated or supersaturated. When an ionic solid dissolves, ions leave the solid and become dispersed in the solvent. Some dissolved ions collide occasionally with the undissolved solute and recrystallize. As long as the rate of dissolving is greater than the rate of recrystallizing, the concentration of ions rises. Eventually, given enough solid, ions are dissolving at the same rate as ions in the solution are recrystallizing. At this point, even though the dissolving and recrystallizing continue, there is no further change in the concentration with time. The system has reached equilibrium; that is, excess undissolved solute is in equilibrium with the dissolved solute:

$$\textbf{Solute (Undissolved)} \rightleftharpoons \textbf{Solute (dissolved)}$$

This solution is called saturated. Therefore, Chemists also characterize solutions by their capacity to dissolve a solute as

- Saturated

- Unsaturated and
- Supersaturated

✓ A saturated solution contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature; the dissolved and undissolved solutes are in dynamic equilibrium. Or a solution that is in equilibrium with respect to a given dissolved substance.

✓ An unsaturated solution contains less solute than it has the capacity to dissolve. Or a solution not in equilibrium with respect to a given dissolved substance and in which more of the substance can dissolve.

✓ A supersaturated solution is a solution that contains more dissolved substance than a saturated solution does.

- Honey is an example of naturally occurring supersaturated solution. It contains glucose, as a solute, and water, as a solvent. If honey is left to stand, the glucose eventually crystallizes.

Supersaturated solutions are not in equilibrium with the solid substance. If a small crystal of ionic solid is added to a supersaturated solution, the excess immediately crystallizes out.

❖ Crystallization is the process in which dissolved solute comes out of solution and forms crystals. Adding small crystals to a supersaturated solution to crystallize out the excess is called seeding.

Activity 4.4

Prepare a saturated solution of sodium thiosulphate ($Na_2S_2O_4$) in beaker containing 50 mL water. Heat the solution so that extra amount of solute dissolves. Filter and divide the solution into two parts in two different beakers. Keep both the solutions to cool slowly undisturbed. After cooling stir one of the solutions and observe what happens. Drop a small grain of crystal in the second one and observe the result.

a. What is the name of such a solution that is made by cooling concentrated solution?
b. What happens when the solution was stirred?
c. What about the solution to which a crystal grain is dropped? Why?
d. What did you understand from the activity?

Exercise 4.4

Instruction: Choose the correct answer from the alternatives given and circle the letter of your choice.

5. The solubility of sodium selenate, $Na_2S_2O_4$, is 84 g/100 g of water at 35°C. If a solution is obtained by dissolving 92 g of $Na_2S_2O_4$ in 200 g of water at 35°C, what do you call this solution? (UEE, 2004)
   A. Diluted B. Saturated C. Unsaturated D. Supersaturated

6. A tiny crystal of solid sodium acetate is added to three aqueous solutions of sodium acetate. Classify each original solution as saturated, unsaturated, or supersaturated.
   a) The added sodium acetate just sits there.
   b) The added sodium acetate causes more solid sodium acetate to form.
   c) The added sodium acetate dissolves.

7. You are given three bottles containing aqueous solutions of X one saturated, one unsaturated and one supersaturated. How can you identify which solution is which?

4.6 WAYS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

The concentration of a solution is the amount of solute present in a given quantity of solution. Chemists use several different concentration units, each of which has advantages as well as limitations. Example, mass percentage, ppm and ppb, mole fraction, molarity, normality and molality.

4.6.1 Mass Percentage, ppm and ppb of Solute

Percent by mass

The percent by mass, also called percent by weight or weight percent, is the ratio of the mass of a solute to the mass of the solution, multiplied by 100.

$$\% \text{ by mass of solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \text{X } 100\%$$

Example 1:

A solution is made by dissolving 13.5 g of glucose, $C_6H_{12}O_6$, in 0.100 kg of water. What is the mass percentage of solute in this solution?

Solution

$$\% \text{ by mass of glucose} = \frac{\text{mass of glucose}}{\text{mass of solution}} \text{X } 100\%$$

$$\% \text{ by mass of solute} = \frac{13.5\text{g}}{13.5\text{g} + 100\text{g}} \text{X } 100\%$$

$$= 11.9\%$$

(b) How would you prepare 425 g of an aqueous solution containing 2.40% by mass of sodium acetate, $NaC_2H_3O_2$?

Solution: The mass of sodium acetate (solute) in 425 g of solution is

$$\% \text{ by mass of } NaC_2H_3O_2 = \frac{\text{mass of sodium acetate}}{\text{mass of solution}} \text{X } 100\%$$

$$\text{Mass of } NaC_2H_3O_2 = \frac{\text{\% by mass of NaC2H3O2 x mass of solution}}{100\%}$$

$$\text{Mass of } NaC_2H_3O_2 = \frac{2.40\% \text{ x } 425\text{g}}{100\%}$$

$$= 10.2\text{g}$$

Therefore, the quantity of water in the solution is

Mass of H_2O=mass of solution − mass of $NaC_2H_3O_2$=425 g−10.2 g=415 g

You would prepare the solution by dissolving 10.2 g of sodium acetate in 415 g of water.

Parts per million (ppm) and parts per billion (ppb)

When the mass of solute in the solution is very small, a widely used expression is parts per million.

$$\text{ppm of solute} = \frac{\text{mass of slute}}{\text{mass of solution}} \text{X } 10^{-6}$$

$$\text{ppm} = \text{mass percentage of solute} \times 10^4$$

Example 2:

A 2.5 g sample of ground water was found to contain 5.4 µg of Zn2+. What is the concentration of Zn^{2+}, in parts per million?

Given:

Mass of sample = 2.5 g

Mass of Zn^{2+} = 5.4 µg = 5.4×10^{-6}g

ppm of Zn^{2+} =?

Solution:

ppm of Zn^{2+}= $\frac{\text{mass of slute}}{\text{mass of solution}}$ X 10^{-6}

ppm of Zn^{2+}= $\frac{5.4\ x}{2.5\ \text{g}}$ X 10^{-6}g

=2.16 ppm

1. Express 5% (m/m) solution of NaCl in ppm.

Given:

% by mass of NaCl = 5% 4

ppm of NaCl = ?

Solution:

ppm = mass percentage of solute × 10^4

= 5 × 10^4 ppm

❖ For solutions that are even more dilute, parts per billion (ppb) is used. A concentration of 1 ppb represents 1 g of solute per billion (10^9) grams of solution.

Exercise: 4.5

1. A sample of 0.892 g of potassium chloride (KCl) is dissolved in 54.6 g of water. What is the percent by mass of KCl in this solution?
2. A solution is prepared by mixing 1.00 g of ethanol with 100.0 g of water. Calculate the mass percent of ethanol in this solution.
3. A 135 g sample of seawater is evaporated to dryness, leaving 4.73 g of solid residue (the salts formerly dissolved in the seawater). Calculate the mass percent of solute present in the original seawater.
4. A commercial bleaching solution contains 3.62 mass % sodium hypochlorite, NaOCl. What is the mass of NaOCl in a bottle containing 2.50 kg of bleaching solution?
5. What mass of solution containing 5.00% potassium iodide, KI, by mass contains 258 mg KI? **(Ans. 5.16 g)**
6. If 150 g of orange juice contains 120 mg of ascorbic acid (Vitamin C), what is the concentration of ascorbic acid, expressed in ppm?
7. Express the concentration of ascorbic acid given in (10) in ppb.
8. Find the concentration of calcium (in ppm) in a 3.50 g pill that contains 40.5 mg of Ca. (Ans.1.16 × 10^4 ppm Ca)

9. The label on a 0.750 L bottle of Italian Chianti indicates "11.5% alcohol by volume." How many liters of alcohol does the wine contain? (**Ans. 0.0862 L)**
10. Seawater contains 0.0079 g Sr^{2+} per kilogram of water. What is the concentration of Sr^{2+} measured in ppm?

Mole Fraction (*X*)

The mole fraction (*X*) of a solute is the ratio of the number of moles of solute divided by the total number of moles of a solution (*moles of solute + moles of solvent*).

Mole fraction for a non-electrolyte (X) = $\frac{\text{Number of moles of solute}}{\text{Number of moles of solute + Number of moles of solvent}}$

$$x = \frac{mole\ of\ solute}{mole\ of\ solution} = \frac{n_{solute}}{n_{solute} + n_{solvent}}$$

$$X_{solute} = \frac{mole\ of\ solute}{mole\ of\ solute + mole\ of\ solvent}\ ;\ X_{solvent} = \frac{mole\ of\ solvent}{mole\ of\ solvent + mole\ of\ solute}$$

$$X_{solute} + X_{solvent} = 1$$

Example:

1. Calculate the mole fraction of ethanol when 23.0g of ethanol is mixed with 18 .0g of water to make aqueous solution of ethanol.

   Solution: Molar mass of ethanol (C_2H_5OH) is 46g/mol; that of water is 18g/mol.

   Mole of C_2H_5OH = $\frac{23g}{46g/mol}$ = <u>0.5mol</u>

   Mole of H_2O = $\frac{18g}{18g/mol}$ = <u>1mol</u>

   Total mole = mole of C_2H_5OH + mole of H_2O = 0.5mol + 1mol =<u>1.5mol</u>

   Mole fraction of ethanol (C_2H_5OH) = $\frac{mole\ of\ ethanol}{Total\ mol} = \frac{0.5mole}{1.5mol}$ = <u>0.3</u>

☞ Mole fraction is unit less.
☞ The total sum of mole fractions is unity (one)

2. A sample of rubbing alcohol contains 142 g of isopropyl alcohol (C_3H_7OH) and 58.0 g of water. What are the mole fractions of alcohol and water?

Solution

First find the number of moles of C_3H_7OH and the number of moles of H_2O:

$$\text{Moles of } C_3H_7OH = \frac{mass\ of\ \text{C3H7OH}}{molar\ mass\ of\ \text{C3H7OH}}$$

$$= 142\ g/60.06g/mol = 2.36\ mole$$

$$\text{Moles of water} = \frac{mass\ of\ \text{water}}{molar\ mass\ of\ \text{water}}$$

$$= 18.09g\ /18.02\ g/mole = 3.22\ mole$$

Calculating mole fractions:

$$\text{Mole fraction of isopropyl alcohol (X)} = \frac{\text{Number of moles of isopropyl alcohol}}{\text{moles of isopropyl alchol+ moles of water}}$$

$$= 2.36\ mole/(2.36\ mole + 3.22\ mole)$$

$$= 0.423$$

$$\text{Mole fraction of isopropyl alcohol } (X_{H2O}) = \frac{\text{Number of moles of water}}{\text{moles of isopropyl alchol+ moles of water}}$$

$$= 3.22\ mole/(2.36\ mole + 3.22\ mole)$$

$$= 0.577$$

3. A solution was prepared by adding 48 g of methanol into 81 g of water (H_2O). What is the mole fraction of methanol in this solution? (UEE, 2005)

   (Answer 0.25)

Molarity (M)

Molarity or molar concentration is the number of moles of solute in 1 L of solution. Molarity is determined by the equation

$$\boxed{\text{Molarity (M)} = \frac{\text{moles of solute (n)}}{\text{liters of solution (L)}}}$$

Thus moles of solute needed to prepare a solution of desired concentration can theoretically be calculated by rearranging the above equation as:

$$\boxed{\text{Moles of solue (n)} = \text{molarity (M)} \times \text{Liters of solution (L)}}$$

Example 1: A solution is prepared by dissolving 1.26g of $AgNO_3$ in a 250 mL volumetric flask and diluting to volume.

a) Calculate the molarity of silver nitrate solution.
b) How many millimoles of $AgNO_3$ were dissolved?

Solution: a) $M = \frac{1.26\ g/169.9\ g/mol}{0.250\ L} = 0.0297\ mol/L$ (or 0.0297 mmol/mL)

b) millimoles = 0.0297 mmol/mL x 250 mL = 7.42 mmol.

Example 2: How do you prepare 500 mL of 0.75M solution of $Cu(NO_3)_2$?

Solution: We have to calculate the number of moles or grams of $Cu(NO_3)_2$ needed for dissolving and prepare the required solution.

Volume of the solution = 500 mL, Molarity = 0.75M, Amount of $Cu(NO_3)_2$ = ?

Moles of $Cu(NO_3)_2$ = molarity x volume of solution

= 0.75M x 0.5L

= 0.375 mol

Mass of $Cu(NO_3)_2$ = 0.375 mol x 187.5g/mol = 70.31g

Thus 500 mL of 0.75M of $Cu(NO_3)_2$ solution can be prepared by dissolving about 70.31g of the salt In sufficient water and the diluting it to 500 mL

NORMALITY (N)

The normality of a solution (*N*) is the number of equivalents of the solute contained in one liter of solution. A one normal solution contains one equivalent per liter.

$$\text{normality of a solution (N)} = \frac{\text{number of gram equivalents of solute}}{\text{liter of solution}}$$

Example

1. What is the normality of a solution made by dissolving 5 g of H_2SO_4 in enough water to make 200 ml of solution?

Solution

Since H_2SO_4 has two ionizable hydrogen then, assuming total dissociation, the equivalent weight of H_2SO_4 is:

$$\text{Equivalent weight of } H_2SO_4 = \frac{Formula\,weight\,of\ H_2SO_4}{Total\ positive\,valence}$$

$$= \frac{98g/mol}{2mol/eq} = 49g/eq$$

$$\text{Normality} = \frac{Given\,mass}{Equivalent\,wt.\,x\ volume}$$

$$\text{Normality} = \frac{5g}{49g/eq} \text{ x } 0.2 \text{ L}$$

Normality = 0.51N H_2SO_4

2. Calculate the normality of a solution of HCl containing 2.2g of Hydrogen chloride in 200mL.

Solution: Volume of the solution = 200mL = 0.20L

Number of equivalents of HCl = actual mass/equivalent wt of HCl

= 2.2g/36.5g/equivalent

= 0.06 equivalent

Normality = no of equivalents/Liters of solution

= 0.06equivalents/0.20L

= 0.3 equivalents/L = 0.3N

3. Iodine (I_2) is an oxidizing agent that in reactions with reducing agents is reduced to iodine ion (I^-). How many grams of I_2 would you weigh out to prepare 100mL of a 0.100N I_2 solution?

Solution: Each molecule of I_2 consumes 2 electrons. $I_2 + 2e^- \rightarrow 2I^-$

Equivalent wt of I_2 = molar mass of I_2 /number of equivalents per mole

= 254g/mol /2eq/mol = 127g/eq

From Normality = (actual mass/ eq. wt)/liters of solution

Actual mass = Normality x eq. wt x liter of solution

= 0.100N x127g/eq x 0.100L = 1.27g

Molality (m)

The molality of a solution is the number of moles of solute per kilogram of solvent contained in a solution.

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass (Kg)of solvent}}$$

Or

$$\text{Molality} = \frac{\text{mass of solute}}{\text{Molar mass of solute} \times \text{Mass (Kg) of solventg)of solvent}}$$

A solution is prepared by dissolving 17.2 g of ethylene glycol ($C_2H_6O_2$) in 0.500 kg of water. If the final volume of the solution is 515 mL, calculate concen-tration of the

solution in: a) molarity b) molality c) percent by mass d) mole fraction, and e) mole percent.

Solution:

Given: Mass of solute = 17.2 g

Mass of solvent = 0.500Kg

Volume of solution = 515 mL = 0.515 L

Molar mass of ($C_2H_6O_2$) = 62 g/mole

Required: Molarity?, molality?, mass percent? Mole fraction? Mole percent?

a) We can calculate molarity using equation

$$Molarity = \frac{actual\ mass\ (g)}{Molar\ mass\ (g/mol)\ x\ volume\ of\ solution(L)}$$

$$M = \frac{17.2\,g}{62\,g/mol\ x\ 0.515\,L}$$

$$= 0.539 mol/L or M$$

b) For molality we will use equation 2.3.8 or 2.3.9. Equation 2.3.8 is a two step process but let's use the second one for direct substitution.

$$m = \frac{m\ (g)}{M\,(g/mol)\ x\ Kg\ (solvent)}$$

$$= \frac{17.2\ g}{62\ g/mol\ x\ 0.500\ Kg}$$

$$= 0.554\ molal$$

c) To calculate mass percent, we use equation

$$mass\ percent = \frac{mass\ of\ solute}{mass\ of\ soltution} x100\%$$

$$= \frac{17.20}{17.70} x100\%$$

$$= 3.33\%$$

d) To determine the mole fraction of the solute we will use equation

Since the solution contains only two components, solute (glycerol) and solvent (water), we must first determine the number of moles of these two components.

$$mole\ of\ C_2H_6O = \frac{actual\ mass(g)}{Molar\ mass(g/mol)}$$

$$n = \frac{17.2\ g}{62\ (g/mol)}$$

$$= 0.28 mol$$

$$mole\ of\ H_2O = \frac{actual\ mass(g)}{Molar\ mass(g/mol)}$$

$$n = \frac{500\ g}{18\ (g/mol)}$$

$$= 27.78 mol$$

Thus equation 2.3.9 will reduce to:

$$x_{C_2H_6O_2} = \frac{mole\ of\ C_2H_6O_2}{mole\ of\ C_2H_6O_2 + mole\ of\ H_2O}$$

$$= \frac{0.28}{0.28 + 27.78}$$

$$= 0.00998$$

e) The percentage of mole fraction of the solute in the solution is 0.998%.

Exercise 4.6

Instruction: Choose the correct answer from the alternatives given and circle the letter of your choice.

1. How many moles are there in 159 g of alanine, $C_3H_7NO_2$? (UEE, 2002)

   A) 0.560 B) 0.992 C) 1.78 D) 3.31

2. What is the molarity of a solution obtained by dissolving 0.01 moles of NaCl in 500 mL of solution? (UEE 2002)

   A) 0.01 M B) 0.005 M C) 0.02 M D) 0.10 M

3. How many grams of $Ca(OH)_2$ are contained in 1500 mL of 0.0250 M $Ca(OH)_2$ solution? (UEE, 2002)

   A) 1.85 g B) 2.78 g C) 3.17 g D) 4.25 g

4. What is the molarity of a solution containing 10 g of sulfuric acid in 500 ml of solution? (UEE, 2004)

   A) 0.02 B) 0.03 C) 0.12 D) 0.20

5. How many moles of sodium hydroxide are present in 2.5 L of 0.5 M aqueous solution? (UEE, 2006)

   A) 0.2 B) 0.5 C) 1.25 D) 12.5

6. What is the molarity of a 5 g hydrogen peroxide (H_2O_2) in 100 mL solution that is used for hair bleaching? (UEE, 2007)

   A) 0.015 M B) 0.15 M C) 1.5 M D) 3 M

7. What is the final concentration of Cl^- ion when 250 mL of 0.20 M $CaCl_2$ solution is mixed with 250 mL of 0.40 M KCl solution? (UEE, 2007)

   A) 1.60 M B) 0.40 M C) 0.20 M D) 0.60 M

8. The concentration of nitrate ion in a solution that contains 0.900 M aluminum nitrate is (UEE, 2007)

   A) 0.90 M B) 0.45 M C) 0.30 M D) 2.70 M

9. How many moles of H_2SO_4 are needed to prepare 5.0 L of a 2.0 M solution of H_2SO_4? (UEE, 2008)

   A) 2.5 B) 5.0 C) 20 D) 10

10. What is the molarity of a solution made by dissolving 10 g of glucose ($C_6H_{12}O_6$) in sufficient water to form 200 mL solution? (UEE, 2008)

    A) 0.18 B) 0.251 C) 0.362 D) 0.278

11. Which one of the following solutions has the greatest concentration of Na^+ ions? (2000)

    A) 0.026 M Na_2CO_3 B) 0.014 M NaCl C) 0.013 M Na_3PO_4 D) 0.032 M $NaNO_3$

12. What is the normality of a 2.3 M sulphuric acid solution? (UEE, 2001)

    A) 1.15 N B) 2.3 N C) 4.6 N D) 6.9 N

13. What is the normality of 1.0 M solution of Na_2CO_3? (UEE, 2002)

    A) 1 N B) 0.5 N C) 2 N D) 3 N

14. What is the mole fraction of a solute in one molal aqueous solution? (UEE, 2003)

A) 0.009 B) 0.018 C) 0.027 D) 0.036

15. An aqueous solution is 70 % nitric acid (HNO_3) by mass. What is the concentration of HNO_3 expressed in molality? (UEE, 2006)

A) 0.55 gm B) 8.62 m C) 11.1 m D) 37 m

Workout

16. 5.85 g of sodium chloride (NaCl) is dissolved in 250 mL of solution. Calculate

a) the molarity of the solution

b) the mass percentage of the solute

17. How would 250 ml of 0.15 M KNO_3 solution be prepared?

18. What is the molarity of each of the following solutions:

(a) 15.0 g $Al_2(SO_4)_3$ in 0.250 mL solution,

(b) 5.25 g $Mn(NO_3)_2.2\ H_2O$ in 175 mL of solution,

4.7 PREPARATION OF SOLUTIONS

A common task in school, medical, industrial and other chemical laboratories is the preparation of solutions of known concentrations.

Solutions are usually prepared from solutes of liquids or solids. Occasionally they are prepared from gases.

Short procedures for preparation of solutions from solids

- First, the solute is accurately weighed and transferred to a volumetric flask,
- Second water is added through a funnel,
- Next, the solid is slowly dissolved by gently swirling the flask,
- After all the solid has dissolved, more water is slowly added to bring the level of solution exactly to the volume mark.

Activity

Dissolve 1g each of NaCl, $CuSO_4$, and $KMnO_4$ in different 50 mL measuring flasks. Note the colour intensity of the solutions. Take 25 mL of solution from each flask and further dilute each solution to 50 mL. Note the colour intensity again.

1. What did you observe?
2. Can you correlate the colour intensity with the concentration of the solution?
3. Does this analogy works for colorless solution also?

Discuss your observations with your classmates.

Preparation of solutions from liquids - Dilution

- **Dilution** is the procedure for preparing a less-concentrated solution from a more concentrated one.

In carrying out a dilution process, Number of moles of solute before dilution = Number of moles of solute after dilution $M_iV_i=M_fV_f$ Or, more generally, C_iV_i=CfVf

Where Ci is initial concentration, C_f is final concentration, V_i is initial volume and V_f is final volume

Example

1. Describe how you would prepare 750 mL of a 0.015 M KBr solution from solid KBr.

Solution

Mass of KBr = Molarity x Molar mass of KBr x Volume of solution

= 0.015 M x 119 g/mol x 0.75 L

= 1.34 g

Weigh out 1.34 g KBr, dissolve in water, dilute with sufficient water by stirring to give a final volume of 750 mL.

2. Describe how you would prepare 500 mL of a 1.75 M H_2SO_4 solution, starting with an 8.61 M stock solution of H_2SO_4

Solution:

MiVi = MfVf

Vf = MfVfMi

=1.75 M×500 mL8.61 M=102 mL

Dilute 102 mL of 8.61 M H_2SO_4 solution with sufficient water to give a final volume of 500 mL.

Activity

1. How do you prepare 60.0 mL of 0.2 M HNO_3 from a stock solution of 4 M HNO_3?
2. You have 100 mL of a 0.5 M HCl solution, and you want to dilute it to exactly 0.1 M. How much water should you add?

Exercise 4.7

Instruction: Choose the correct answer from the alternatives given and circle the letter of your choice.

1. How would you prepare 0.90 L of 1.2×10^{-2}M NaCl aqueous solution? (2003 E.C)
   A. Weigh 0.012 g of NaCl, dissolve in a small amount of water and dilute to 0.09 L
   B. Weigh 0.63 g of NaCl, dissolve in a small amount of water and dilute to 0.09 L
   C. Weigh 1.2 g of NaCl, dissolve in a small amount of water and dilute to 0.09 L
   D. Weigh 1.4 g of NaCl, dissolve in a small amount of water and dilute to 0.09 L
2. How much water has to be evaporated from 250 mL of 1 M $Ca(OH)_2$ to make it 3 M? (UEE, 2004)
   A) 100 mL B) 150 mL C) 167 mL D) 200 mL
3. How many mL of water is required to dilute 50 mL of 3.5 M H_2SO_4 to 2.00 M H_2SO_4? (UEE, 2004)
   A) 37.5 B) 45 C) 75 D) 87.5
4. What is the quantity of water in mL, required to prepare 0.5 M of HCl from a concentrated solution of 3.5 M in 50 mL? (UEE, 2005)
   A) 50 B) 100 C) 300 D) 350
5. How many mL conc. HNO_3 and how many mL of water are required to prepare 500 mL of 0.1 M HNO_3 from a conc. 13 M HNO_3?
   A. 1 mL HNO_3 and 496.15 mL of H_2O
   B. 3 mL HNO_3 and 500 mL H_2O
   C. 3.85 mL HNO_3 and 500 mL H_2O
   D. 3.85 mL HNO_3 and 496.15 mL H_2O

6. A lab instructor is preparing 5.0 L of a 0.10 M $Pb(NO_3)_2$ (molecular mass = 331) solution. What is the mass required/ (UEE, 2006)
   A. 165.5 g $Pb(NO_3)_2$ and add 5.0 Kg of H_2O
   B. 165.5 g of $Pb(NO_3)_2$ and add H_2O until the solution has a volume of 5.0 L
   C. 31.1 g of $Pb(NO_3)_2$ and add H_2O until the solution has a volume of 5.0 L
   D. 31.1 g $Pb(NO_3)_2$ and add 5.0 L of H_2O
7. If a student wishes to prepare approximately 100 ml of an aqueous solution of 6 M HCl using 12 M HCl. Which procedure is correct? (UEE, 2007)
   A. Adding 50 mL of 12 M HCl to 50 mL of water while stirring the mixture steadily.
   B. Adding 25 mL of 12 M HCl to 50 mL of water while stirring the mixture steadily.
   C. Adding 50 mL of water to 50 mL of 12 M HCl while stirring the mixture steadily.
   D. Adding 25 mL of water to 50 mL of 12 M HCl while stirring the mixture steadily.
8. What is the mass of $CuCl_2.6H_2O$ required to prepare 300 mL of 0.1 M aqueous solution? (UEE 2000)

   A) 1.19 g B) 2.19 g C) 7.28 g D) 11.9 g

Answer key

Exercise 4.1

1. B 2. B 3. A 4.D 5. A

Exercise 4.2

1. D 2. B 3. C 4. A

Exercise 4.3

1. C
2. a) saturated b) supersaturated c) unsaturated
3. By adding a crystal of X in each solution. The size of the crystal decreases, remains the same and increases when added into unsaturated, saturated and super saturated solutions, respectively.

Exercise 4. 4

1. A 2. B C. D 4. D

Exercise 4.6

1. D 2. C 3. B 4. D 5. C 6, C 7. B 8. D

9. D 10.D 11. A 12. C 13. C 14.B 15. D

Exercise 4. 7

1. B 2. C 3. A 4. C 5. D 6. B 7. A 9. C

Chapter 6

Chemical equilibrium

6.1 introductions

A reversible reaction is a chemical reaction that results in an equilibrium mixture of reactants and products.

$$H_{2(g)} + I_2(g) \rightleftharpoons 2HI(g)$$

Chemical equilibrium is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.

When a chemical reaction takes place, the reactants are consumed and the products are formed. As a result the concentrations of reactants decrease with time and that of products increase. If the reaction is reversible in nature and it takes place in a closed vessel then the products decompose to give back reactants.

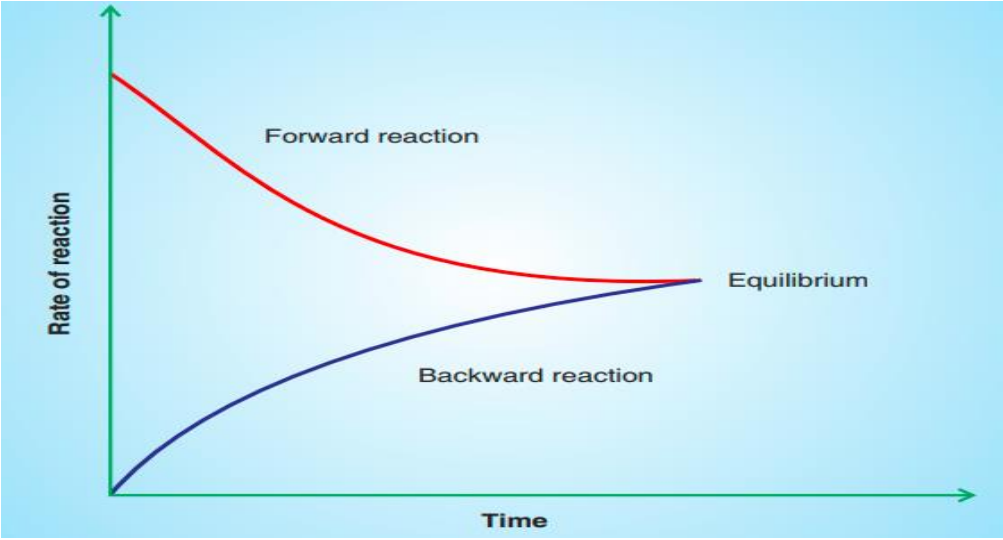


Fig 6.1 Change in the rate of reaction with time for the forward and reverse reactions.

The chemical equilibrium is also dynamic in nature since the reaction does not stop at equilibrium. The macroscopic properties remain constant because the rate of forward

reaction becomes equal to the rate of reverse reaction and hence no net reaction takes place.

The general equation that represents a reversible reaction is

$$aA + bB \rightleftharpoons mM + nN \qquad \text{------(1)}$$

For the forward reaction A and B are reactants and M and N are products. It is assumed that the reaction is homogeneous in nature, that is all the reactants and the products are present in the same state. The rate of forward reaction (r_f) depends upon the concentrations of A and B and is given by the expression

$$\mathbf{r_f = k_f\,[A]^a\,[B]^b}$$

The rate of reverse reaction is given by the expression

$$\mathbf{r_b = k_b\,[M]^m\,[N]^n}$$

where [A], [B], [M] and [N] are the concentrations of A, B, M and N respectively. k_f and k_b are rate constants for forward and reverse reactions, respectively.

At equilibrium, the rate of forward reaction is equal to the rate of reverse reaction.

$$\mathbf{r_f = r_b} \quad \text{or} \quad \mathbf{k_f\,[A]^a\,[B]^b = k_b\,[M]^m\,[N]^n}$$

$\mathbf{k_f}$ and $\mathbf{k_b}$ are constant. Therefore, the ratio of k_f to k_b is also a constant.

$$\frac{k_f}{k_b} = \frac{[M]^m\,[N]^n}{[A]^a[B]^b} = K_{eq}$$

The ratio of k_f and k_b is represented by Keq. Since this constant represents the reaction at equilibrium it is known as equilibrium constant. [M], [N], [A] and [B] are concentrations at equilibrium. When the concentrations are expressed in molarities, the equilibrium constant is represented by Kc .

When all the reactants and the products are in the gaseous state, their concentrations can be written in terms of partial pressures. In such cases the **Keq** is denoted by Kp. The expression for K_p is

$$K_p = \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b}$$

Units of Kc from rxn (1) will be

$$K_c = \frac{[M]^m[N]^n}{[A]^a[B]^b} = \frac{[\text{mol L}^{-1}]^m\,[\text{mol L}^{-1}]^n}{[\text{mol L}^{-1}]^a[\text{mol L}^{-1}]^b} = (\text{mol L}^{-1})^{(m+n)-(a+b)}$$

Unit of Kp is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of Kp , will be:

$$K_p = \frac{(p_M)^m (p_N)^n}{(p_A)^a (p_B)^b} = \frac{(\text{atm})^m (\text{atm})^n}{(\text{atm})^a (\text{atm})^b} = (\text{atm})^{(m+n)-(a+b)}$$

Example:

Write the concentration-based expression for each of the following reactions:

a) $3O_2(g) \rightleftharpoons 2O_3(g)$

b) $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$

Solution a) $Kc = \frac{[O_3]^2}{[O_2]^3}$ b) $Kc = \frac{[NH_3]^2}{[N_2][H_2]^3}$

$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$, the concentrations at equilibrium are $[SO_2]$ = 0.90 *M*, $[O_2]$ = 0.35 *M*, and $[SO_3]$ = 1.1 *M*. What is the value of the equilibrium constant, K_c?

Solution:

$$Kc = Qc = \frac{(SO_3)^2}{(SO_2)^2(O_2)^1}$$

$$= \frac{(1.1)2}{(0.9)2x(O2)}$$

$$= \mathbf{4.27}$$

6.2 Characteristics of chemical equilibrium

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient (*Q*).** For a reversible reaction described by

$$\boldsymbol{mA + nB + \rightleftharpoons xC + yD}$$

The reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$\boldsymbol{Qc = \frac{[C]^x[D]^y}{[A]^m[B]^n}}$$

The constant value of *Q* exhibited by a system at equilibrium is called the **equilibrium constant,** *K*: $\boldsymbol{K = Q}$, at equilibrium. A reaction exhibiting a large *K* will reach equilibrium when most of the reactant has been converted to product, whereas a small *K* indicates the reaction achieves equilibrium after very little reactant has been converted. The magnitude of *K* does *not* indicate how rapidly or slowly equilibrium will be reached.

The value of equilibrium constant predicts the extent of reaction at equilibrium. It also tells about the relative concentrations of products and reactants present at equilibrium, that is, the position of equilibrium. Kc can have three types of values.

When Kc >1: This indicates that the value of numerator is greater than the denominator. So the formation of products is favoured at equilibrium.

When Kc < 1: This indicates that the value of numerator is less than the denominator. So the formation of products is not favoured at equilibrium.

When Kc =1: This indicates that the rate of forward reaction is equal to the rate of backward reaction.

When Q is less than K, then the reaction will proceed in the forward direction and more products will be formed till the equilibrium is reached. When Q is greater than K, then the reaction will proceed in the reverse direction and more reactants will be formed till the equilibrium is reached. When Q is equal to K, then the reaction has attained equilibrium.

Calculating the Equilibrium Concentrations:

Not only can we estimate the extent of reaction from the Kc value, but also the expected concentrations at equilibrium can be calculated from knowledge of the initial concentrations and the Kc value. In these types of problem it will be very helpful to use the following approach.

1. Express the equilibrium concentrations of all the species in terms of the initial concentrations and an unknown x, which represents the change in concentration.

2. Substitute the equilibrium concentrations derived in part 1 into the equilibrium constant expression, and solve for x. The equilibrium concentration is given by: equilibrium concentration = initial concentration ± the change due to the reaction where the + sign is used for a product, and the – sign for a reactant.

3. Use x to calculate the equilibrium concentration of all the species.

Example:

Calculate the pH of a 0.50 M HF solution at 25°C. The ionization of HF is given by

$$HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \text{ is } 6.8\times10^{-4}$$

Solution:

The species that can affect the pH of the solution are HF, and the conjugate base F^-, Let x be the equilibrium concentration of H_3O^+ and F^- ions in molarity (M). Thus,

	$HF(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$F^-(aq)$
Initial, M	0.50	0.00	0.00
Change, M	$-x$	$+x$	$+x$
Equilibrium, M	$(0.50 - x)$	x	x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$\frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50} = 6.8 \times 10^{-4}$$

Rearranging this equation gives

$x^2 = (0.5)(6.8 \times 10^{-4}) = 3.4 \times 10^{-4}$

x = ∫ 3.4× 10^{-4} = 1.8 × 10–2 M Thus, we have solved for x without using the quadratic equation. At equilibrium, we have

[HF] = (0.50 – 0.018) M = 0.48 M, $[H_3O^+]$ = 0.018 M $[F^-]$ = 0.018 M and the pH of the solution is pH = –log(0.018) = 1.74

The equilibrium constant depends upon the following factors:

1. Temperature at which the experiment is performed.

2. The form of equations which describe the equilibrium.

For example, for the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

If the reaction is multiplied by 2,

2N2(g) + 6H2(g) → 4NH3(g) the expression for Kc becomes

$$K_c' = \frac{[NH_3]^4}{[N_2]^2[H_2]^6} \qquad K_c' = (K_c)^2$$

If the reaction is reversed, $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ the Kc becomes

$$K_c'' = \frac{[N_2][H_2]^3}{[NH_3]^2} \qquad K_c'' = 1/K_c$$

The equilibrium constant does not depend upon the initial concentrations of the reactants. Kc and K p are independent of pressure.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products are present in the same phase. Homogeneous equilibria take place in solutions.

These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$C_2H_2(aq) + 2Br_2(aq) \rightleftharpoons C_2H_2Br_2(aq) \qquad K_C = \frac{[C_2H_2Br_2]}{[C_2H_2][Br_2]^2}$$

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K_C = \frac{[I_3^-]}{[I_2][I^-]}$$

Water is *not* included in the reaction quotient in the second reaction. The reason for this omission is related to the *relative concentrations for liquids and solids are equal to 1 and needn't be included*. The equilibria below all involve gas-phase solutions:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + (g)H_2 \qquad K_C = \frac{[C_2H_4][H_2]}{[C_2H_6]}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p). A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

$$PV = nRT$$

$$\boldsymbol{P = \left(\frac{n}{V}\right) RT = MRT}$$

For the gas-phase reaction

$$\boldsymbol{mA + nB \rightleftharpoons xC + yD}:$$

$$\boldsymbol{K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n}}$$

$$\boldsymbol{= \frac{([C]xRT)^x ([D]xRT)^y}{([A]xRT)^m ([BxRT)^n}}$$

$$\boldsymbol{= \frac{[C]^x [D]^y}{[A]^m [B]^n} x \frac{(RT)^{x+y}}{(RT)^{m+n}}}$$

$$\boldsymbol{= K_C (RT)^{(x+y)-(m+n)} \ = K_C (RT)^{\Delta n}}$$

And so, the relationship between K_C and K_P is

$$\boldsymbol{K_P = K_C (RT)^{\Delta n}}$$

Where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\boldsymbol{\Delta n = (x + y) - (m + n)}$$

Example:

Write the equations relating K_c to K_P and calculate $\boldsymbol{K_P}$ for each of the following reactions $\boldsymbol{K_c}$ is equal to 0.28 at 900 °C:

$$\boldsymbol{CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)}$$

$$K_P = K_C (RT)^{\Delta \mathrm{n}} = \frac{0.28}{[(0.0821)(1173)]^2} = 3.0X10^{-5}$$

Heterogeneous Equilibria

- A heterogeneous equilibrium involves reactants and products in two or more different phases:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_C = [Pb^{2+}][Cl^-]^2$$

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad K_C = \frac{1}{[CO_2]}$$

$$C(s) + 2S(g) \rightleftharpoons CS_2(g) \qquad K_C = \frac{[CS_2]}{[S]^2}$$

6.3The Le Chatelier's principle

Châtelier's principle (T,P,V&C) if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium. It gives the effect of any one or more of the reaction parameters namely, temperature, pressure or concentration on equilibrium.

Le Chatelier's principle describes the effect of the change in parameters on the position of equilibrium. That is, it predicts whether the changes in reaction parameters will favor the formation of reactants or products.

Effect of Change in Temperature on the Position of Equilibrium

If the **temperature** of the reaction at equilibrium is increased then the reaction will proceed in that direction where heat is absorbed so as to undo the effect of heating. Similarly if the temperature of the reaction at equilibrium is lowered then the reaction will proceed in that direction where the heat is produced so that the equilibrium is again attained.

$$heat + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Raising the temperature of the system is causing to increasing the amount of a product, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left.

For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed. A +B →C + heat, when the temperature is lowered, more products are formed. That is, the decrease in temperature favors exothermic reactions.

Effect of Change in Pressure on the Position of Equilibrium

If the **pressure** at equilibrium is increased then the reaction will proceed in that direction where the pressure is reduced. Since the pressure depends upon the **number of moles**, on increasing the pressure the reaction will precede in that direction where the number of moles are reduced.

For a general reaction,

$$\boldsymbol{aA + bB \rightleftharpoons mM + nN}$$

The effect of pressure is decided by Δn. $\boldsymbol{\Delta n = (m + n) - (a + b)}$

- If **Δn > 0,** that means the total moles of products is greater than the total moles of reactants.
  - Lowering of pressure will favor the reaction in reverse direction.
- If **Δn < 0**, that means the total moles of products is less than the total moles of reactants.
  - Increasing the pressure will favor the reaction in forward direction.
- If **Δn = 0**, then the change in pressure has no effect on the position of equilibrium.

Effect of Change in the Concentration on the Position of Equilibrium

At equilibrium, on increasing the amount of a substance, the reaction proceeds in that direction where the substance is consumed. When the amount of the reactants is increased the reaction proceeds in the forward direction and when the amount of products is increased, the reaction proceeds in the backward direction. The forward reaction is favored if the products formed are removed from the vessel.

Effect of a Catalyst

Catalysts are substances that enable a reaction to proceed via a different mechanism with an accelerated rate. The catalyzed reaction mechanism involves a lower energy transition state than the uncatalyzed reaction, resulting in lower activation energy, E_a Consequently, both forward and reverse reactions are accelerated, and equilibrium is achieved more quickly *but without a change in the equilibrium constant*.

6.3.1. Calculation of equilibrium constant

Iodine molecules react reversibly with iodine ions to produce tri iodide ions.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3}M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4}M, what is the equilibrium constant for the reaction?

Solution: To calculate the equilibrium constants, constant are needed for all the reactant and products:

$$\boldsymbol{K_c = \frac{[I^{3-}]}{[I_2][I^-]}}$$

- The initial concentrations of the reactants and the equilibrium concentration of the product.

  Use this information to derive terms for the equilibrium concentrations of reactants, presenting all the information in the reaction table.

	$\boldsymbol{I_2(aq)}$	$+$ $\boldsymbol{I^-(aq)}$	$\rightleftharpoons$ $\boldsymbol{I_3^-(aq)}$
Initial concentration (M)	1.000×10^{-3}	1.000×10^{-3}	0

Change (M)	-x	-x	+x
Equilibrium conc.(M)	$1.000x10^{-3}$-x	$1.000x10^{-3}$-x	X

At equilibrium the concentration of $I_2$is $6.61x10^{-4}$M so that

$1.000x10^{-3}$-x =$6.61x10^{-4}$

X = $1.000x10^{-3}$-$6.61x10^{-4}$ = $3.39x10^{-4}$M

	$\boldsymbol{I_2(aq)}$ +	$\boldsymbol{I^-(aq)}$ ⇌	$\boldsymbol{I_3^-(aq)}$
Initial concentration (M)	$1.000x10^{-3}$	$1x10^{-3}$	0
Change (M)	$-3.39x10^{-4}$	$-3.39x10^{-4}$	$+3.39x10^{-4}$
Equilibrium conc.(M)	$6.61x10^{-4}$	$6.61x10^{-4}$	$3.39x10^{-4}$

Substitute the equilibrium concentrations into the K expression and solve:

$$\boldsymbol{K_c = \frac{[I^{3-}]}{[I_2][I^-]}}$$

$$= \frac{3.39x10^{-4}M}{(6.61x10^{-4}M)(6.61x10^{-4}M)} = 776$$

6.4 IONIC EQUILIBRIA

6.4.1 Acid-Base Equilibria

6.4.1.1. Theories of Acids and Bases

I. Arrhenius (Classical) Acid-Base Definition

An ***acid*** is a substance that dissociates in water to yield a H_3O^+ and a ***base*** is a substance that dissociates in water to yield OH^-

Neutralization is the reaction of an H^+ (H_3O^+) ion from the

Eg. Acids: HCl, H_2SO_4, HNO_3 etc

Bases: NaOH, KOH, $Mg(OH)_2$ etc.

- Three limitations:

1. Applied only to substances in aqueous solutions.
2. Restricted to substances that produce H^+ and OH^- ions
3. Does not explain why some compounds containing hydrogen such as CH_4 dissolve in water and do not give acidic solutions

II. Brønsted-Lowry Acid-Base Definition

- An acid is a **proton donor**, any species that donates an H^+ ion.
  - It must contain H in its formula.

Eg. HCl, HNO_3, $H_2PO_4^-$ etc.

- All Arrhenius acids are Brønsted-Lowry acids.
- A base is a **proton acceptor**, any species that accepts an H^+ ion.
  - It must contain a lone pair of electrons to bind the H^+ ion.

Eg. NH_3, CO_3^{2-}, F^-, OH^- etc.

- Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH^-.
- Therefore in the Brønsted-Lowry perspective, ***one species donates a proton and another species accepts it and hence, an acid-base reaction is a proton transfer process.***
- Based on the number of proton donated acids can be classified into 3:

i. **Monoprotic acid:** yields one hydrogen ion upon ionization

Eg. $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

Diprotic acid: give up two H^+ ions, in two separate steps:

Eg.
$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

Triprotic acids: yield three H^+ ions, are relatively few in number.

Eg.
$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$
$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^-(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

Conjugate Acid-Base Pairs

- The concept of the conjugate acid-base pair, arises from the Brønsted definition of acids and bases.
- The conjugate base of a Brønsted acid is the species that remains after the acid donates a proton.
- Conversely, a conjugate acid results from the addition of a proton to a Brønsted base.
- Every Brønsted acid has a conjugate base, and vice versa.

Example:

$$\underset{acid_1}{CH_3COOH(aq)} + \underset{base_2}{H_2O(l)} \rightleftharpoons \underset{base_1}{CH_3COO^-(aq)} + \underset{acid_2}{H_3O^+(aq)}$$

- ✓ ***weak acids have strong conjugate bases***
- ✓ ***weak bases have strong conjugate acids***

Lewis Acid-Base Definition

A ***base*** is any species that ***donates*** an electron pair. Whereas an ***acid*** is any species that ***accepts*** an electron pair. Protons act as Lewis acids in that they accept an electron

$$B: + \quad H^+ \rightleftharpoons \quad B \quad H^+$$

A Lewis base has a lone pair of electrons to donate. And a Lewis acid is a vacant orbital

6.4.1.2 Dissociation of strong and weak

monoprotic acids and bases

Strong and Weak Acids: The reaction of an acid with its solvent (typically water) is called an acid dissociation reaction. Acids are divided into two categories based on the ease with which they can donate protons to the solvent.

- A strong acid is completely dissociated in aqueous solution.
- They almost completely transfer their protons to the solvent molecules.
- That is, the equilibrium constants for the following reactions are very large:

$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

- Weak acids, of which aqueous acetic acid is one example, cannot completely donate their acidic protons to the solvent.
- Instead, most of the acid remains undissociated, with only a small fraction present as the conjugate base.

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-{}_{(aq)}$

The Acid-Dissociation Constant (K_a)

Strong acids dissociate completely into ions in water:

In a dilute solution of a strong acid, almost no HA molecules exist:

$[H_3O^+] = [HA]_{init}$ or $[HA]_{eq} = 0$

$HA_{(g\ or\ l)} + H_2O_{(l)} \qquad H_3O^+_{(aq)} + A^-_{(aq)}$

$$Q_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \text{at equilibrium, } Q_c = K_c >> 1$$

Nitric acid is an example: $HNO_{3\,(l)} + H_2O_{(l)} \qquad H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$

Weak acids dissociate very slightly into ions in water:

$HA_{(aq)} + H_2O_{(aq)} \qquad H_3O^+_{(aq)} + A^-_{(aq)}$

In a dilute solution of a weak acid, the great majority of HA

molecules are undissociated: $[H_3O^+] << [HA]_{init}$ or $[HA]_{eq} = [HA]_{init}$

$$Q_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \text{at equilibrium, } Q_c = K_c << 1$$

Strong and Weak Bases: the basicity of an aqueous solution

- is a measure of the concentration of the hydroxide ion, OH^-. The most common example of a strong base is an alkali metal hydroxide, which completely dissociates to produce the hydroxide ion. $NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$
- Weak bases only partially accept protons from the solvent and are characterized by a base dissociation constant, Kb.
- For example, the base dissociation reaction and base dissociation constant for the acetate ion are:

$CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COOH_{(aq)}$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Amphiprotic Species: Some species can behave as either an acid or a base.

- A species that can serve as both a proton donor and a proton acceptor is called amphiprotic.

  $HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$ ..... $K_{a2} = 4.69\times10^{-11}$

  $HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-{}_{(aq)} + H_2CO_{3(aq)}$ .....$K_{b2} = 2.25\times10^{-8}$

- Whether an amphiprotic species behaves as an acid or as a base depends on the equilibrium constants for the two competing reactions.

  Since, $k_{b2} > k_{a2}$, we expect that aqueous solutions of HCO_3^- will be basic.

6.4.1.3 Dissociation of water and pH of aqueous solutions

- Water is an amphiprotic solvent in that it can serve as an acid or a base.

- An interesting feature of an amphiprotic solvent is that it is capable of reacting with itself as an acid and a base.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+ + OH^-$$

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

- For pure water the concentration of hydroxyl and hydronium ions must be equal:

  The ion-product for water, K_w:

  $K_c[H_2O]^2 = K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ (at 25°C)

  $[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$ (at 25°C)

  <u>pH</u>: a way to express acidity -- the concentration of H^+ in solution

- $pH = \log(1/[H^+]) = -\log[H^+] = -\log[H_3O^+]$

Acidic solution	pH < 7
Neutral	pH = 7
Basic solution	pH > 7

Eg. What is the pH of a solution that is 10^{-12} *M* in hydronium ion?

Solution: pH = -log[H_3O^+] = (-1)log 10^{-12} = (-1)(-12) = 12

6.4.1.4 Common ion effect

- The shift in the position of anequilibrium on addition of a substance that provides an ion in common with one of the ions already involved in the equilibrium.
- Equilibrium is shifted in the direction that reduces the concentration of the common ion
  - ✓ Sources of common ions are
    - Strong acid
    - Strong bases
    - Soluble salts
- The Common Ion Effect is important to
  - ✓ Buffers
  - ✓ Solubility Equilibrium

6.4.1.5. Buffer solutions

- A buffer solution resists changes in pH when it is diluted or when acids or bases are added to it.

  Generally, buffer solutions are prepared from a conjugate acid/base pair, such as acetic acid/sodium acetate or ammonium chloride/ammonia.
- Has two components, one component is able to neutralize the acid and other component is able to neutralize base

- Can be prepared from
  - weak acid and its conjugate base Eg CH_3COOH/CH_3COO^-
  - weak base and its conjugate acid eg NH_3/NH_4^+
  - weak acid and strog base, if the weak acid is excess eg. $CH_3COOH/NaOH$ in 2:1mole ratio
  - weak base and strog acid, if the weak base is excess eg. NH_3/HCl in 2:1mole ratio
- it is used to:
  - human blood
  - protein studies often must be performed in buffer media
  - control of P^H is often important in industrial process
  - enzyme activity always working with P^H 6&8

for a weak acid HA the dissociation equation and Ka expression are given by

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$Ka = [H_3O^+][A^-]/[HA]$, $[H_3O^+] = Ka.[HA]/[A^-]$

Put logarithm on both sides of the equation and rearranging

$P^H = Ka .\log \frac{[HA]}{[A-]}$ for any acid- base pair $P^H = PKa + \log \frac{[conj.base]}{[acid]}$

For bases $P^{OH} = Kb.\log\frac{[B]}{[BH+]}$ $P^{OH} = PKb + \log \frac{[conj.\ acid]}{[base]}$

Example: calculate the PH of a buffer solution containing 0.1M acetic acid and 0.2M potassium acetate.

Solution:

$P^H = PKa + \log \frac{[conj.base]}{[acid]}$

$P^H = -\log Ka + \log \frac{[0.2M]}{[0.1M]} = -Log(1.8x10^{-5}) + \log 2 =$ **5.05**

6.4.1.6. Hydrolysis of salts

- **<u>Hydrolysis</u>** is a term applied to reactions of aquated ions that change the pH from 7

- The interactions between salts and water are called **<u>hydrolysis</u>**

❖ There are 4 salt forming processes of acid base reactions:

1. Salt of a strong acid and a strong base:

   Eg: NaCl, KBr, and $Ba(NO_3)_2$.

   ➢ Neither the cation nor anion hydrolyzes, and the solution has a pH of 7.

   2. Salt of a strong acid and a weak base:

   Eg: NH_4Br, $ZnC1_2$, and $Al(NO_3)_3$.

➢ The cation hydrolyzes, forming H^+ ions, and the solution has a pH less than 7.

   3. Salt of a weak acid and a strong base:

   Eg: $NaNO_2$, $KC_2H_3O_2$, and $Ca(OCl)_2$.

➢ The anion hydrolyzes, forming OH-ions, and the solution

   has a pH greater than 7.

   4. Salt of a weak acid and a weak base:

   Eg: NH_4F, $NH_4C_2H_3O_2$, and $Zn(NO_2)_2$.

➢ Both ions hydrolyze.

   The pH of the solution is determined by the relative extent to which each ion hydrolyzes.

6.4.2 Solubility Equilibria

- Many natural processes depend on the precipitation or dissolving of a **slightly soluble salt.**

- **Insoluble does not mean 100% insoluble.**

– In the next section, we look at the **equilibria** of slightly soluble, or nearly insoluble, ionic compounds.

– Their equilibrium constants can be used to answer questions regarding **solubility** and **precipitation**.

The Solubility Product Constant

- When an excess of a slightly soluble ionic compound is mixed with water, an equilibrium is established b/n the solid and the ions

- The equilibrium constant for this process is called the solubility product constant, K_{sp}.

$$CaC_2O_4(s) \qquad Ca^{2+}(aq) + C_2O_4^{2-}(aq), \qquad K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

- K_{sp} basically relationship of amount of ions in solution at saturation point

- once product of concentration of ions = K_{sp}, ppt occurs

- In general, $\mathbf{K_{sp}}$ is the equilibrium constant for the solubility equilibrium of a slightly soluble ionic compound.

- It is a constant that relates to amount of substance that is dissolve in solution at saturation point <u>not</u> amount in flask

- It equals the **product of the equilibrium concentrations** of the ions in the compound.

- Each concentration is **raised to a power** equal to the number of such ions in the formula of the compound.

Calculating Ksp from the Solubility

A 1L sample of a saturated CaC2O4 contains 0.0061g of the salt at 25°C. Calculate the Ksp for this salt at 25°C.

- We must first convert the solubility of calcium oxalate from 0.0061 g/liter to moles per liter.
- Note to calculate the K_{sp} must have data on a saturated solution, if below saturation point can't determine K_{sp}.

$$M\ CaC_2O_4 = \left(\frac{0.0061g\ CaC_2O_4}{L}\right) \times \frac{1\,mol\ CaC_2O_4}{128g\ CaC_2O_4} \qquad = 4.8\times10^{-5}\ mol\,CaC_2O_4 / L$$

When 4.8 x 10^{-5} mol of solid dissolve it forms 4.8 x 10^{-5} mol of each ion.

$$CaC_2O_4(s) \underset{}{\overset{H_2O}{\rightleftharpoons}} Ca^{2+}(aq) + C_2O_4^{\ 2-}(aq)$$

Equilibrium 4.8 x 10^{-5} 4.8 x 10^{-5}

You can now substitute into the equilibrium-constant expression

$$K_{sp} = [Ca^{2+}][C_2O_4^{\ 2-}] \qquad K_{sp} = (4.8\times10^{-5})(4.8\times10^{-5}) \qquad K_{sp} = 2.3\times10^{-9}$$

The common-ion effect

- Caused by the addition of a compound having an ion in common with the dissolved substance that shift the equilibrium.
- The presence of the common ion suppresses the ionization of a weak acid or a weak base. For example, if sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH3COO$^-$ ions

$$CH_3COONa\ (s) \rightarrow CH_3COO^-\ (aq) + Na^+\ (aq)$$
$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

- Sodium acetate, CH3COONa, is a strong electrolyte, so it dissociates completely in solution, but acetic acid, CH3COOH, is a weak acid and ionizes partially.
- According to Le Chatelier's principle, the addition of CH3COO$^-$ ions from CH3COONa to a solution of CH3COOH will suppress the ionization of

CH3COOH and decrease the concentration of hydrogen ions. Therefore, a solution containing both CH3COOH and CH3COONa will be less acidic than a solution containing only CH3COOH of the same concentration.

- The shift in equilibrium of the acetic acid ionization is caused by the acetate ions from the sodium acetate. CH3 COO– is the common ion because it is supplied by both CH3COOH and CH3COONa.

Exercise: Determine the [H3O+] and [CH3COO$^-$] in a solution that is 0.10 M in both CH3COOH and HCl?

6.4.3 Factors affecting stability of complexes

The main factors affecting stability of complexes are:

- ✓ Charge on the metal ion.
- ✓ Principal quantum number.
- ✓ Nature of ligands
- ✓ Macro cyclic ligands
- ✓ Hardness and softness
- ✓ Surrounding conditions

Unit 8

8. Introduction to organic chemistry (16 hours)

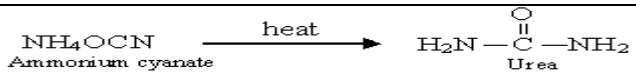
8.1 Introduction

Organic Chemistry was originally known by studying the compounds of carbon, which occurred in living organisms. However, in 1828 a German chemist, Friedrich Wohler, synthesized the organic compound Urea, CO $(NH_3)_2$, an animal waste product, from inorganic compound ammonium cyanate, NH_4OCN. Therefore, the meaning of Organic chemistry has to be extended to include the compounds of carbon whether or not they occur in living organisms.

Activity 8.1

1. Do you agree with the notion that says: "carbon compounds can be synthesized only by animals and plants"?
2. Draw diagrams to show how carbon atoms can link to one another in different ways to form a variety of compounds by considering only four carbon atoms.

Discuss with your group and present it to the class.



Urea was the first organic compound synthesized in the laboratory. The synthesis of urea by Friedrich Wöhler and subsequent synthesis of other organic compounds marked the downfall of the 'life force' theory.

How do you explain organic compounds at present and define organic chemistry?

The common feature of organic compounds is that they all contain the element carbon. Organic compounds are the compounds of carbon found in and derived from plants and animals.

They also include those substances synthesized in laboratories except the oxides of carbon, carbonates, hydrogen carbonates, cyanides and cyanates.

Besides carbon, these compounds contain a few other elements such as hydrogen, oxygen, nitrogen, sulphur, halogens and phosphorus. The branch of chemistry that studies carbon compounds is called organic chemistry. This branch of chemistry was developed, starting from the theory of 'life force' to the era in which synthetic organic compounds

are used in our daily lives. The number of inorganic compounds discovered and prepared may be in the region of some hundred thousand. At present, millions of organic compounds have been discovered, synthesized, and used.

1.2 Classification of organic compounds

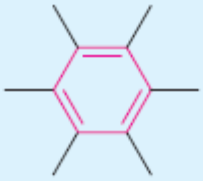
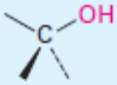
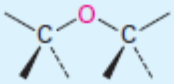
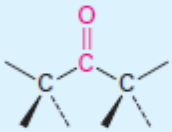
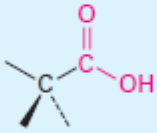
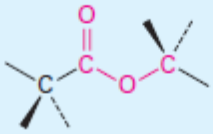
Activity 8.2

CH_3CH_2CHO and CH_3COCH_3 have the same chemical formula C_3H_6O. Write their detailed structures and observe their difference? Why do these compounds have different properties? Discuss with your group and present it to the class.

Organic compounds are generally classified based on their functional group.

***What are functional groups and what groups of organic compounds are known on the basis of this classification*?**

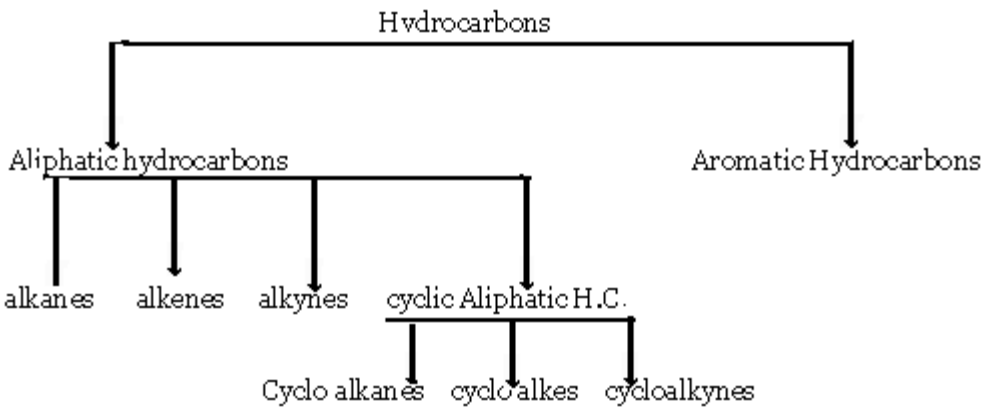
The functional group is the part of a molecule or a compound that determines the chemical properties of that molecule or compound. This group also determines some of the physical properties of a compound. Based on the functional groups they possess, the most common classification of organic compounds including alkanes, alkenes, alkynes, aromatics, alcohols, aldehydes, ketones, carboxylic acids and esters. The common functional groups of some organic compounds are given in Table 8.1.

Name	Structure*	Name ending	Example
Alkene (double bond)		*-ene*	$H_2C{=}CH_2$ Ethene
Alkyne (triple bond)	—C≡C—	*-yne*	HC≡CH Ethyne
Arene (aromatic ring)		None	Benzene
Halide	(X = F, Cl, Br, I)	None	CH_3Cl Chloromethane
Alcohol		*-ol*	CH_3OH Methanol
Ether		*ether*	CH_3OCH_3 Dimethyl ether
Aldehyde		*-al*	$CH_3CH(=O)$ Ethanal
Ketone		*-one*	$CH_3C(=O)CH_3$ Propanone
Carboxylic acid		-oic acid	$CH_3C(=O)OH$ Ethanoic acid
Ester		*-oate*	$CH_3C(=O)OCH_3$ Methyl ethanoate

8.3 Hydrocarbons (classification, Naming, uses, and general Properties)

Hydrocarbons are the simplest **organic compounds**, containing only carbon and hydrogen, they can be straight-chain, branched chain, or cyclic molecules. Carbon tends to form four bonds in a tetrahedral

geometry. **Hydrocarbon derivatives** are formed when there is a substitution of a **functional group** at one or more of these positions.



8.3.1 ALKANES, CYCLOALKANES AND ALKYL GROUPS

Alkanes are saturated hydrocarbons containing only carbon-carbon single bond; they are also known as paraffin. (i.e. small tendency for a chemical reaction). Alkanes have C – C single bond functional group. Functional group is a part of a compound that determines its physical and chemical property. For example: C - C single bond is a functional group of Alkanes.

Write the general formula for homologous series of alkanes.

Alkanes have the general formula C_nH_{2n+2}, where n is the number of carbon atoms. Alkanes have endings ***"ane"***.

The first member of alkane is methane with carbon number one. Table 8.2 shows some of the physical states of Alkanes.

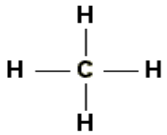
Formula	Name	Boiling point (^{0}C)	Density (g/cm^3)	State at room

				temperature
CH_4	Methane	-161.7	0.42	Gas
C_2H_6	Ethane	-88.5	0.57	Gas
C_3H_8	Propane	-4.2	0.59	Gas
C_4H_{10}	Butane	-0.4	0.60	Gas
C_5H_{12}	Pentane	36.2	0.63	Liquid
C_6H_{14}	Hexane	68.8	0.66	Liquid
C_7H_{16}	Heptane	98.5	0.68	Liquid
C_8H_{18}	Octane	125.8	0.70	Liquid
C_9H_{20}	Nonane	150.9	0.72	Liquid
$C_{10}H_{22}$	Decane	174.4	0.73	Liquid

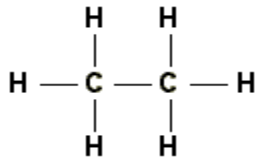
SATURATED HYDROCARBONS OR ALKANES

Those hydrocarbons which contains as many hydrogen atoms as possible are said to be saturated. On the other hand saturated hydrocarbons contains only a carbon-carbon single bond. The saturated hydrocarbons are also known as alkanes. The simplest allkane is methane (CH_4).

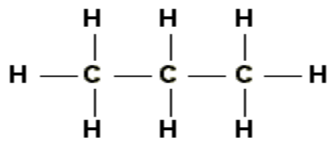
The structural formula for methane is:



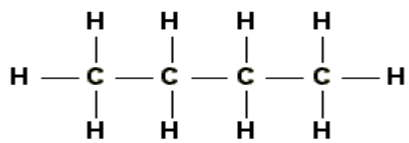
The second member of alkane is ethane with formula C_2H_6



The third member of alkane is propane which has a formula C_3H_8



The fourth member of alkane is Butane which has a formula of C_4H_{10}



If we see the above consecutive members of alkane each consecutive members differ only by a constant – CH_2 group.

A series of compounds in which each member differs from the next members by a constant amount is called a Homologous series & the members of the series are called homologous.

The general formula for alkanes is $C_nH_{2n}+2$ where n=1, 2, 3…

Alkyl radicals are obtained by removing one hydrogen atom from the corresponding alkanes. Their general formula is C*n*H2*n*+1, where *n* = 1, 2, 3 . . . . The names of alkyl radicals are derived from the names of the corresponding parent alkanes by changing the suffix -ane to -yl.

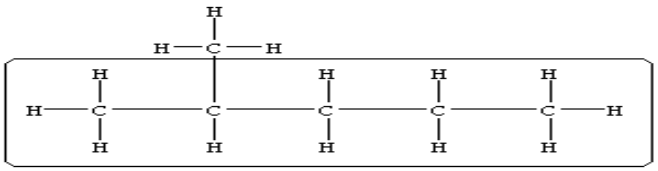
Table 8.3 indicates formulas, names and structures of some alkyl groups.

Formula of alkane	Formula of alkyl radical	Condensed structure of alkyl radical	Common name of alkyl radical
CH_4	CH_3–	CH_3–	Methyl
C_2H_6	C_2H_5–	CH_3CH_2–	Ethyl
C_3H_8	C_3H_7–	$CH_3CH_2CH_2$– $CH_3-CH(CH_3)-$	*n*-Propyl Isopropyl
C_4H_{10}	C_4H_9–	$CH_3CH_2CH_2CH_2$– $CH_3CH(CH_3)-CH_2-$ $H_3C-CH_2-C(CH_3)(H)-$ $H_3C-C(CH_3)_2-$	*n*-Butyl Isobutyl sec-Butyl (s-Butyl) tert-Butyl (t-Butyl)

NOMENCLATURE OF ALKANES:-

Common names such as pentane, isopentane and neopentane are sufficient to differentiate between the three isomers with the formula C_5H_{12}. However as the size of the hydrocarbon chain increases an international naming is required. The international union of pure and applied chemistry (IUPAC) has developed a systematic approach to naming of alkanes based on the following rules.

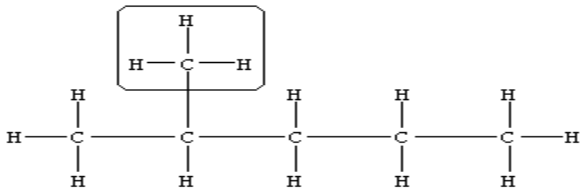
Rule – 1: Find the longest continuous chain atoms in the skeletal structure & name the compound as the derivative of the alkane with this n^o of carbon atoms.



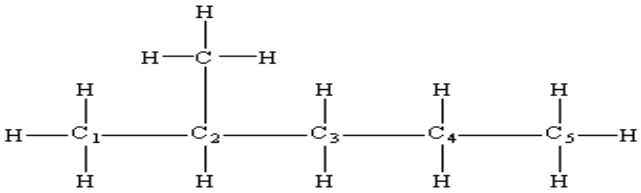
The names of the straight chain hydrocarbons is derived from Latin or Greek origin some of the 1st 10 straight chain alkane are given in the above table.

Rule- 2: Nam the substituents on the chain, substituents derived from alkanes are named by replacing the-ane ending with –yl.

Example: The substituent derived from methane is methyl (CH_3-)

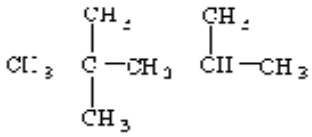


Rule- 3: Number the longest chain starting at the end nearest to the first substitute and specify the n° of carbon atoms on which the substituents are located use the lowest possible numbers.



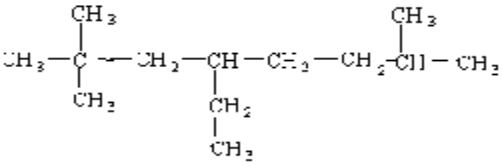
This compound is named as 2-methylpentane, not 4-methyl pentane.

Rule- 4: Use the prefixes di-,tri-, and tetra- to describe substituents that are found two, three of four times respectively on the same chain.



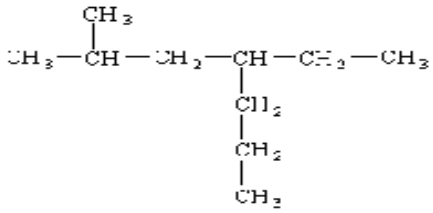
This compound is named as 2,2,4-trimethyl pentane.

Rule- 5: Arrange the names of the substituents in alphabetical order.



Is named as 4-ethyl- 2,2,7-trimethyl octane

Activity: Name the following compound



PHYSICAL AND CHEMICAL PROPERTIES OF ALKANES

What are four physical properties of alkanes?

- Insoluble in water.
- Less dense than water.
- Boiling point is directly related to length of chain.
- At standard conditions:
  - ✓ Methane to butane are gases
  - ✓ Pentane to heptadecane $C_{17}H_{36}$ are liquids
  - ✓ Octadecane and up are solids (as indicated in table 2.1 above)

What are the chemical properties of alkanes?

Alkanes are also called paraffins which comes from Latin meaning lacking affinity. Therefore, alkanes have low level of reactivity secondary to stable C-H and H-H bonds.

ISOMERS

Isomers are compounds which have the same molecular formula but different arrangement of atoms and because of this difference in their structures isomers have different physical properties such as (boiling point, refractive indexes, vapor pressures, heat of combustions, solubility etc.)

Saturated hydro carbons shows structural isomerism. The maximum number of structural isomers of alkane is determined by the general formula of $2^{n-4}+1$ where n is the number of carbon atoms.

Example: How many isomers does pentane have?

Solution: n=5

n^{o} of isomers = $2^{n-4}+1$

$= 2^{5-4}+1$

$= 3$

i.e. $CH_3CH_2CH_2CH_2CH_3$, $CH_3-CH(CH_3)CH_2CH_3$, $CH_3-C(CH_3)_2-CH_3$

Preparations of alkanes:

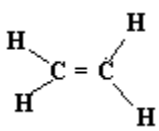
Alkanes are prepared in the laboratory by decarboxylation of carboxylate salts.

i.e. $RCOONa + NaOH \xrightarrow{heat} R\text{-}H + Na_2CO_3$

Carboxylate salt alkane

ALKENES STRUCTURE

The chemical bonding in alkenes can be illustrated by reference to the simplest alkene, ethene. This compound has the following structural form.



The double bond represents a four electron bond (i.e. two shared pairs of electrons). However, the two bond between the carbon atoms have significantly different chemical properties, and are formed in different ways. The first bond between the carbon atoms in ethene is a s bonds (sigma bonds) and is similar to the carbon to carbon bond found in the alkane series. However, the second bond between the carbon atoms in ethene is a p-bond (pi-bond), which is much more reactive than the sigma bond and behaves differently in a variety of experimental conditions.

The ethene molecule is planar (i.e. all atoms lie in the same plane) and the bond angle between all the bonds (i.e. carbon to carbon and carbon to hydrogen) is 120 degrees. This observed structure for ethene can be explained in terms of sp2 hybridisation of the orbitals on the carbon atom.

Thus, ethene is a flat molecule, the distance between the carbon atoms being less than that in ethene.

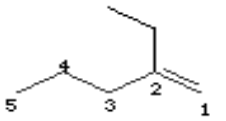
ALKENE NOMENCLATURE

Alkenes represent one of the most common functional groups in organic chemistry. An alkene contains only carbon and hydrogen (a **hydrocarbon**) and contains at least one double bond (termed an **unsaturated hydrocarbon**). Alkenes have the general formula $\mathbf{C_nH_{2n}}$,(n>2) thus, an alkene with 10 carbons (n = 10) will have 2(10) = 20 hydrogen, or themolecular formula $C_{10}H_{20}$; each double bond therefore contributes one *degree of unsaturation*.

The root, or parent name for an unbranched alkene is taken directly from the number of carbons in the chain according to a scheme of nomenclature established by the International Union of Pure and Applied Chemistry **(IUPAC)**, as described previously for alkanes.

To name alkenes:

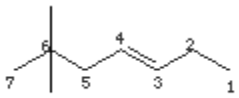
1. Find the longest chain containing the alkene(double bond)
The IUPAC name for an alkene is constructed of two parts: 1) a prefix (meth... eth... prop..., etc.) which indicates the number of carbons in the main, or parent, chain of the molecule, and 2) the suffix ...**ene** to indicate that the molecule is an alkane. For branched-chain alkanes, the name of the parent hydrocarbon is taken from the **longest continuous chain** of carbon atoms **containing the double bond**.



2-ethyl-1-pentene

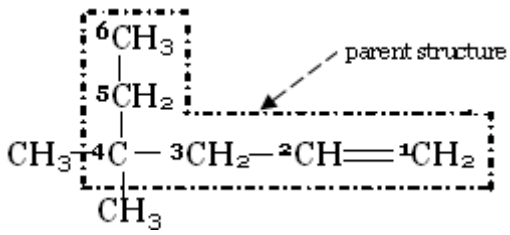
2. Number the chain, giving the double bond the lowest possible number.
Numbering of the carbons in the parent chain is always done in the direction that gives the **lowest number to the double bond**, or, **the lowest number at the first point of difference**. If there are different substituents at equivalent positions on the chain, the constituent of lower alphabetical order is given the lowest number.
If the same constituent occurs more than once in a molecule, the number of each carbon of the parent chain where the constituent occurs is given and a multiplier is used to indicate the total number of identical substituents; i.e., **di**methyl... **tri**methyl... **tetra**ethyl..., etc.

In constructing the name, substituents are arranged in alphabetical order, without regard for multipliers.



6,6-dimethyl-3-heptene

Example*:* Give IUPAC name for the following alkene



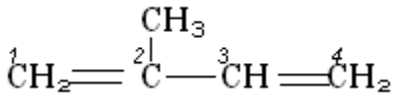
Parent name – Hexane

Position of double bond = 1- ene

Substitutes = 4, 4 – dimethyl

Therefore, the IUPAC name of the compound is: 4, 4- dimethyl-1-hexene.

Example*:* Give IUPAC name for the following Alkene



-1, 3- diene

- 2- methyl

Hence, **IUPAC** name is 2-methyl-1, 3-butadiene

ALKENES PHYSICAL PROPERTIES

The first three alkenes are gases, the intermediate alkenes are liquids and higher members of the olefin series are wax like solids at room temperature. The alkenes are insoluble in water, but are soluble in organic solvents. The liquids and solids have a density less than water.

Compound	Formula	MP degC	BP degC	Density (g/ml)
Ethylene	**C_2H_4**	**-170**	**-102**	**0.6128**

Propene	**C_3H_6**	**-185**	**-47**	**0.6142**
1-Butene	**C_4H_8**	**-130**	**-6.5**	**0.6356**

ISOMERISM IN ALKENES

Unlike alkanes alkenes have geometric isomerism in addition to its position isomerism& constitutional isomerism.

- **Constitutional (structural) isomerism** is due to substituents.
- **Position isomerism** is due to the position of the double bond.

Now let us look geometric isomerism.

GEOMETRIC ISOMERISM

Geometric isomerism (also known as cis-trans isomerism or E-Z isomerism) is a form of stereoisomerism.

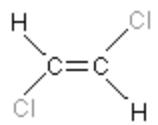
The E-Z system is better for naming more complicated structures but is more difficult to understand than cis-trans. The cis-trans system of naming is still widely used - especially for the sort of simple molecules you will meet at this level.

Where the atoms making up the various isomers are joined up in a different order, this is known as structural isomerism. Structural isomerism is *not* a form of stereoisomerism.

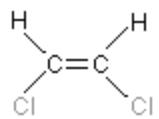
How geometric isomers arise?

These isomers occur where you have restricted rotation somewhere in a molecule. At an introductory level in organic chemistry, examples usually just involve the carbon-carbon double bond - and that's what this page will concentrate on.

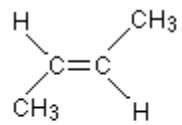
Think about what happens in molecules where there is *unrestricted* rotation about carbon bonds - in other words where the carbon-carbon bonds are all single. The next diagram shows two possible configurations of 1,2-dichloroethane.



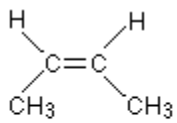
trans-1,2-dichloroethene



cis-1,2-dichloroethene



trans-but-2-ene

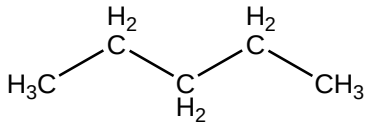


cis-but-2-ene

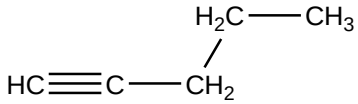
ALKYNES

- Have a general form of R–C≡C–R. Where R- is alkyl group
- Have the general formula of $\mathbf{C_nH_{2n}\text{-}2}$ where n= 2,3,4,…..
- They are isomeric with ***cyclo alkenes***

Each triple bond reduces the number of hydrogen atoms by 4. For example, consider compounds having the formula C_5H_8. The formula of the five-carbon alkane pentane is C_5H_{12} so the difference in hydrogen content is 4. The formula of 5 carbon alkyne is C_5H_8. Their structures are shown below.



pentane



pentyne

NOMENCLATURE OF ALKYNES

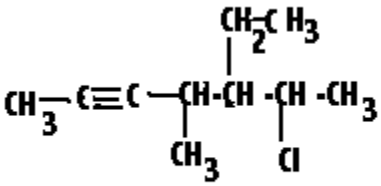
THE *IUPAC* NAMING OF ALKYNE IS SIMILAR TO THAT OF ALKENE EXCEPT THAT THE ENDING SUFFIX –'YNE' REPLACES THE SUFFIX-'ENE' OF THE ALKENE.

RULES:

1. Determine the longest continuous chain of carbons that have the triple bond.
2. Decide whether to number beginning on the right end or left end of the chain. If it makes no difference to the triple bond then shift attention to the branched groups.

3. Name the branched groups in alphabetical order attaching (hyphenating) the carbon number it is attached to along the continuous chain. of carbons to the front of the branch name. If more than one of the same kind of branched group is attached to the chain, identify the number carbon each group is attached to as a series of numbers separated by commas between each number then a hyphen and finally use a greek prefix attached to the branch name.
4. Attach a numerical prefix indicating the lowest carbon number the triple bond is between onto the normal alkane name
5. Drop the "ane" ending and add the "yne" ending.

Let's try an example. Determine the IUPAC name of the following structure:

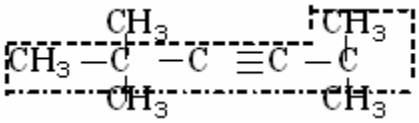


1. Determine the longest continuous chain of carbons that have the triple bond. The chain does not necessarily have to be straight. That would be seven carbons long. Actually there are two alternate continuous chains of carbpn that have seven carbons, but *teh rules* say that we choose the one that results in the greatest number of substituents.
2. Number the carbons in the chain so that the triple bond would be between the carbons with the lowest designated number. This means that you have to decide whether to number beginning on the right end or left end of the chain. If it makes no difference to the triple bond then shift attention to the branched groups. We would number from the left end and go toward the right end of the continuous chain.
3. Identify the various branching groups attached to this continuous chain of carbons by name There is a methyl group on carbon #4, an ethyl group on carbon #5, and a Chloro group on carbon #6

4. Name the branched groups in alphabetical order attaching (hyphenating) the carbon number it is attached to along the continuous chain of carbons to the front of the branch name. If more than one of the same kind of branched group is attached to the chain, identify the number carbon each group is attached to as a series of numbers separated by commas between each number then a hyphen and finally use a greek prefix attached to the branch name. 6-Chloro-5-ethyl-4-methyl
5. Attach a numerical prefix indicating the lowest carbon number the triple bond is between onto the normal alkane name 6-Chloro-5-ethyl-4-methyl-2-heptane
6. Drop the "ane" ending and add the "yne" ending associated with the Alkene family 6-Chloro-5-ethyl-4-methyl-2-heptyne

Example:

a) $^{1}CH_3\,^{2}C \equiv\,^{3}C\,^{4}CH_2\,^{5}CH_2\,^{6}CH_3$ 2 – Hexyne

b 

2, 2, 5- trimethyl-3- hexyne

ALKYNES PHYSICAL PROPERTIES

Alkynes are compounds which have low polarity, and have physical properties that are essentially the same as those of the alkanes and alkenes.

- They are insoluble in water.
- They are quite soluble in the usual organic solvents of low polarity (e.g. ligroin, ether, benzene, carbon tetrachloride, etc.).
- They are less dense than water.
- Their boiling points show the usual increase with increasing carbon number.
- They are very nearly the same as the boiling points of alkanes or alkenes with the same carbon skeletons.

Table 8.4 below show the physical properties of Alkynes

Name	**Formula**	**MP degC**	**BPdegC**	**Density(20C)**
Acetylene	HCCH	-82	-75	
Propyne	$HCCCH_3$	-101.5	-23	
1-Butyne	HCCCH2CH3	-122	91	
1-Pentyne	$HCC(CH_2)_2CH_3$	-98	40	0.695
1-Hexyne	$HCC(CH_2)_3CH_3$	-124	72	0.719
1-Heptyne	$HCC(CH_2)_4CH_3$	-80	100	0.733
1-Octyne	$HCC(CH_2)_5CH_3$	-70	126	0.747
1-Nonyne	$HCC(CH_2)_6CH_3$	-65	151	0.763
1-Decyne	$HCC(CH_2)_7CH_3$	-35	182	0.770
2-Butyne	CH_3CCCH_3	-24	27	0.694
2-Pentyne	$CH_3CCCH_2CH_3$	-101	55	0.714

ALCOHOLS

Alcohols are one of the oxygen derivative hydrocarbons. They have a general form of R-OH ; where R= alkyl or aryl group & -OH= the functional group.

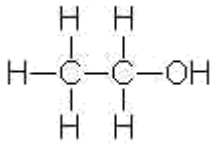
NOMENCLATURE OF ALCOHOLS

The systematic (IUPAC) nomenclature for alcohols adds the ending ***-ol*** to the name of the parent alkane and uses a number to identify the carbon that carries the OH group. The systematic name for isopropyl alcohol, for example, is 2-propanol.

Formula	**IUPAC name**	**Common name**
CH_3-OH	Methanol	methyl alcohol
CH_3CH_2-OH	Ethanol	ethyl alcohol
$CH_3CH_2CH_2OH$	Propanol	propyl- alcohol
$CH_3CHOHCH_3$	*2-Propanol*	isopropyl alcohol

1) Prefix: Take the alkane (or alkene) name that corresponds to the correct number of carbon atoms and remove the final ***e*** from the name.
2) Position number: Count the number of carbon atoms from the nearest chain end to where the hydroxyl group, ***-OH***, is attached. Put hyphens around this number and place it after the prefix.
3) Suffix: Finally the suffix ***ol*** is added to denote an alcoh***ol.***

Examples:



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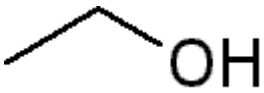
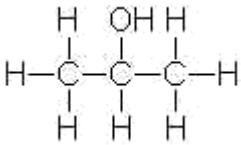


Ethanol



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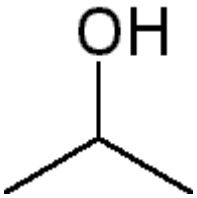
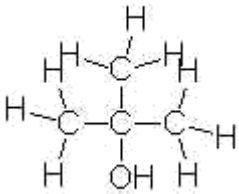


2-propanol



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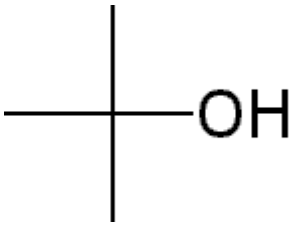


2-Methylpropan-2-ol

Physical property of Alcohols

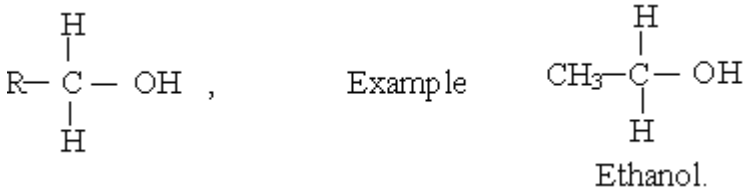
Lower alcohols are colorless and toxic liquids. They have a characteristic odor. The boiling point of alcohol increases with increasing number of carbon atoms.

Between isomers as branching increases, the boiling point decreases. Boiling point of alcohol is much higher than the corresponding alkenes because of the strong hydrogen bond in OH. Lower alcohols (from C_1 to C_3) are completely soluble in water.

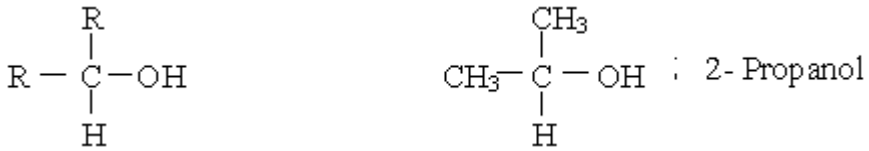
Classification of Alcohols

Alcohols are classified as either *primary* (1^0), *secondary* (2^0), or *tertiary* (3^0) on the basis of their structures.

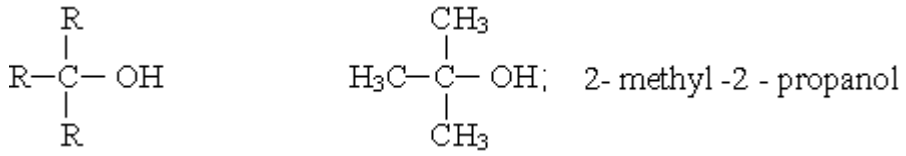
a. **Primary alcohols**: there is only one hydrocarbon group (R-group) attached to the carbon containing "OH" functional group.



b. **Secondary alcohols**: alcohols containing two "R"–groups bonded to the carbon containing OH- group. For example:

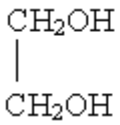


c. **Tertiary alcohols**: Contain three 'R' groups bonded to the carbon containing OH^- group. For example:



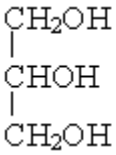
All the above alcohols have only one OH, and hence they are called monohydric alcohols. And their general formula is $\mathbf{C_nH_{2n+1}}$ **OH.** Alcohols containing more than one hydroxyl group are also known as polyhydric alcohol. These are:

I. **Dihydric alcohols**: alcohols with two hydroxyl group, and their name ends in prefix '**diols**'. They are commonly known as **glycol**. For example:



, Ethane 1, 2-diol (glycol)

II. **Trihydric alcohols**: alcohols that contain three OH groups and their name ends in prefix 'triol'. For example:



propane –1, 2, 3- triol (glycerol)

PREPARATION OF ETHANOL

a. **Fermentation:** This basic and ages old procedure involves the action of zymase (***yeast***, an ***enzyme***) on an aqueous solution of ***sucrose*** (***a simple sugar***). The by-products of the consumption of the sugar by the yeast are ***carbon dioxide*** and ***ethanol***. The carbon dioxide simply bubbles out of the solution, leaving behind a weak aqueous solution of ethanol.

$$C_6H_{12}O_{6(aq)} \longrightarrow 2CH_3CH_2OH_{(aq)} + 2CO_2$$

This weak solution of ethanol in water can be made more concentrated by the process of (***fractional***) ***distillation***,

b. **Hydration of ethene:**

The fermentation of sucrose doesn't produce enough ethanol to be commercially viable, so a different process is needed to produce the volumes of ethanol needed for industry.

The process of ***hydration*** is where the elements of water (2 H atoms and 1 O atom) are added to a molecule. In this particular case water can be added to ethene to produce ethanol, with no other by-products. It is not a straight forward process and requires a high temperature and high pressure to generate the steam. The reaction also uses a catalyst of sulphuric acid to speed up the whole process.

$$CH_2{=}CH_2 + H_2O \longrightarrow CH_3CH_2OH$$

REACTIONS OF ETHANOL

a. **Combustion**: Ethanol (along with all organic compounds) burns in excess oxygen to give carbon dioxide and water as the only products.

$$CH_3CH_2OH + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

N.B.: Less oxygen is needed to ensure complete combustion of an alcohol, than a corresponding alkane, because it contains an oxygen atom already.

b. **With sodium metal:** Just as with water, sodium metal will react with ethanol, though not nearly as violently. The ***products*** are ***hydrogen*** gas (exactly the same as with water) and ***sodium ethoxide*** (different to the reaction with water).

$$2CH_3CH_2OH + 2Na_{(s)} \longrightarrow 2CH_3CH_2ONa + H_{2(g)}$$

The hydrogen gas produced does not ignite, as the enthalpy change of reaction is not high enough. This is because the oxygen atom in water has two hydrogen atoms attached to it and only one in ethanol.

c. **Oxidation:** Refluxing ethanol with oxidizing agents such as acidified manganate $(VII)_{(aq)}$ and acidified dichromate$(VI)_{(aq)}$ ions changes it into ethanoic acid.

$$CH_3CH_2OH + [O] \longrightarrow CH_3COOH$$

Purple manganite (VII) ions (MnO_4^-) turn ***colorless*** (Mn^{2+}) and ***orange*** dichromate (VI) ions ($Cr_2O_7^{2-}$) turn ***green*** (Cr^{3+}).

d. **Halogenation:** Whilst it is easy to hydrolyse haloalkanes into alcohols, the reverse reaction requires quite extreme conditions.

A concentrated mixture of halide ions and acid are used (for example, sodium chloride in concentrated sulphuric acid) along with heat, to ensure that the -OH group leaves the alcohol (as water) and the carbon atom will accept a Cl^- ion.

$$CH_3CH_2OH + Cl^- + H^+ \longrightarrow CH_3CH_2Cl + H_2O$$

There is an old test involving the halogenation of an alcohol to determine whether an alcohol is primary, secondary or tertiary. A solution of zinc chloride in hydrochloric acid is added to the alcohol. A primary alcohol will be the slowest to show a reaction and the tertiary will be the fastest.

e. **Dehydration:** This process is the ***removal*** of the elements ***of water*** (2 H atoms and 1 O atom) from ethanol leaving ***ethene***. It is accomplished by refluxing ethanol with a

catalyst of concentrated sulphuric or phosphoric acid, or by passing ethanol vapour over heated aluminium oxide.

$$CH_3CH_2OH \longrightarrow CH_2{=}CH_2 + H_2O$$

f. **Esterification:** An ester is formed by reacting an ***alcohol*** with a ***carboxylic acid***. It is a similar type of reaction to the neutralization of an acid with a base. A catalyst of concentrated sulphuric acid removes the water produced and helps to push the equilibrium towards the products side of the equation.

$$CH_3CH_2OH + CH_3COOH \longrightarrow CH_3COOCH_2CH_3 + H_2O$$

Carboxylic acids

Carboxylic acid, any of a class of organic compounds in which a carbon (C) atom is bonded to an oxygen (O) atom by a double bond and to a hydroxyl group (—OH) by a single bond. The carboxyl (COOH) group is so-named because of the carbonyl group (C=O) and hydroxyl group. The general formula of a carboxylic acid is R−COOH or R−CO_2H, with R referring to the alkyl, alkenyl, aryl, or other group. Carboxylic acids occur widely.

Structure of Carboxylic Acids

Carboxylic acids are organic compounds that contain at least one carboxyl group in their structure. A carboxyl group is a functional group consisting of a carboxyl and a hydroxyl which is usually written as —COOH or —CO_2H

Nomenclature of Carboxylic Acids

Common names carboxlic acids

a. **Straight chain monocarboxylic acids**

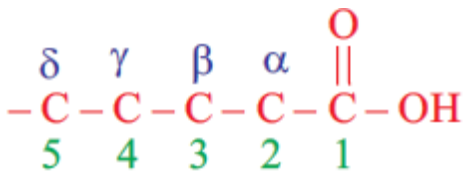
A large number of carboxylic acids have widely used common names. Those with an even number of carbon atoms ranging from 4 to 22 may be obtained by hydrolysis of animal and vegetable fats and oils. They are referred to as fatty acids, and they have common names derived from various sources. Formic acid derives its name from the Latin word for ants, because it is one of the toxic ingredients of the secretion injected by the stinging ant. Butanoic acid (butyric acid) derives its name from butter, in which it is found when the butter becomes rancid. Caproic, caprylic, and capric acids are involved in the odor of a goat, and their names derive from the Latin word, caper, for goat.

Table 8.5 lists common names of some of the most important monocarboxylic acids.

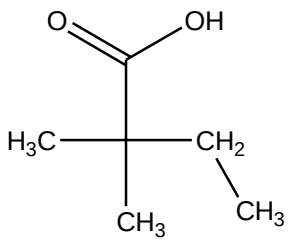
Structure	Common name	Source of name
HCOOH	Formic acid	Ant (Latin, formica)
CH_3-COOH	Acetic acid	Vinegar (Latin, acetum)
CH_3-CH_2-COOH	Propionic acid	Milk (Greek, propion)
$CH_3-CH_2-CH_2-COOH$	Butyric acid	Butter (Latin, butyrum)
$CH_3-CH_2-CH_2-CH_2-COOH$	Caproic acid	Goat (Latin, caper)

b. Branched chain and substituted carboxylic acids

In common naming system, the branched chain and substituted acids are named as derivatives of straight chain carboxylic acids. In this case, the position of the side chain or substituents is indicated by Greek letters, α, β, γ, δ... for designating the 1st, 2nd, 3rd,… position of carbon atoms as shown below:



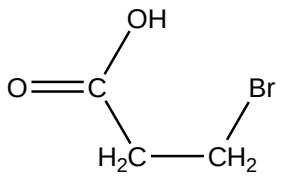
Example: Write the common names for:



a.

Solution:

It is monocarboxylic acid that consists of four carbon atoms. So, it is common name is butyric acid. In addition to this, two methyl groups are attached to α -and β-positon carbon atoms in the structure. Now, the complete common name is α, β -dimethylbutyric acid.



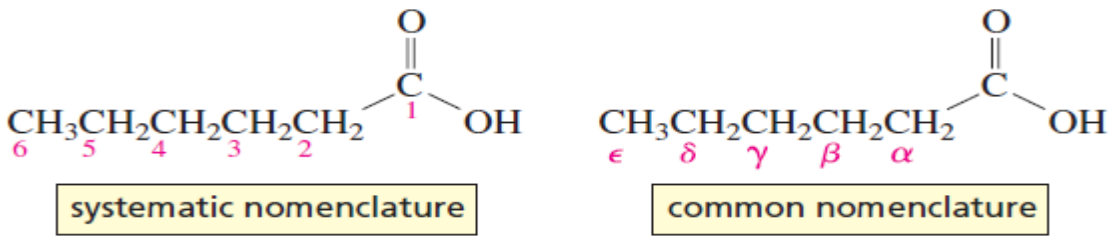
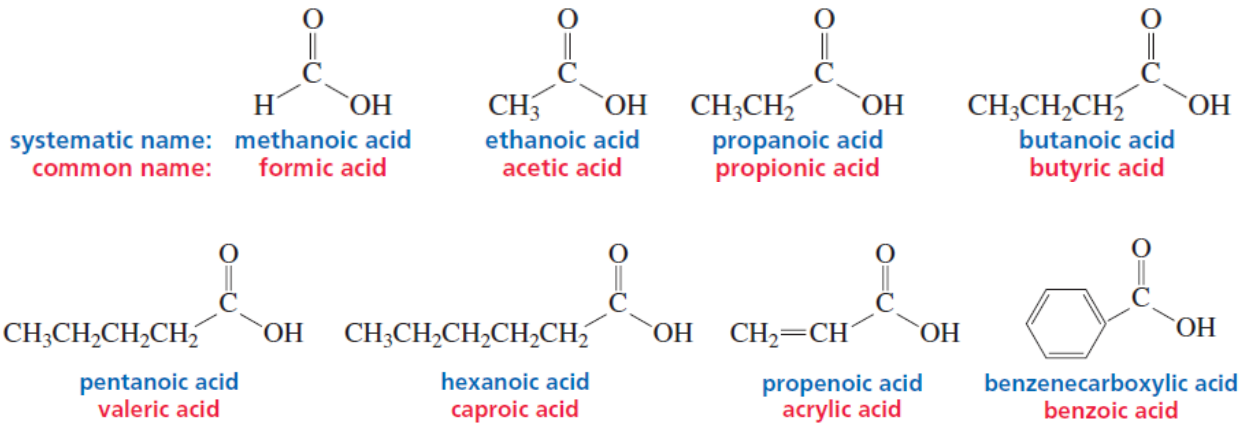
b.

Solution:

Similarly, the given acid contains three carbon atoms. Hence, the common name is propionic acid. Next, the position of bromo group, which is attached to α-carbon atom in the structure. This gives the complete common name as β -bromopropionic acid.

The IUPAC name of a carboxylic acid is derived from that of the longest carbon chain that contains the carboxyl group by dropping the final -e from the name of the parent alkane and adding the suffix -oic followed by the word "acid." The chain is numbered beginning with the carbon of the carboxyl group.

In systematic nomenclature, the position of a substituent is designated by a number. The carbonyl carbon of a carboxylic acid is always the C-1 carbon. In common nomenclature, the position of a substituent is designated by a lowercase Greek letter, and the carbonyl carbon is not given a designation. The carbon adjacent to the carbonyl carbon is the α-carbon, the carbon adjacent to the α-carbon is the β-carbon and so on.



In systematic nomenclature, a **carboxylic acid** is named by replacing the terminal "e" of the alkane name with "oic acid." For example, the one-carbon alkane is methan*e*, so the one-carbon carboxylic acid is methan*oic acid*.