



General chemistry (Chm 101)
First year
Molecular Biotechnology Group

2024-2025
First semester

Atom structure

The earliest thoughts about the composition of matter were developed by the ancient Greek philosophers.

Empedocles stated that all matter was composed of 4 elements: earth, air, fire, and water.

Democritus thought that all forms of matter were composed of tiny indivisible particles. He called these tiny indivisible particles “atoms” (from the Greek word “atomos” which means indivisible). This hypothesis was not based on experiment or scientific observations.

Aristotle rejected the theory of Democritus and modified the **Empedocles** theory. The ideas of Aristotle dominated the thinking of philosophers and scientists until the beginning of the 17th century.

Dalton's model of the Atom

John Dalton, proposed his model of the atom (which was based on facts and experiment) about 2000 years after Aristotle. Dalton model is based on the law of conservation of mass and the law of constant composition. The law is based on the idea of different kind of atoms for different elements.

From experiments it was clear that particular compounds always contain the same elements in the same proportions by mass. Thus, if pure samples of any compound are analyzed the samples always contains the same elements and in these samples, the elements are always present in the same ratio by mass.

For example, if pure samples of water were analyzed, each sample always contains **hydrogen** and **oxygen** and the ratio of **hydrogen** to **oxygen** is always equals **11.1%: 88.9%**.

A compound made of hydrogen and oxygen with a different ration between hydrogen and oxygen than this, would not be water.

For example, H_2O_2 is also composed of **hydrogen** and **oxygen** but the ratio between **hydrogen** and **oxygen** is **5.9%: 94.1%**, which is different from that of water (**11.2%: 88.8%**).

The law of definite proportions

A chemical compound always has exactly the same proportion of elements by mass.

A chemical compound is made up of two or more elements that are present in a definite proportion by mass regardless of the method by which the compound was obtained.

The law of simple multiple proportions

Atoms of two (or more) elements may combine in different ratios to form more than one compound.

Whenever two elements form more than one compound, the masses of **one element** (that combine with the same mass of the **other element**) are in a ratio of a small whole number.

Nitrogen and **oxygen** forms **NO_2** and **NO**

The ratio of **oxygen** in the two molecules = 2

For NO_2 , **N:O** = **14:32** (1: **2.286**)

For NO , **N:O** = **14:16** (1: **1.143**)

$2.286/1.143 = 2$

Carbon and oxygen form CO_2 and CO . The ratio of the mass of oxygen in the two compounds is 2.

Dalton's atomic theory

According to this model:

- Elements are composed of minute indivisible particles known as atoms.
- Atoms of the same element are alike in mass and size.
- Atoms of different elements are different in masses and sizes.
- Chemical reactions occurs through rearrangements of atoms.
- Chemical compounds are formed by the union of two or more atoms of different elements (CO , H_2CO_3).
- Atoms combine to form compounds in simple numerical ratios, such as 1:1, 2:2,and so on. (CO , H_2O_2).
- Atoms of two elements may combine in different ratios to form different compounds (CO , CO_2 , H_2O , H_2O_2 , ...etc.)

The nature and properties of electric Charge

Electric charges may be positive (+) or negative (-). Like electric charges repel while unlike electric charges attract. Electric charges can be transferred from one object to another (through contact).

The smaller the distance between two charges, the greater the force (F) of attraction between unlike charges (or repulsion between similar charges).

$F = kq_1q_2/r^2$, q_1 and q_2 are charges, r is the distance between them and k is a constant.

Discovery of Ions

Michael Faraday discovered that some substances conduct an electric current when they are dissolved in water (like the solutions of electrolytes). He also found that **atoms of some elements** migrated towards the cathode (**a negative electrode**) and **some** migrated towards the anode (**a positive electrode**). He concluded that these species were electrically charged and he called them **ions**.

According to Arrhenius, an **ion** is an atom (or a group of atoms) carrying a **positive** or a **negative** electric charge. Arrhenius accounted for the electrical conduction of molten sodium chloride (NaCl) by proposing that molten NaCl dissociated into the charged ions, **Na⁺** and **Cl⁻**:



Positive **Na⁺** ions migrated to the **cathode** and thus positive ions were called **cations** while negative **Cl⁻** ions migrated to the **anode** and accordingly negative ions were called **anions**.

Positive ions were explained by assuming that a neutral atom loses electrons ($\text{Na} \rightarrow \text{Na}^+ + \text{e}$).

Negative ions were explained by assuming that atoms gain electrons ($\text{Cl} + \text{e} \rightarrow \text{Cl}^-$).

When one or more electrons are lost from an atom, a **cation** is formed while when one or more electrons are added to a neutral atom, an **anion** is formed

Subatomic Parts of the Atom

Stoney suggested that there must be a fundamental unit of electricity and he named it (electron).

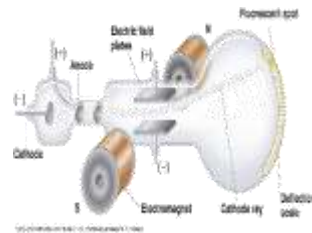
William Crookes invented the Crookes tube. It is a vacuum-sealed glass container capable of carrying electrical current. It is used in the studies of electrical discharge. Crookes tube emissions were called cathode rays.

Crookes tube experiments paved the way for understanding the subatomic structure of the atom.

It was demonstrated that cathode rays travel in straight lines, are negatively charged, deflected by the electric and magnetic fields,...etc.

Thomson's experiment and the charge-to-mass (e/m) ratio of the electron

The cathode ray tube, shown below, was used for measuring the e/m ratio.



The cathode ray tube used for the determination of the e/m ratio

As it was mentioned before, cathode rays travel in straight lines and as a consequence will cause a fluorescent spot on the fluorescent screen.

In the presence of a magnetic field (perpendicular to the direction of motion of the cathode rays) the electron beam will deviate from its straight line direction, **affected by the force of the magnetic field (Hev)**, where, H is the magnitude of the magnetic field, e is the electron charge and v is the electron velocity.

Under these conditions, the electron moves in a circular pass of a radius = r . In the circular pass, the electrons are affected also by **the centrifugal force** (mv^2/r) m is the mass of electron, v is the electron velocity and r is the radius of the circular pass.

In the circular pass of the electrons, the attraction force and centrifugal force are equal: $Hev = mv^2/r$ (i)

Rearrangement of the previous relation gives:

$$e/m = v/Hr \text{ (ii)}$$

An electric field (perpendicular to direction of the magnetic field) is applied so that the electron retunes to the straight line pass again (causing fluorescent in the original spot before applying the electrical field). Under these conditions **the electric field force equals** the **magnetic field force**:

$$Ee = Hev \text{ (iii)}$$

Deleting e from both sides in the previous relation and rearrangements gives:

$$v = E/H \text{ (iv)}$$

substituting this value of v in relation (ii) gives:

$$e/m = E/H^2r.$$

in the last relation, E and H are known while r can be determined experimentally from the geometry of the tube and hence e/m was found to be $1.7588196 \times 10^{11} \text{ C Kg}^{-1}$

Thompson model of the atom

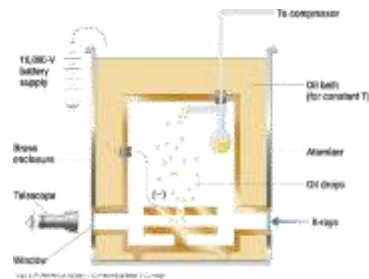
This model visualizes the atom as a sphere of positive charge with the negative electrons embedded in it.

Anode rays

Eugen Goldstein discovered anode rays and it was shown that they were positively charged particles (ions) produced from gases in certain gas-discharge tube. However, since particles from different gases had different (e/m) values, they could not be identified with a single particle.

Millikan Experiment

In 1906, Robert Millikan was able to determine the value of the charge on the electron in his famous "oil drop" experiment. A schematic of his experiment is shown below:



Apparatus used for the determination of the electron charge

Millikan used a fine spray of oil droplets in his experiment. These droplets enter the space between two charged plates through a hole in the upper plate where they acquire an electric charge.

Under the act of gravity, these oil droplets move downwards.

Under the effect of electric field opposite to gravity, these droplets move upwards.

It is also clear that by tuning the electric field, the **force** due to the pull of gravity and the **that** due to the electric field can be balanced so that the oil droplets remain suspended in space between the two electrodes.

The force due to gravitational pull = mg and the force due to electric field = Ee , where e is the charge acquired by a droplet, m is the mass of the droplet, g is the acceleration due to gravitational pull and E is the magnitude of the electric field.

When the droplet remains suspended in space, the force due to gravity equals the force due to electric field: $mg = Ee$ (assuming that the droplet acquired a single charge)

- In the absence of the electric field however, the oil drop falls downward with a velocity (U_d) proportional to mg ,

$$U_d \propto mg. \quad (i)$$

- When an electric field is applied so that the drop moves upward with a velocity (U_u). The upward velocity is proportional to $nEe - mg$. (n is the number of charges, mainly, 1)

$$U_u \propto nEe - mg \quad (ii)$$

From relation (i) and (ii) we get:

$$U_d/U_u = (mg)/(nEe - mg) \quad (iii)$$

The previous relation can be rearranged to give:

$$ne = (mg/E) (1 + U_u/U_d) \quad (iv)$$

In the previous equation U_u and U_d can be determined experimentally using the telescope so, only the value of m (the mass of the oil droplet) is required to evaluate the charge.

It is known from **Stokes**

law that: $U_d = 2gr^2/9\zeta$, where, U_d is the downward velocity of the oil droplet, (r) is the radius of the oil droplet, (g) is a constant (the acceleration in gravitational pull) and (ζ) is the

viscosity of air. When (r) is calculated from the previous relation, m can be calculated as follows: $m = \frac{4}{3} \pi r^3 d$.

From Milliken experiment, the electron charge was calculated to be 1.602×10^{-19} C.

Radioactivity

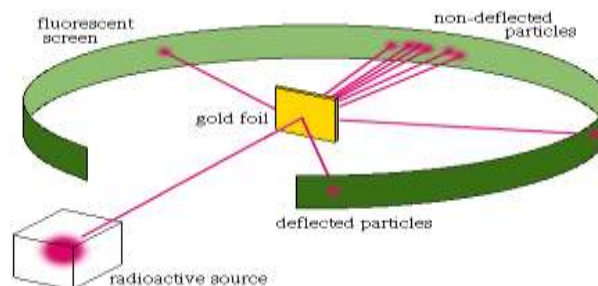
The phenomenon of radioactivity was discovered by **Becquerel** in 1896. Radioactive elements spontaneously emit alpha particles, beta particles and gamma rays from their nuclei.

Alpha particles emitted by certain radioactive elements are helium nuclei.

The Rutherford Experiment

In this experiment **Rutherford** used alpha particles emitted from a radioactive source as probes to explore the unseen atomic structure.

Alpha particles were directed towards a gold foil as shown in the diagram below.



A Diagram of Rutherford experiment

In this experiment most of the particles went through the foil (non-deflected) but a few were deflected.

To interpret these unexpected results, Rutherford presented his own physical model for the atom structure (the nuclear model atom). In his model, Rutherford suggests a small central region of a very high positive charge surrounded by a cloud of orbiting electrons.

It is worth mentioning that it was possible from the results of this experiment to calculate the radius of the nucleus.

Consider the movement of a high speed α particle through an atom having a positive central charge Ze , and surrounded by a compensating charge of Z electrons.

Alpha particles will be deflected by an angle of 180° when their kinetic energy ($1/2mv^2$) equals the repulsion force ($2Ze^2/r^2$) between the nucleus (Ze) and alpha particles ($2e$)

$$1/2mv^2 = 2Ze^2/r^2$$

Rearrangement of the previous relation gives:

$$r^2 = 4Ze^2/mv^2$$

where, m is the mass of α particle, (v) is its velocity, (e) is the charge, (r) is the distance at which α particles are reflected by 180° . According to result of this calculation, the radius of the nucleus should be less than 3.4×10^{-14} meters.

According to Rutherford model

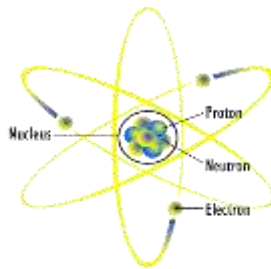
- The mass of the atom is concentrated in the nucleus
- The atom is neutral because the number of negative charges equals the number of positive charges
- The electrons orbit the nucleus at very large distances
- The centripetal force needed for the electron to orbit the nucleus arises from the attraction force between the electron and the nucleus.

It was suggested that the atom also contains neutral particles and were called neutrons and **James Chadwick** discovered the real existence the neutron in 1932. The actual mass of the neutron is slightly greater than the mass of a proton.

Inside an atom there are:

- i- electrons (e) having a charge of (-1), a mass of 5.4×10^{-4} (amu, atomic mass unit) or of 9.1095×10^{-28} gm.
- ii- protons (p) having a charge of (+1), a mass of 1.00 (amu) or a mass of 1.6725×10^{-24} gm.
- iii- neutrons having a charge of (0), a mass of 1.00 (amu) or a mass of 1.6750×10^{-24} gm. $1 \text{ amu} = 1.6605 \times 10^{-24} \text{ g}$.

Protons and neutrons are found in the nucleus, and electrons are found as cloud outside the nucleus.



The Rydberg equation

The Rydberg equation, $E=R(1/n_1^2-1/n_2^2)$, had been known experimentally.

R is the Rydberg constant, $= 1.097 \times 10^{-7} \text{m}^{-1}$,

E is measured as the wave number, $\nu = 1/\lambda$

The experimentally obtained energy of the spectral lines of atomic hydrogen can be derived from this formula by substitution with different values for n_1 and n_2 , where n_1 is always less than n_2 . For example, the experimentally observed spectral lines of Lyman ($n_1=1$ and $n_2 = 2, 3, \dots$ etc.), Balmer ($n_1 =2$ and $n_2 = 3, 4, 5 \dots$ etc), and Paschen ($n_1 =3$ and $n_2 = 4, 5, 6, \text{Brackett} (\dots) \dots$ etc).

However, the Rydberg equation did not have a theoretical explanation until the introduction of Bohr model.

Bohr model

Bohr model **depicts** the atom as a small, positively charged nucleus surrounded by electrons. The electrons move in circular orbits around the nucleus.

Bohr model succeeded to explain the Rydberg formula for the spectral emission lines of atomic hydrogen and it is considered a suitable introduction to quantum mechanics.

Why there was a need for a new model of the atom?

According to Rutherford model, the atom consists of a diffuse cloud of electrons surrounding the nucleus (small, dense and positively charged). According to the laws of classical mechanics, Rutherford model describes unstable atoms because the electron would release energy (electromagnetic radiation) while orbiting the nucleus. This means that the electron loses energy and rapidly spiral inwards, collapsing into the nucleus in a short time. Also, as the electron spirals inward, the emission would rapidly increase in frequency (as the orbit gets smaller).

Planck showed that atoms will only emit light (electromagnetic radiation) at certain discrete frequencies. $E = h\nu$ (h is Planck's constant and ν is the frequency).

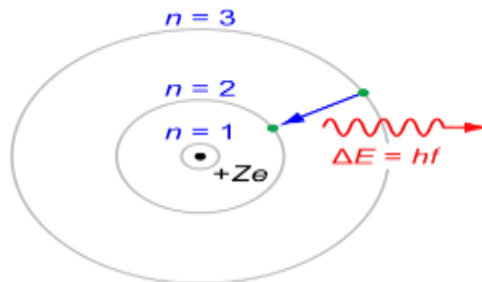
Bohr proposed his own model of the atom based upon Planck's quantum theory of radiation.

Postulates of the Bohr model

Bohr suggested that:

- 1-Electrons in atoms orbit the nucleus **stably** (not radiating) in certain orbits exist at certain distances from the nucleus (fixed energy levels). These energy levels, which are associated with definite energies, are given integer numbers 1, 2, 3 ...etc. and assigned corresponding symbols, K. L. M. N ...etc.
- 2- Electrons gain and lose energy by jumping from one allowed orbit to another. By doing so, the electron absorbs or emits electromagnetic radiation. The is energy emitted or absorbed is determined by the energy difference between the levels

involved according to the Planck's equation: $\Delta E = E_2 - E_1 = h\nu$
(where ν is the frequency and h is Planck's constant)



Electromagnetic radiation due to electron jump from the second to the first orbital

3- The angular momentum, mvr (m is the electron mass, v is the velocity and r is the radius of the orbital) is restricted to be an integer multiple of \hbar : $n\hbar$.

Where, $n = 1, 2, 3, \dots$ is called the **principal quantum number**, and $\hbar = h/2\pi$.

Starting from the angular momentum quantum rule ($mvr = nh/2\pi$) Bohr was able to calculate the energies of the allowed orbits of the hydrogen atom.

Calculation of the radius of electron shell and the velocity of the electron:

Suppose that an electron having a charge (e) and a mass (m) orbiting the nucleus (charge = Ze , Z is the number of positive protons in the nucleus) with a velocity (v) at a distance = r .

(r) is the radius of the electron shell.

The attraction force between the nucleus and the electron (Ze^2/r^2) equals the centripetal force (mv^2/r):

$$Ze^2/r^2 = mv^2/r \dots\dots\dots (1)$$

$$\text{Hence, } r = Ze^2/mv^2 \dots\dots\dots (2)$$

In the previous relation Z , m and e are known but v is not.

$$\text{But Bohr postulated that } mvr = nh/2\pi \dots\dots\dots (3)$$

Substituting for (r) from equation number (2) in the last equation (3) gives: $mvZe^2/mv^2 = nh/2\pi \dots\dots\dots (4)$

$$v = 2\pi Ze^2/nh \dots\dots(5)$$

$$\text{and } v^2 = 4\pi^2 Z^2 e^4/n^2 h^2 \dots\dots\dots (6)$$

using this value for V^2 and substituting in relation (2) gives:

$$r = n^2 h^2 / 4m\pi^2 Z e^2 \dots\dots(7).$$

From this equation it is clear that (r) increases with increasing the value (n).

Calculation of the energy of the electron

The total energy of the electron equals the potential energy ($-Ze^2/r$) and kinetic energy ($1/2 mv^2$).

$$E = (-mV^2) + (1/2mv^2) = -mv^2/2 \dots\dots\dots(8)$$

Substituting for v^2 from equation (6) in equation 8 gives:

$$E = -2m \pi^2 Z^2 e^4/n^2 h^2 \dots\dots\dots(9)$$

From the last equation it can be clearly seen that the energy increases with increasing the value of n.

The source of radiation:

When the electron jump from an orbital of higher energy n_2 to another of lower energy n_1 it emits energy (radiation).

The energy difference $\Delta E = E_2 - E_1 = (-2m \pi^2 Z^2 e^4/n_2^2 h^2) - (-2m \pi^2 Z^2 e^4/n_1^2 h^2)$

$$\Delta E = hv = 2m \pi^2 Z^2 e^4/h^2 (1/n_1^2 - 1/n_2^2)$$

$$hc/\lambda = 2m \pi^2 Z^2 e^4/h^2 (1/n_1^2 - 1/n_2^2)$$

$$1/\lambda = 2m \pi^2 Z^2 e^4/ch^3 (1/n_1^2 - 1/n_2^2)$$

$E = R(1/n_1^2 - 1/n_2^2)$ where, $R = 2m \pi^2 Z^2 e^4/ch^3 = \text{Rydberg constant } (1.079 \times 10^7 \text{m}^{-1})$

It is worth mentioning that:

Bohr's condition that the angular momentum is an integer multiple of \hbar was reinterpreted by de Broglie as a standing wave condition: a whole number of wavelengths must fit along the circumference of the electron's orbit: $n\lambda = 2\pi r$

Substituting de Broglie's wavelength of $\lambda = h/p$ in the previous relation reproduces Bohr's rule ($mvr = n\hbar$).

Bohr model gives almost exact results only for systems similar to the hydrogen atom (two charged points orbit each other at speeds much less than that of light).

The lowest value for n is 1 is related to the smallest possible orbital radius value of 0.0529 nm. which is known as the Bohr radius.

Once an electron is in this lowest orbit, **it can get no closer to the proton.**

The energy calculated from the Bohr model for the hydrogen atom is quantized:

$$E = 13.6/n^2 \text{ eV}$$

It is noteworthy that when $n = 1$, the radius is called Bohr radius (a_0):

$$r_0 = a_0 = (1)^2 h^2 / 4\pi^2 m Z e^2 = 0.0529 \text{ nm}$$

$$r = n^2 (a_0)$$

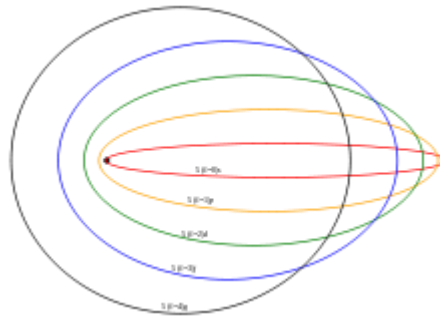
Shortcoming and disadvantages of Bohr model

- The Bohr theory failed to explain the spectra of larger atoms.
- The model also violates the uncertainty principle of Heisenberg ($\Delta p \times \Delta x \geq h/2\pi$, which implies that we cannot know both the position and speed of a particle like electron with perfect certainty).
- The model neglects the fact that the electron behaves as a particle and as a wave (the dual nature of the electron).
- Bohr model uses flat energy levels rather than spherical.

Refinements

Sommerfeld model

Instead of the Bohr model's which use circular orbits, Sommerfeld model suggested that electrons travel in **elliptical orbits** around a nucleus and that each energy level (shell) consists of a number of subshells, the number of which equals the value of n .



This suggestion implies that for each elliptical orbit around the nucleus, there are two perpendicular axes. The ratio between the lengths of these two axes is the same as that between the value of n and another quantum number, the azimuthal quantum number k ($n/k =$ the length of the longer axis/the length of the shorter axis).

For each value of n there is only one circular orbit while the others are elliptical orbits.

According to Sommerfeld model, each spectral line splits into a number of fine lines. For example, the spectral lines due to electron transition from the third level to the second level should split into 6 fine lines (because there are six possibilities for this transitions). However, experimentally, only 3 lines were observed. This was explained by the selection rule which controls electron transition. The selection rule suggests that a transition is allowed only when the difference in the azimuthal quantum number k is $+1$ or -1 .

Planck equation

The energy according to Planck = $h\nu = hc/\lambda$

h is Planck constant =

c is the speed of light

λ is the wave length

Einstein equation The energy = mc^2

m is the mass

c is the speed of light

de Broglie equation

$$\lambda = h/mv = h/p$$

v is the speed of the particle

m is the mass of the particle

λ is the wave length of the wave accompanying the moving particle

h is Planck constant

p is the momentum

The energy of a particle in a box

$$E_n = (h^2/mL^2)n^2$$

h is Planck constant

m is the mass of the particle

L is the length of the box

n is an integer number, 1, 2, 3, 3, 4,

the energy is quantized (due to the boundary conditions)

The wave function

$$\Psi_{(x)} = Ae^{ikx}$$

Ψ is the wave function

K is the wave number = $2\pi/\lambda$

A is a constant

$$d^2\Psi/dx^2 = -(2\pi/\lambda)^2 \Psi_{(x)}$$

$\Psi \Psi^* = |\Psi|^2 =$ probability of finding the particle in a certain place on the x axis

Schrödinger equation

Quantum mechanics was proposed by Werner Heisenberg. In the treatment of quantum mechanics, the idea of Bohr's model, which suggests that the energy levels of the atom are quantized, was extended into a more accurate model of electron motion.

Wave mechanics was discovered by Schrödinger. In this case, matter waves of de Broglie were employed for solutions of a three-dimensional wave equation. The wave equation describes electrons that are constrained to move about the nucleus of the hydrogen atom (or a hydrogen-like atom) while it is trapped by the potential of the positive charge of the nucleus.

The simplest form of the Schrödinger equation is: $H\psi = E\psi$, where ψ is the wave function, H is the Hamiltonian and E is the energy. The equation can be solved for the hydrogen atom and quantum numbers are originating naturally from the solution of the equation.

According to the Schrodinger equation, the probability of finding the electron around the nucleus can be determined. Also, according to this treatment of the atoms, the electron do not orbit the nucleus in definite trajectories or orbits instead, the concept orbital was used to express the probability of finding the electron in certain space in the atom.

Energy levels

The wave mechanical treatment of the atom and the solution of the Schrodinger equation to the hydrogen atom predicts principle energy levels within the atom. Each energy level is divided into sub energy levels. Sub energy levels contain orbitals with certain orientation within sublevels. Each orbital can hold 2 electrons

Quantum numbers

Principle quantum number (n) shows the place and size of the electron cloud. It is an integer positive number, 1, 2, 3, 4, 5, 6, 7 and takes corresponding symbols, K, L, M, N, O, P, Q (representing principle energy levels)

Angular momentum quantum number (l) (secondary, subsidiary or azimuthal quantum number), describes energy sublevels and the shape of orbitals (s for spherical, p for principal, d for diffuse, f for fundamental)

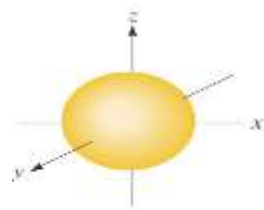
For s, $l=0$ for p, $l=1$ for d, $l=2$ for f, $l=3$

Magnetic quantum number (m_l) determines the number of orbitals and describe the orientation of the orbital in subshell.

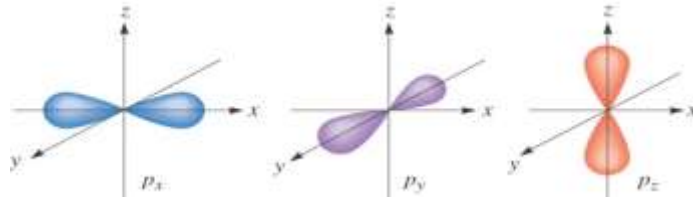
$$m_l = 2l + 1$$

Example:

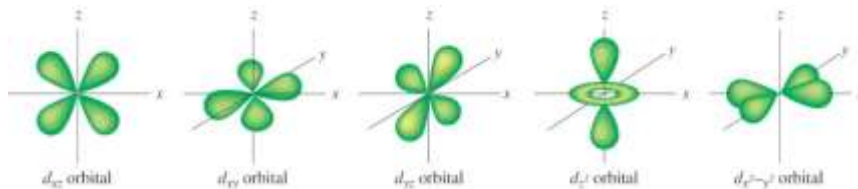
for s, it = $2 \times 0 + 1 = 1$,



for p, $m_l = 2 \times 1 + 1 = 3$, these correspond to 3 different orientations P_x, P_y, P_z and three different values (-1, 0, 1)



for d, $m_l = 2 \times 2 + 1 = 5$ these correspond to 5 different orientations d_{xz} , d_{xy} , d_{yz} , d_{z^2} , $d_{x^2-y^2}$ and 5 different values (-2, -1, 0, 1, 2)



The spin quantum number (m_s) (shows the direction of rotation of the electron about the electron own axis)

It takes two values $+1/2$ or $-1/2$

Thus, the number of electrons in each level = $2n^2$ (n is the principle quantum number)

Principles of electronic distribution

The Aufbau principle states that orbitals are filled starting with the lowest energy. The following order is right for the sublevels within a certain principle energy level $s < p < d < f$.

The sublevel of the lower (n+1) value is filled first. If the sublevels have the same value of (n+1), the electrons fill the one of the lower (n) value.

The Pauli exclusion principle states that the maximum number of electrons occupying an orbital is two, with opposite spin. In this way no two electrons exist (in the same atom) have the same 4 quantum numbers.

Hund's rule states that when there are several AO's (atomic orbitals) with equal energy, the electrons occupy the AO's one at a time before two electrons occupy the same AO (this means that pairing of two electrons cannot take place in orbitals of equivalent energy before these orbitals are singly occupied)

Example, N atom contains 7 electrons. Two of these electrons occupy the 1s sublevel, another two electrons occupy the 2s sublevel. The last three electrons occupy the three orbitals of 2p sublevel which are equivalent. Thus, an electron fills in the p_x , an electron fills in the p_y and an electron fills in the p_z .

In case of oxygen atom which contains 8 electrons, the electron filling follows the same order as in case of the nitrogen atom till electron # 7. The electron # 8, of the oxygen atom then is paired with one of the electrons singly occupying the 2p orbitals.

The electronic structure of atoms can be represented by the electronic configuration of the atom and can be illustrated as follows:



The **number** just before the **symbol** represent the **principle quantum number**

The **symbol** represents the type of **sublevel**

The **exponent** represents the number of electrons in the orbitals of the sublevel

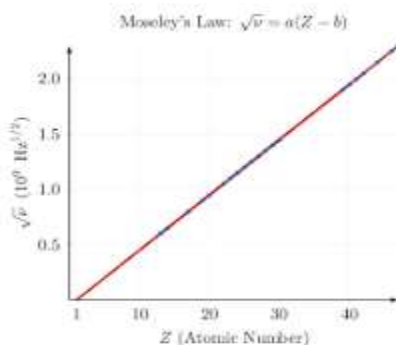
The electronic structure also can be represented in a diagram form (orbital diagram). In this orbital diagram illustration, small boxes are used to represent orbitals. An electron in a box is represented by an upward arrow. Two electrons is represented by two arrows (one upward and the other downward).

The periodic table

The periodic table is a tabular arrangement of the chemical elements. The arrangements of the elements in the early versions of the periodic table was based on the atomic masses of elements.

It was proposed that atomic number of an element equals the charge of its nucleus (A. Van den Broek). This was confirmed experimentally by Henry Moseley using X-ray spectra:

Moseley equation: $1/\lambda = a(Z-b)^2$, where $(1/\lambda)$ is the wave number, a and b are constants (b represents the shielding effect of inner electrons, Z is the atomic number).



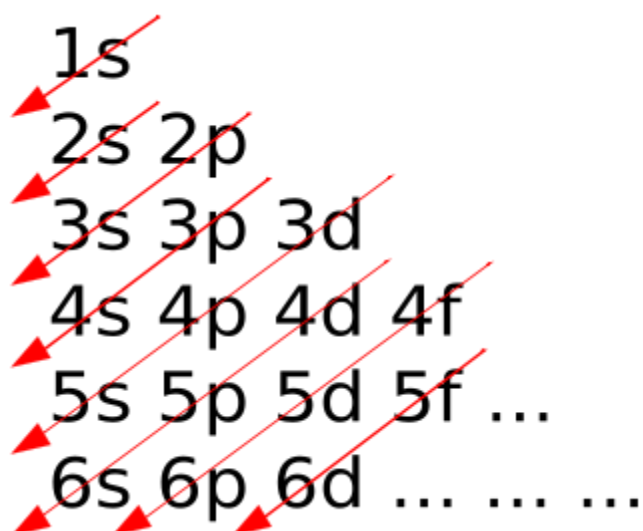
The order in which the different elements appear in the modern periodic table is related to:

- i- The atomic number (the number of protons in the nucleus). The elements in the table are placed so that the nucleus of each element has a number of protons more than the number of protons in the nucleus of the previous element by a value = 1.
- ii- The energy of sublevels.

As was mentioned before, the electron configurations of an atom is obtained through filling the energy of sublevels following some rules. For example, the $(n+1)$ value for any sublevel is calculated. The sublevel of the lower $(n+1)$ value is filled first. If the sublevels have the same value of $(n+1)$, the electrons fill the one of the lower (n) value.

Example: for 4s and 3d sublevels, the value of $(n+1)$ is 4 and 5, respectively. Therefore, 4s sublevel is filled first. For 4p and 3d, the value of $(n+1)$ is 5 for both. Because n for 3d is less than n for 4p, 3d is filled first (check the electronic configuration of K, Ca and Sc and their position in the periodic table).

The following is a simple method to fill in different orbitals with electrons:



This order in which the sublevels are arranged following the order of increasing energy according to the Madelung rule. Each diagonal red arrow corresponds to a certain value of $(n+1)$.

The order in which the elements appear in the periodic table have an impact on the periodic nature of properties of elements such as atomic size, ionization energy, metallic character,etc.

The rows of the periodic table are called periods. The number of a period is related to the outermost energy level containing electron (for all elements in the period within a row).

The elements are metals on the left hand side and non-metals on the right hand side in periods. For example, in period 3 sodium (metal) appears on the left hand side while fluoride (nonmetal) appears on right hand side.

- The columns of the periodic table are called groups. These groups also are given numbers. For example groups are given numbers from 1 to 18 starting from left to right. Letters also are used.

Representative elements groups are assigned the letter A. representative groups elements are those of s and p blocks. Transition elements are assigned the letter B (thus transition metals consists of B elements + group 8 elements)

Some groups have names as well as numbers. For example:

- Group 1 elements are called alkali metals
- Group 2 elements are called alkaline earth metals
- Group 17 elements are called the halogens;
- Gases in group 18 are called the noble gases.

The periodic table can be used to predict the properties of the elements, explain their chemical behavior and to correlate their properties.

Periodic Table of the Elements

Number of electrons in each shell

6 (Carbon example)

Atomic Number
Symbol
Name
Atomic Mass

Metals (Yellow)
Transition Elements (Red)
Inner Transition Elements (Orange)
Nonmetals (Light Blue)
Noble Gases (Pink)

1 New designation
1A Original designation

***** Synthetic
▲ Radioactive

() Atomic weight of most stable isotope

Unknown elements 113 - 118 are shown in their predicted positions

The s block elements, the electronic configuration shows that the elements in this block have their valance electrons in the s orbital. The electronic configuration is $[ng] ns^{1-2}$ (except helium, it is located on the top of the noble gases, group 18).

In the p block elements, the last electron enters the p orbital. The electronic configuration is $[ng] ns^2 np^{1-6}$.

In the d block elements, the electronic configuration varies from $[ng] (n-1) d^{1-10} (n)s^{1-2}$

The f block elements, the electronic configuration

$[ng] (n-2) f^{1-14} (n-1) d^{0-1} (n)s^2$

The elements in these blocks have some approximately similar chemical properties.

The electronic configuration of the valance electrons of the elements of a group is the same. For example, the electronic configuration of the elements of group 1A is ns^1 , for group 2A elements, it is ns^2 .

Generally, the electronic structure of an element can be represented simply using the following notation:

[noble gas] principle quantum number sublevel^{number of electrons in the orbitals of the sublevel}

For example, the electronic configuration of potassium, K (Z=19): [Ar]3s¹

Periodic trends in the periodic table

Atomic number

The atomic number represents the number of protons in the nucleus and as mentioned before, the atomic number determines the position of the element in the periodic table. It is worth mentioning that most elements have differing isotopes. The isotopes of an element have the same atomic number but have different numbers of neutrons. For example, carbon has three different isotopes all of these naturally occurring isotopes have six protons in their nuclei but each have different number of neutrons (6, 7 and 8 neutrons).

The nucleus of C-12 contains (six protons + 6 neutrons)

The nucleus of C-13 contains (six protons + 7 neutrons)

The nucleus of C-14 contains (six protons + 8 neutrons)

Hydrogen has three isotopes, protium, deuterium and tritium, the nucleus of them has (1 proton, 1 proton+1 neutron, 1 proton + 2 neutrons, respectively)

Atomic radius

Atomic radii increase down a group (due to the addition of a new energy level in each step below) and decrease from left to right in a period (in each step to left, electrons are added to the same level and at the same time the number for protons in the nucleus increases and so do the attraction forces which pulls the electrons closer to the nucleus)

Ionization energy

It is the energy required to remove an electron from the atom.

The first ionization energy is the energy required to remove one electron from an atom ($M \rightarrow M^+ + e$).

The second ionization energy is the energy required to remove a second electron from the atom ($M^+ \rightarrow M^{2+} + e$) and so on.

Example: the ionization energies of magnesium:

Number	Ionization step	Ionization energy
1 st ionization energy	$Mg \rightarrow Mg^+ + e$	738 kJ.mol ⁻¹
2 nd ionization energy	$Mg^+ \rightarrow Mg^{2+} + e$	1450 kJ/mol
3 rd ionization energy	$Mg^{2+} \rightarrow Mg^{3+} + e$	7730 KJ.mol ⁻¹

It is clear that the second ionization energy is larger than the first ionization energy because the formation of Mg^{2+} involves the removal of an electron from a positive Mg^{1+} . Also, the third ionization energy of magnesium corresponds to removal of an electron from a complete electron shell and as a result a sharp increase is observed for the ionization energy.

Ionization energy increase upwards in groups and to the right across periods. This can be explained by the fact that electrons in closer orbitals to the nucleus experience greater attraction forces and therefore their removal requires increasingly more energy.

Metallic character

Generally, the lower the values of ionization energy, the more the metallic character of the element is. On the contrary, the nonmetallic character increases with the higher values of ionization energy.

Example, sodium has low ionization energy but high metallic character while chlorine has high ionization energy but low metallic character.

Metallic character tends to decrease across a period. The most metallic element (Caesium) is located at the bottom left of the periodic table while the most nonmetallic element (fluorine) is found at the top right of the periodic table.

Ionic bond

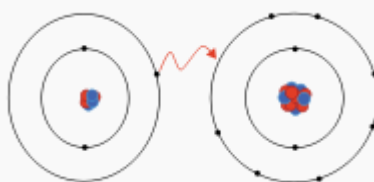
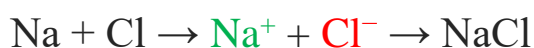
The ionic bond is formed due to the electrostatic attraction between **cations** and **anions**. In the simplest example, the cation is a metal atom like sodium (group 1A) and the anion is a nonmetal atom like chlorine (group 7A). However, the ions of the ionic bond may be of a more complex nature like NH_4^{4+} or SO_4^{2-} (i.e. molecular ions).

The ionic bond involves the transfer of an electron (or electrons) from a metal atom to a non-metal atom so that both atoms become having a full valence shell (of lower energy).

Ionic bonding, therefore, can result from a redox reaction. Atoms of an element (whose ionization energy is low) can easily give an electron to achieve a stable electron configuration. In doing so, **cations** are formed ($\text{Na} \rightarrow \text{Na}^+ + e$, attains the configuration Ne). The atom of another element (a nonmetal like Cl) accepts the electron and becomes an **anion** (to attain a stable electron configuration, $\text{Cl} + e \rightarrow \text{Cl}^-$ (attains the configuration of Ar)).

The ionic bond is thus formed through the electrostatic interaction between the **positive cation** and the **negative anion**. The electrostatic attraction between the anions and cations leads to the formation of a solid with a crystal lattice in which the ions are arranged in an alternating fashion.

When sodium (Na, $Z=11$) and chlorine (Cl, $Z=17$) are combined, the sodium atoms lose electrons to form **cations** (Na^+), and the chlorine atoms gain an electrons to form **anions** (Cl^-). These ions are then attracted to each other in a 1:1 ratio to form sodium chloride (NaCl).



It is well known that the unit cell of the crystal lattice of sodium chloride is a face centered cube (fcc, face centered cube).

Generally, in the compounds of representative elements, the elements have the electron configuration of the nearest noble gas.

Properties of the ionic compounds

Ionic compounds are those containing an ionic bond. Generally, these compounds have a high melting point. The higher the charges of the ions participating in the ionic bonding, the stronger the cohesive forces and the higher the melting point.

The ionic compound also tend to soluble in water (water is an example of polar solvents). The lower the ionic charge, the weaker the cohesive forces, the greater is the solubility. Metallic compounds have high melting and boiling points.

Covalent bond

A covalent bond is a type of chemical bonds that involves the sharing of electron pairs between atoms involved in bonding. These electron pairs are called shared pairs or bonding pairs.

The process of sharing of electrons allows each atom to attain the stable electronic configuration of lower energy. This means that the electronic configuration attained by the atoms through sharing pairs of electrons in covalent bonding is an equivalent of a full outer shell of lower energy.

The bond between the two atoms in the hydrogen molecule is formed through sharing the two electrons (1s electron, from each atom) via covalent bonding.

Covalent bonding occurs between two atoms of two different elements such as in HCl and methane CH₄,

Lewis notation is used for representing the covalent bond. In this notation valence electrons are represented as dots around the atomic symbols. A pair of electrons between two atoms represent a covalent bond (a single bond).

Multiple pairs represent multiple bonds (double bonds and triple bonds).

An alternative way of representing a covalent bond involves using a **solid line** to represent an electron pair between two atoms (H-H).

The octet rule

An atom forms enough covalent bonds to form a full outer electron shell. In methane carbon forms four covalent bonds according to this rule.

The duet rule

Hydrogen and helium may have no more than two electrons in their valence shells. In the hydrogen molecule, each atom is surrounded by two electrons (one electron from each atom).

The nature of covalent bonds and the prediction of the structures and properties of simple molecules can be understood in the light of quantum mechanics. Thus, the **valence bond model** provides a successful explanation of a chemical bond. This **theory** assumes that a chemical bond is formed when there is a good **overlap** between the atomic orbitals of participating atoms.

Types of covalent bonds

Because atomic orbitals (except for s orbitals) have specific orientation, there are different types of covalent bonds.

Sigma bonds (σ bonds) are the strongest covalent bonds. Sigma bonds are formed through **head-on overlapping** of orbitals of two atoms. A single bond is usually a σ bond.

Pi bonds (π bonds) are weaker than sigma bonds. They are formed due to a **lateral overlap** between p (or d) orbitals. A double bond between two atoms consists of one σ bond and one π bond while a triple bond consists of one σ bond and two π bonds.

The electronegativity of atoms of the bond determines the polarity of the bond. Two atoms with equal electronegativity make a nonpolar covalent bond such as H–H. An unequal

values of electronegativity of the two atoms involved in the covalent bonding results in the formation of a polar covalent bond such as with $\delta^+\text{H}-\text{Cl}\delta^-$.

It is important to notice that there are several types of structures for **covalent substances**:

Covalent substances may be **individual molecules**. Individual molecules like HCl, CO₂, and CH₄ have strong bonds within the molecule holding the atoms together but the forces of attraction between the molecules themselves is negligible. **Covalent substances** may be liquids of low boiling point such as ethanol. In this case, the attraction forces between molecules of are weak.

Covalent substances also may be solids like iodine which has a low melting point. Large numbers of atoms can be linked by covalent bonds **to form macromolecular structures**. Polymers and biopolymers are examples of macromolecular structures. Moreover, atoms in some structures such as graphite are linked covalently forming sheets (graphite has high melting and boiling points, brittle and conduct electricity). Atoms are also linked in 3-dimensional structures like in diamond (diamond has high melting and boiling points, very hard, insulator). These are **giant covalent structures** contain large numbers of atoms.

For a covalent bond to be formed, it is required that the two atoms are of comparable electronegativity where large values of differences in electronegativity of the atoms leads to the formation of ionic compounds (when the difference in electronegativity is ≥ 2 , the bond is ionic).

It is worth noting that when $0.4 < \text{electronegativity difference} < 2$ the bond is polar covalent while if the electronegativity difference ≤ 0.4 the covalent bond is nonpolar.

Molecular orbital diagram

In the **MO** theory, the molecular orbitals are formed by the overlap of atomic orbitals and, therefore, MO modelling is valid

when the atomic orbitals have comparable energy and also have the appropriate (similar) symmetry.

The molecular orbital (**MO**) diagram is used to explain and describe chemical bonding in molecules **qualitatively**.

The diagram is constructed in light of the **molecular orbital theory** and the concept of **linear combination of atomic orbitals (LCAO)**. Accordingly, atoms bond to form molecules so that a certain number of atomic orbitals combine to form the same number of molecular orbitals.

MO diagrams can explain why some molecules exist while others do not (enables calculating the bond order).

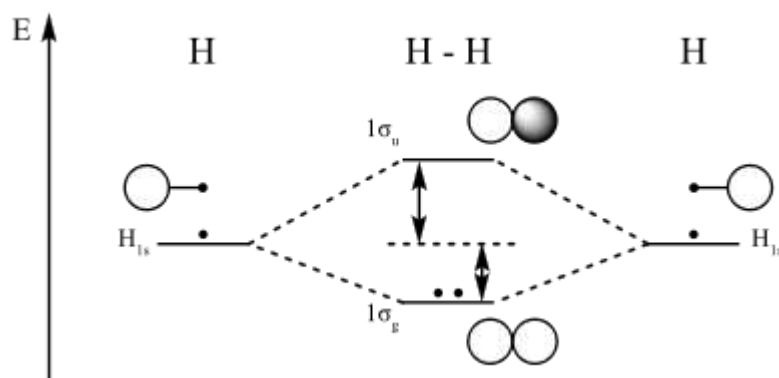
They can also predict bond strength (the type of bond (sigma or pi) and if it is single, double or a triple bond)

The electronic transitions that can take place when an electron is given energy ($\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$).

The energy in the **molecular orbital diagram** increases from the bottom to the top and the molecular orbitals are presented as short horizontal lines in the center. For comparison, these are flanked by the constituent **atomic orbitals (AO)** energy levels.

Dashed diagonal lines (connecting MO levels with their constituent AO levels) are commonly used.

Because the σ bond includes greater overlap than the π bond, it is clear that σ and σ^* (the bonding orbital and the antibonding orbital, respectively) show greater energy separation than π and π^* orbitals. Also, a more electronegative atom holds its electrons more tightly and this lowers the energy of its AO.



MO diagram for dihydrogen. Here electrons are shown by dots.

Orbital **phase** is shown either by a plus (+) or minus (-) signs or by shading one lobe. It is worth mentioning that, the **sign** of the phase does not have any physical meaning except when there is mixing for the orbitals to form molecular orbitals. Thus, two same-sign atomic orbitals undergo a constructive overlap and form a molecular orbital. In this case the bulk of the electron density is found between the two nuclei. This MO is called bonding molecular orbital and its energy is lower than those of the original atomic orbitals.

Sigma bonds are symmetric with respect to **rotation about the bond axis** (i.e. does not change phase) while a pi bond (π -bond) change phase with respect to the same operation.

If the orbital maintains its original character after an inversion about its center, it is a gerade, g. If the orbital does not maintain its original character after performing the same operation, it is ungerade, u.

The following rules apply in filling the newly formed molecular orbitals with electrons.:

The Aufbau principle states that orbitals are filled starting with the lowest energy

The Pauli exclusion principle states that the maximum number of electrons occupying an orbital is two, with opposite spins. MO levels are filled with electrons according to the Pauli

Exclusion Principle. Small vertical arrows, whose directions indicate the electron spins, are commonly used for this purpose.

Hund's rule states that when there are several MO's with equal energy, the electrons occupy the MO's one at a time before two electrons occupy the same MO.

In more complex molecules the filled MO which has the highest energy is called the **Highest Occupied Molecular Orbital** or **HOMO** and the empty MO just above it is then has the **Lowest Unoccupied Molecular Orbital** or **LUMO**.

The electrons in the bonding MO's are called bonding electrons and any electrons in the antibonding orbital would be called antibonding electrons.

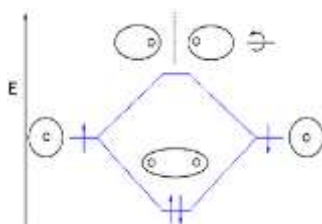
It is worth mentioning that the reduction in energy of the electrons is the driving force for chemical bond formation.

For a stable bond, the bond order, defined as:

Bond order = $\frac{1}{2}$ (no. of electrons in the bonding MOs – the no. of electrons in the anti-bonding orbitals), **must be positive**.

Dihydrogen molecular orbital diagram

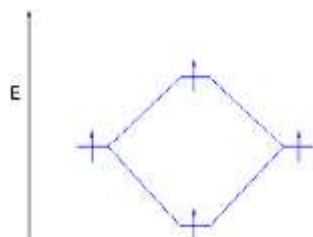
The smallest molecule, hydrogen gas exists as a dihydrogen H_2 with a single covalent bond between the two hydrogen atoms (H-H). Because each hydrogen atom has a single 1s atomic orbital for its electron, the bond forms by overlap of these two atomic orbitals. In figure the two atomic orbitals are shown on the left and on the right. The vertical axis always represents the orbital energies. Each atomic orbital is singly occupied with an up or a down arrow representing an electron.



The molecular orbital diagram of H_2

Application of MO theory for dihydrogen results in having both electrons in the bonding MO with electron configuration $1\sigma_g^2$. The bond order for dihydrogen is $(2-0)/2 = 1$.

The dihydrogen MO diagram helps explain how a bond breaks. When applying energy to dihydrogen, a molecular electronic transition takes place when one electron in the bonding MO is promoted to the antibonding MO.



In carbon monoxide (CO, isoelectronic with dinitrogen, i.e. both have 14 electrons) the oxygen 2s orbital is much lower in energy than the carbon 2s orbital and therefore the degree of mixing is low.

The electron configuration $1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ is identical to that of nitrogen.

Another representation is $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2py}^2 \pi_{2pz}^2 \sigma_{2px}^2$

The bond order = $1/2 (10-4) = 3$

The bond order for H_2^+ , H_2^- , He_2^+ is $1/2$, for He_2 is zero and thus He_2 cannot exist.

It is noteworthy that the order of energy of MO of molecules having average value of $Z < 8$ is slightly different from the order of those of molecules having average $Z \geq 8$.

The hydrogen bond

It is the electrostatic attraction that occurs when a hydrogen atom bound to a highly electronegative atom such as oxygen,

(OH) experiences attraction to some other nearby **highly electronegative atom** (H_2O).

Hydrogen bonds are commonly represented by dashed lines (see below).

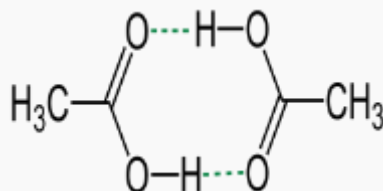
Hydrogen bond attractions occurring between molecules are termed (**intermolecular**). **Intermolecular** hydrogen bonding is responsible for the high boiling point of water ($100\text{ }^\circ\text{C}$) compared to the other group 6A hydrides that have no hydrogen bonds

Hydrogen bonds within different parts of the same molecule are termed (**intramolecular**). The **intramolecular** hydrogen bonding determines the DNA structure.

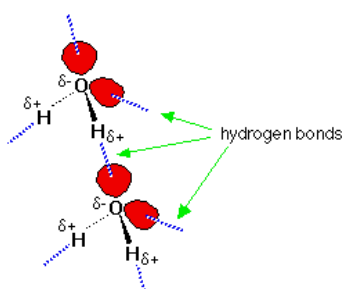
The hydrogen bond is stronger than the van der Waals interaction, but weaker than covalent or ionic bonds.

Examples:

Cyclic dimer of acetic acid



Water molecule



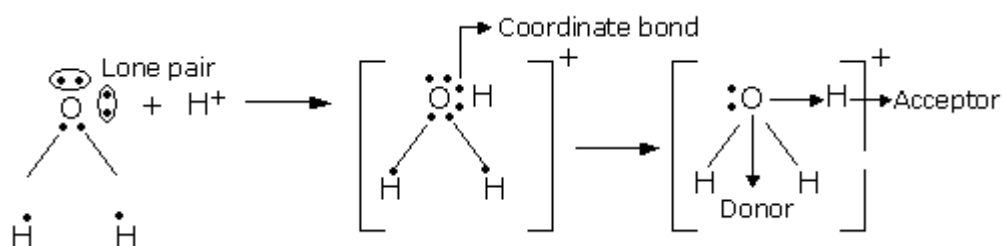
Metallic bond

Metallic bonding arises from the electrostatic attractive force between valence electrons (in the form of an electron cloud of delocalized electrons) and positively charged metal ions. It may be described as the sharing of free electrons among a lattice of positively charged ions (cations).

Metallic bonding accounts for many physical properties of metals such as strength, ductility, thermal conductivity, electrical conductivity, opacity, luster,etc.

The strength of the metallic bond depends on the charge of the nucleus, the size of the ions and the number of delocalized electrons.

Coordinate bond



A coordinate bond (a dative covalent bond or dipolar bond) is a kind of 2-center, 2-electron covalent bond. The two electrons are derived from the same atom and at the same time they are shared by the two atoms.

Example: R_3NO ($R_3N \rightarrow O$)

The **amine** donates 2 electrons to the oxygen atom.

An alternative view for this bond is that the amine gives one electron to the oxygen atom. A covalent bond (from the electron transferred to the oxygen atom and the remaining unpaired electron on the nitrogen atom) is formed.

The later process in which an electron was transferred from nitrogen to oxygen creates formal charges. Therefore, this process leaves the nitrogen positive and the oxygen negative. The structure resulting from the process may be depicted as $R_3N^+O^-$ (ionic?).

Another example of a **dative covalent bond** is that between a molecule of ammonia (a Lewis base, there is a lone pair of electrons on the nitrogen atom) and BF_3 (a Lewis acid, it is

electron deficient where the boron atom have an incomplete octet of electrons). In forming the adduct, the boron atom attains an octet configuration.



The Adduct of NH_3 and boron BF_3

Hybridization

The shape and structure of molecules affect their physical and chemical behavior. The spatial arrangements of atoms in molecules can be determined experimentally and also theoretically through modelling.

A relatively simple way to predict the structure is the Lewis structure.

According to the VSEPR (valance shell electrons pairs repulsion) theory the electron pairs repel each other and they tend to lower this repulsion. Thus, the electron pairs will arrange themselves around the central atom as far apart as possible. This process determines the shape of the molecule.

For example, BeCl_2 and CO_2 are linear molecules, ammonia NH_3 is trigonal pyramidal (the electron pairs arrangement is tetragonal, the molecule contains one unbonded electron pair), CH_4 is tetrahedral (the electron pairs arrangement is also tetrahedral, there is no unbonded electron pairs), water H_2O is a bent molecule, (the electron pairs arrangement is tetragonal and water contains two pairs of unbonded electrons)

Hybridization

Hybridization is the process of combining or mixing of atomic orbitals of an atom to create new hybridized orbitals.

The hybrid orbitals have the same shape and, energyetc.

The hybrid orbitals are different from the constituting orbitals in shape and energy,... etc.

The number of atomic orbitals combined or mixed equals the number of hybrid orbitals formed.

Hybridization is used to explain the orientation of bonds and lone pairs of electrons in molecules. The energy required for hybridization is compensated for by the energy released during bond formation (electron excitation occurs from the (s) to a (p) or a (d) orbital and from a (p) orbital to (d) orbital according the type of hybridization)

Covalent bonds are formed from the overlap between hybrid orbitals together or hybrid orbitals and non-hybrid orbitals.

Examples

Carbon forms a huge number of compounds. In these compounds it usually uses hybrid orbitals instead of pure orbitals.

Whenever one (s) orbital and one (p) orbital combine, an sp hybridization occurs (this type explains linear geometry). When one (s) orbital and two (p) orbitals combine an sp^2 hybridization occurs (this type explains trigonal planar geometry). When one (s) orbital and 3 (p) orbitals combine an sp^3 hybridization occurs (this type explains tetrahedral geometry). When one (s) orbital, three (p) orbitals and one (d) orbital combine an sp^3d hybridization occurs (this type explains trigonal pyramidal

geometry), when one (s) orbital, three (p) orbitals and two (d) orbital combine an sp^3d^2 hybridization occurs (this type explain the octahedral geometry).

It is worth meaning that (i) orbitals of the central atom only would undergo hybridization, (ii) the orbitals of almost the same energy level can mix to form hybrid orbitals

Examples: Carbon is sp in acetylene, sp^2 in ethylene and sp^3 in methane.

In diamond carbon is sp^3 while in it graphite, it is sp^2 . The layers of carbons in graphite are held together by the weak Van der Waals forces.

Van der Waal forces is a type of intermolecular forces and they are weak interactions due to dipole-dipole ($\delta^+HBr\delta^- \delta^+HBr\delta^-$) or ion -dipole ($Na^+ (\delta^-OH_2)$). Van der Waal forces are weaker than London dispersion forces.

London dispersion forces is type of intermolecular forces between non polar molecules like H_2 . The temporary shift of electron density in the molecules creates temporary dipoles. London forces is due to the interaction between these temporary dipoles of molecules.