Structure of an Atom

The atomic theory of matter was first proposed on a firm scientific basis by John Dalton in 1808. His theory, called Dalton's atomic theory, regarded the atom as the ultimate particle of matter.

Dalton's Atomic Theory (1808)
- Matter is composed of indivisible particles - atoms.
- An element is composed of only one kind of atom. These atoms in a particular element have the same properties such as mass, size, or even shape.
- A compound is composed of two or more elements combined in fixed ratios or proportions.
- In a chemical reaction, the atoms in the reactants recombine, resulting in products which represent the combination of atoms present in the reactants. In the process, atoms are neither created, nor destroyed. So a chemical reaction is essentially a rearrangement of atoms.

Ramifications of Dalton's Theory:
- The *Law of Conservation of Mass* states that mass is neither created nor destroyed in a chemical reaction or physical change.
- The *Law of Definite Proportions* states that every chemical compound is made up of elements in a definite ratio by mass.

Experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century established that atoms can be further divided into subatomic particles, i.e., electrons, protons and neutrons - a concept very different from that of Dalton. The major problems before the scientists at that time were:
- To account for the stability of atom after the discovery of sub-atomic particles,
- To compare the behaviour of one element from other in terms of both physical and chemical properties,
- To explain the formation of different molecules by the combination of different atoms,
- To understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms.

SUB-ATOMIC PARTICLES

Dalton's atomic theory failed to explain the results of many experiments e.g. substances like glass or ebonite when rubbed with silk or fur generate electricity.

Discovery of Electron

In mid 1850s, Faraday began to study electrical discharge in partially evacuated cathode ray discharge glass tube containing two thin electrodes (**Fig. 1**). The pressure of different gases could be adjusted by evacuation. When sufficiently high voltage was applied across the electrodes, current started flowing through a stream of particles moving in the tube from the cathode to the anode. These were called cathode rays or particles. The flow of current was further confirmed by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide (ZnS). When the rays struck the ZnS coating, a bright spot was developed (same thing happens in a television set) [Fig. 1(b)].
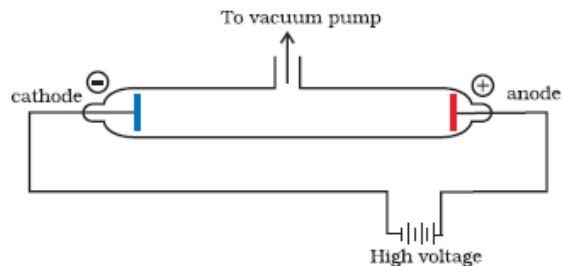
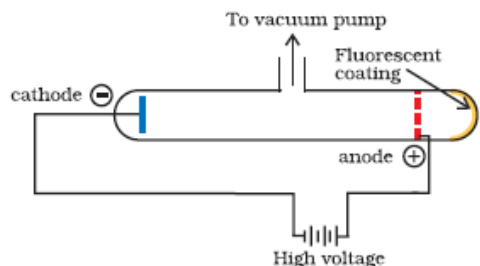**Fig. 1(a)** *A cathode ray discharge tube*

Fig. 1(b) *A cathode ray discharge tube with perforated anode*

The results of these experiments are summarized below:

i.   The cathode rays start from cathode and move towards the anode.

ii. These rays themselves are invisible but can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them.

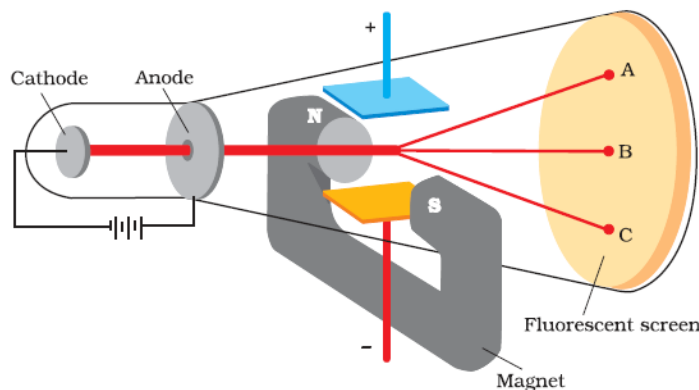iii. In the absence of electrical or magnetic field, these rays travel in straight lines (**Fig. 2**).

Fig. 2 *The apparatus to determine the charge to the mass ratio of electron*

iv. In the presence of electrical or magnetic field, the cathode rays behave like negatively charged particles, implying that cathode rays are negatively charged particles, electrons.

v.   The behaviour of cathode rays (electrons) is independent of the material of electrodes and the nature of the gas in the cathode ray tube. Thus, we can conclude that electrons are basic constituent of all the atoms.

Charge to Mass Ratio of Electron

In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (me) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (**Fig. 2**). Thomson argued that the deviation of the rays from their path in the presence of electrical or magnetic field depends upon:

   i.   The magnitude of the negative – the greater the magnitude of the charge on the particle, the greater is the interaction with the field and thus greater deflection.
   ii.   The mass of the particle – lighter the particle, greater the deflection.
   iii. The strength of the field – the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field.

- When only electric field is applied, the electrons hit the cathode ray tube at point **A**.
- When only magnetic field is applied, electron strikes the cathode ray tube at point **C**.
- Carefully balancing of the field strengths brings back the electron to hit the screen at point **B**.
- Thomson was able to determine the value of e/m by accurate measurements on the amount of deflections observed by the electrons on the electric or magnetic field strength,

$$\frac{\text{Charge}}{\text{Mass}} = \frac{e}{m} = -1.76 \times 10^{11} \; C/kg$$

Where *m* is mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C).
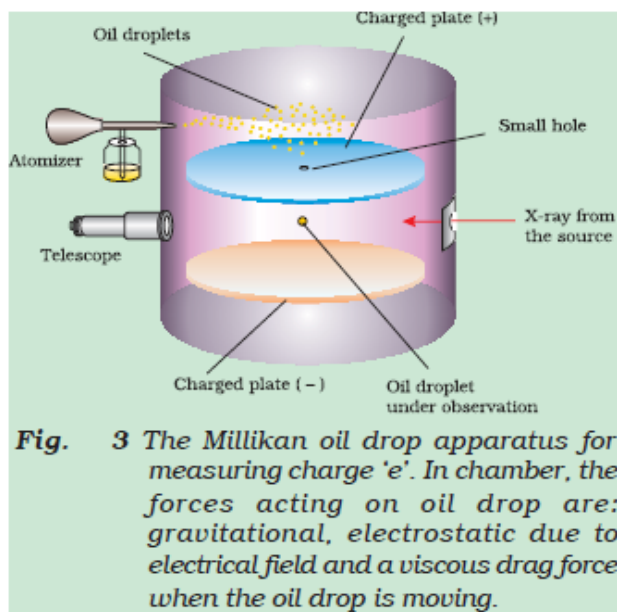
Charge on the Electron

R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found the charge on the electron to be – 1.6 x 10^{-19} C. The present accepted value of electrical charge is – 1.6022 x 10^{-19} C. The mass of the electron (m_e) was determined by combining these results with Thomson's value of e/m_e ratio.

$$m_{electron} = \frac{e}{e/m} = \frac{-1.6 \times 10^{-19} \; C}{-1.76 \times 10^{11} \; C/kg} = 9.1 \times 10^{-19} \; kg$$

Millikan's Oil Drop Method

Oil droplets in the form of mist, produced by the atomizer, were allowed to enter through a tiny hole in the upper plate of electrical condenser and their motion viewed through a telescope. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending on the charge of the droplets and the polarity and strength of the voltage applied to the plate. From the rate of fall of the droplets, Millikan was able to measure the mass of oil droplets. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the

magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, $q = n e$, where $n = 1, 2, 3….$

Fig.   3 *The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving.*

Discovery of Protons and Neutrons

Electrical discharge carried out in the modified cathode ray tube led to the discovery of particles carrying positive charge, also known as canal rays. The characteristics of these positively charged particles are listed below.

- The positively charged particles depend on the nature of gas used in the cathode ray tube.
- The charge to mass ratio of the particles depends on the gas from which these originate.
- Some of these particles carry a multiple of the fundamental unit of electrical charge.
- Their behaviour in magnetic or electrical field is opposite to that observed for electrons.

The smallest and lightest positive ion was obtained from hydrogen and was called proton, characterized in 1919. Later, Chadwick (1932) discovered the presence electrically neutral particles by bombarding a thin sheet of beryllium by α-particles, where electrically neutral particles (neutrons) having a mass slightly greater than that of the protons were emitted. The important properties of these fundamental particles are given below.

NAME	SYMBOL	ABSOLUTE CHARGE/C	RELATIVE CHARGE	MASS/KG	MASS/U	APPROX. MASS/U
Electron	e	-1.6022×10^{-19}	-1	9.10939×10^{-31}	0.000554	0
Proton	p	$+1.6022 \times 10^{-19}$	+1	1.67262×10^{-27}	1.00727	1
Neutron	n	0	0	1.67493×10^{-27}	1.00867	1

ATOMIC MODELS

The first atomic theory by John Dalton in 1808 regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century, it was proved experimentally that atoms are divisible and consist of three fundamental particles: electrons, protons and neutrons. The discovery of sub-atomic particles led to the proposal of various atomic models to explain the structure of atom.

Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model considered the mass of the atom to be evenly spread over the atom but was proved wrong by Rutherford's famous alpha-particle scattering experiment.
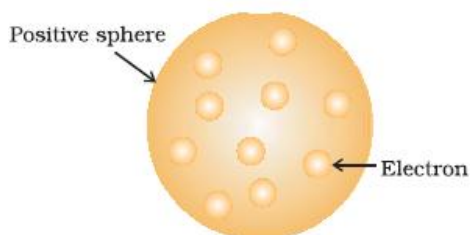
Fig. 4 Thomson model of atom

Rutherford's scattering experiment (1909) led to the conclusion that atom is made of a tiny positively charged nucleus, at its centre with electrons revolving around it in circular orbits. Rutherford model, which resembles the solar system, was no doubt an improvement over Thomson model but it could not account for the stability of the atom i.e., why the electron does not fall into the nucleus.
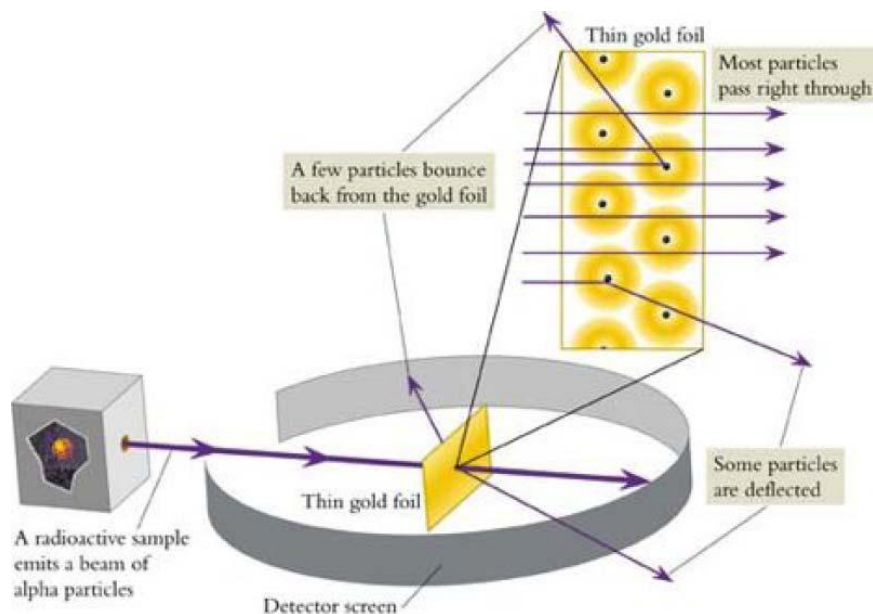

Fig. 5: Rutherford's scattering experiment. When a beam of alpha particles is "shot" at a thin gold film, most of them pass through without effect. Some are, however deflected.

Rutherford was also silent about the electronic structure of atoms i.e., about the distribution and relative energies of electrons around the nucleus. The difficulties of the Rutherford model were overcome by Niels Bohr in his model of the hydrogen atom.

Niels Bohr (1913) postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. He calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. Bohr model, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. This is because he regarded an electron as a charged particle moving in a well defined circular orbit about the nucleus. He ignored the wave character of the electron.

An orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts Heisenberg uncertainty principle.

The **Heisenberg Uncertainty Principle (**1927) by Werner Heisenberg (1901–1976): It is impossible to determine accurately both the momentum and the position of an electron (or any other very small particle) simultaneously.

 Erwin Schrödinger (1926) proposed an equation called Schrödinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This equation incorporates de Broglies concept of wave-particle duality and is consistent with Heisenberg uncertainty principle. When Schrödinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy [and the corresponding wave function(s) (ψ) (which are the mathematical functions) of the electron associated with each energy state].

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) + V\psi = E\psi$$

Wave nature for electron: De Broglie (1925) proposed that not only does light have the dual properties of waves and particles, but also particles of matter have properties of waves. The wavelength of those particle waves is given by:

$$\lambda = h/mv$$

$$h = 6.626 \times 10^{-34} \, Js$$

where m and v are the mass and velocity of the particle. Planck's constant, h, is so small that the wavelengths are in an observable range only for particles of atomic or subatomic mass.

Basic ideas of quantum mechanics:

- Atoms and molecules can exist only in certain energy states. In each energy state, the atom or molecule has a definite energy. When an atom or molecule changes its energy state, it must emit or absorb just enough energy to bring it to the new energy state (the quantum condition).
- When atoms or molecules emit or absorb radiation (light), they change their energies. The energy change in the atom or molecule is related to the frequency or wavelength of the light emitted or absorbed by the equations:

$$\Delta E = h\nu \qquad \text{or} \qquad \Delta E = hc/\lambda$$

- The allowed energy states of atoms and molecules can be described by sets of numbers called *quantum numbers*.
- The mathematical approach of quantum mechanics involves treating the electron in an atom as a *standing wave*.

1 half-wavelength

2 half-wavelengths (or one full wave)

3 half-wavelengths
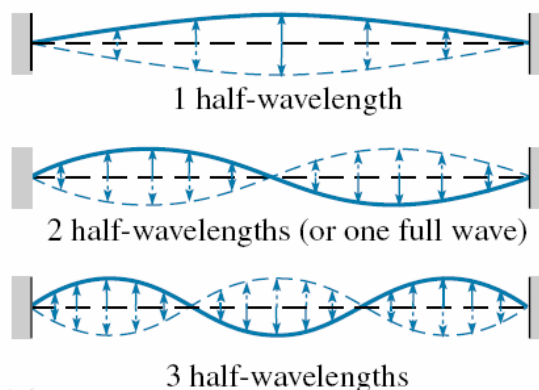
Orbitals:

- A solution to the Schrödinger equation for an electron must satisfy three quantum conditions corresponding to the three dimensions of space.
- Each quantum condition introduces an integer, called a *quantum number*, into the solution.
- A separate solution, describing a probability distribution of finding the electron at various locations, exists for each allowed set of three quantum numbers.
- Such a solution is called an *orbital.*

Quantum number:

- **Principal quantum number (n)** denotes the energy level of electrons. The larger the principal quantum number is, the larger the energy.
- The orbital size depends on n. This means that the larger the n value, the larger the orbital. Orbitals with the same n belong to the same shell.

n	1	2	3	4	5	6	7
Designation	K	L	M	N	O	P	Q

- **Angular momentum quantum number (l)** denotes the shape of the orbital. The values range from 0 to n − 1.
- The angular momentum quantum numbers correspond to different subshells.

l	0	1	2	3	4
Designation	s	p	d	f	g

- **Magnetic quantum number (m_l)** defines the different spatial orientations of the orbitals. The values range from $-l$ to $+l$.
- There are three p orbitals corresponding to $m_l = 1$, 0, and −1. However, it is usually more convenient in chemistry to use a new set of three orbitals oriented along the x, y, and z axes to display the shapes and directions of these orbitals.
- Further, there are 5 d orbitals and 7 f orbitals having different shapes and orientations in space.

s orbital

p orbitals

2 p_x orbital   2 p_y orbital   2 p_z orbital
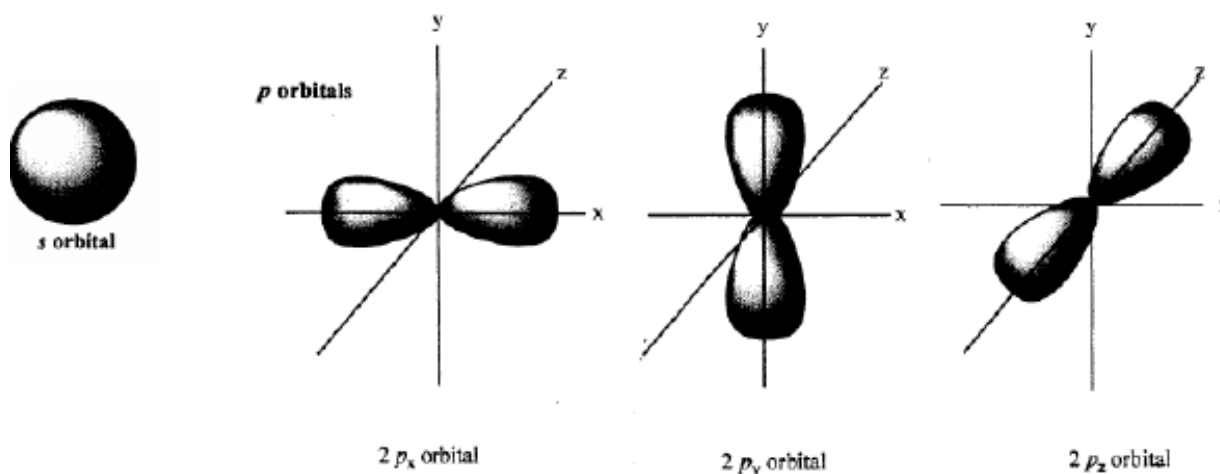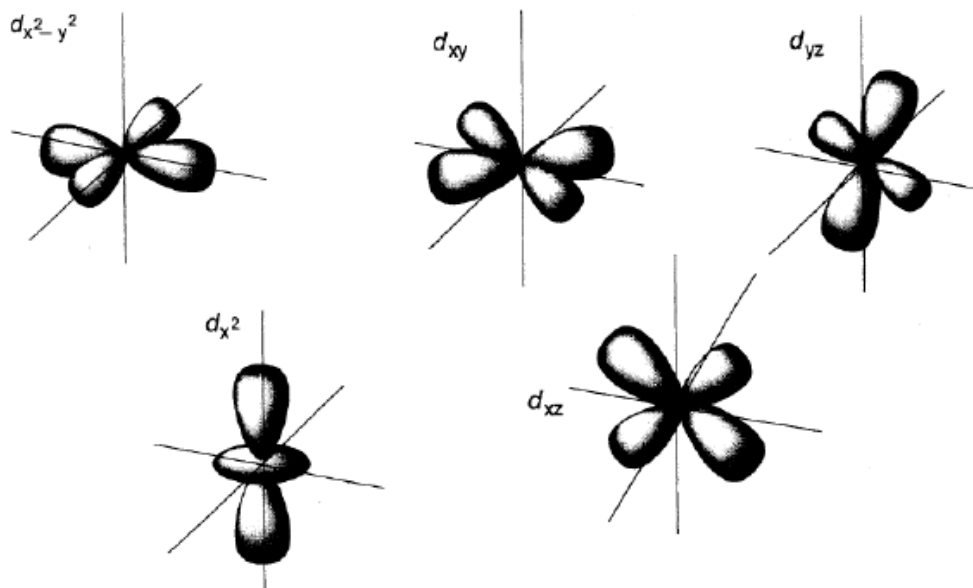
- **Spin quantum number** *(m_S)* has to do with the spin orientations of an electron. The two possible spins are denoted by the spin quantum numbers + ½ and - ½.
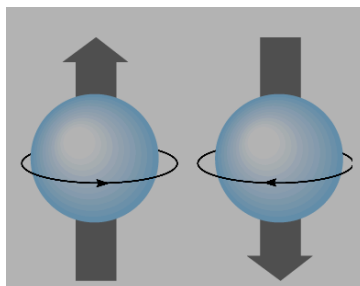
- The values of n, l, and ml describe a particular atomic orbital. Each atomic orbital can accommodate no more than two electrons, one with $m_S = +\frac{1}{2}$ and another with $m_S = -\frac{1}{2}$.
- **A set of quantum numbers: (n, l, m₁, mₛ).**

Permissible Values of the Quantum Numbers

n	ℓ	m_ℓ	m_s	Electron Capacity of Subshell = $4\ell + 2$	Electron Capacity of Shell = $2n^2$
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
	1 (2p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	18
	1 (3p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (3d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
4	0 (4s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
	1 (4p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (4d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
	3 (4f)	−3, −2, −1, 0, +1, +2, +3	$\pm\frac{1}{2}$ for each value of m_ℓ	14	

In an atom, many such orbitals are possible and electrons are filled in those orbitals in order of increasing energy in accordance with Pauli exclusion principle (no two electrons in an atom can have the same set of four quantum numbers) and Hund's rule of maximum multiplicity (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied). This forms the basis of the electronic structure of atoms.

Examples : The following examples will illustrate the applications of Hund's rule.

1. Nitrogen has atomic number 7 and hence will have the following configuration.
    $1s^2\ 2s^2\ 2p^3$

$\uparrow\downarrow$		$\uparrow\downarrow$		$\uparrow$	$\uparrow$	$\uparrow$
1s		2s		$2p_x$	$2p_y$	$2p_z$

    and not

$\uparrow\downarrow$		$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow$	
1s		2s		$2p_x$	$2p_y$	$2p_z$

2. Oxygen has atomic number 8 and the following configuration $1s^2, 2s^2, 2p^4$

$\uparrow\downarrow$		$\uparrow\downarrow$		$\uparrow\downarrow$	$\uparrow$	$\uparrow$
1s		2s		$2p_x$	$2p_y$	$2p_z$

3. Carbon has atomic number 6. In ground state its electronic configuration is $1s^2\ 2s^2\ 2p^2$

$\uparrow\downarrow$		$\uparrow\downarrow$		$\uparrow$	$\uparrow$	
1s		2s		$2p_x$	$2p_y$	$2p_z$

In excited state the energies of 2s and 2p come further close and hence the four electrons (all in 2s and 2p) divide themselves between four orbitals. Thus covalency of carbon is four.

$\uparrow\downarrow$		$\uparrow$		$\uparrow$	$\uparrow$	$\uparrow$
1s		2s		$2p_x$	$2p_y$	$2p_z$
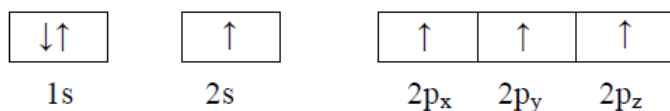
Electron configurations by the Aufbau Principle

- No two electrons in an atom may have identical sets of four quantum numbers (Pauli exclusion principle).
- Orbitals are filled in the order of increasing energy (Klechkowski´s rule).
- Electrons occupy all the orbitals of a given subshell singly before pairing begins. These unpaired electrons have parallel spins (Hund´s rule).

Example:

Iron has atomic number 26. Electronic configuration according to Aufbau principle will be: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^6$.

But empty (p^0 d^0), half filled (p^3 d^5) and completely filled (p^6 d^{10}) orbitals of a sub shell provide symmetry and are more stable as compared to other arrangements. Thus, the other stable configuration for iron will be: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^5$, $4p^1$.

Deviations from Aufbau Principle:

The deviations from regularity may occur due to one of the following reasons:

a) half filled and completely filled orbitals are more stable than partially filled orbitals,

b) diamagnetic nature of atom,

c) to explain the observed properties of elements like lanthanides and actinides.

Electron configurations

Two general rules help us to predict electron configurations:

- Electrons are assigned to orbitals in order of increasing value of $(n + l)$.
- For subshells with the same value of $(n+l)$, electrons are assigned first to the subshell with lower n.
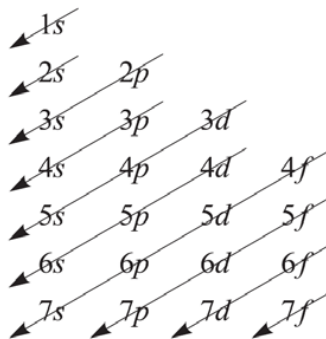
1s < 2s < 2p <3s < 3p<4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d...

Degenerate orbitals – The orbitals having equal energy are called degenerate orbitals. So p has three equivalent energy orbitals or three fold degeneracy, d orbital has 5 fold degeneracy and f has seven fold degeneracy. While filling the orbitals, no differentiation is made between three p, five d or seven f levels.

Atomic orbital	Degeneracy
s	No degeneracy
p	Triple degeneracy
d	Fivefold degeneracy
f	Sevenfold degeneracy

Electromagnetic spectrum

Visible light, infrared radiation, microwaves, radio waves, ultraviolet, x-rays and gamma rays are all types of electromagnetic radiation.
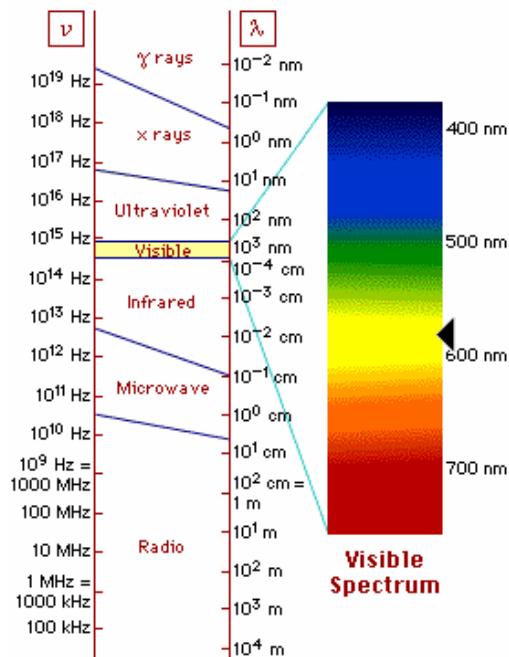
Wave character of light

- The distance between two waves, usually measured from the peak of the waves, is the **wavelength**, given the symbol lambda, λ.
- The **frequency** is a statement of the number of waves passing a point in space per second; it is given the symbol nu, ν. (The *hertz* is commonly used as the unit for frequency; 1 Hz = 1 s^{-1})
- The product of the wavelength and the frequency is equal to the velocity of light, usually designated by *c*:

$$c = \lambda\nu$$

(*The value of c can be rounded to* c=2.998 $\times 10^8$ m/s *for most calculations.*)
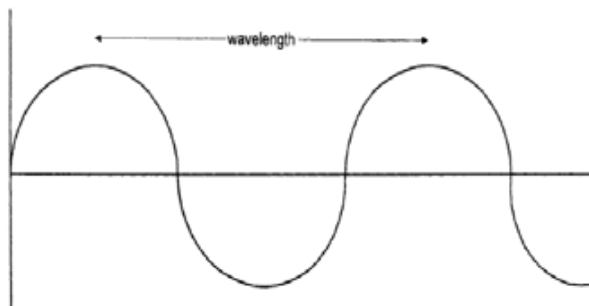
Particle character of light

- The energy of light is emitted, absorbed, or converted to other forms of energy in individual units referred to as *quanta* (singular: *quantum*).
- The unit of light energy is often referred to as the particle of light called the *photon*.
- The energy of a photon is proportional to the frequency:

$$\varepsilon = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})\nu$$

Planck's constant, *h,* is the universal proportionality constant.

Atomic spectra

- In the late 19th century, Johann Balmer (1825–1898) and Johannes Rydberg (1854–1919) showed that the wavelengths of the various lines in the hydrogen spectrum can be related by a mathematical equation:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

- Here R is 1.097 x 10^7 m^{-1} and is known as the Rydberg constant. The n's are positive integers, and n_1 is smaller than n_2.

Bohr's Model of Hydrogen Atom (1913)

The radius is given by $r = n^2 a_0$

a_0 = 5.292 x 10^{-11} m = 0.5292 Å (*Bohr radius)*

The potential energy is given by:

$$E = -\frac{1}{n^2}\left(\frac{h^2}{8\pi^2 m a_0^2}\right) = -\frac{2.180 \times 10^{-18} \text{ J}}{n^2}$$

where h Planck's constant, m the mass of the electron.

Each line in the emission spectrum represents the *difference in energies* between two allowed energy levels for the electron.

$$E \text{ of photon} = E_2 - E_1 = \left(-\frac{2.180 \times 10^{-18} \text{ J}}{n_2^2}\right) - \left(-\frac{2.180 \times 10^{-18} \text{ J}}{n_1^2}\right)$$

$$E \text{ of photon} = 2.180 \times 10^{-18} \text{ J}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{hc}{\lambda} = 2.180 \times 10^{-18} \text{ J}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = \frac{2.180 \times 10^{-18} \text{ J}}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$ **(Comparing this to the Balmer-Rydberg equation)**
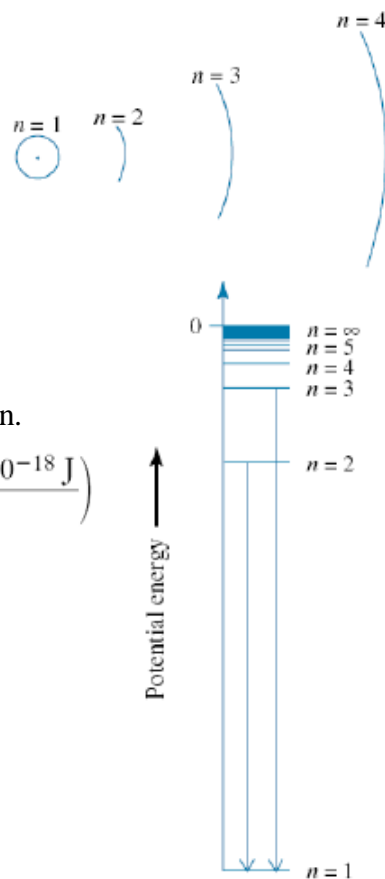
Example:

The figure shows the line spectra and the electron transitions of the hydrogen atom with its characteristic three spectral series, Lyman, Balmer and Paschen. Calculate the wavelength (in nm) of spectral line associated with the $n = 6$ to $n = 3$ electron transition in a hydrogen atom.
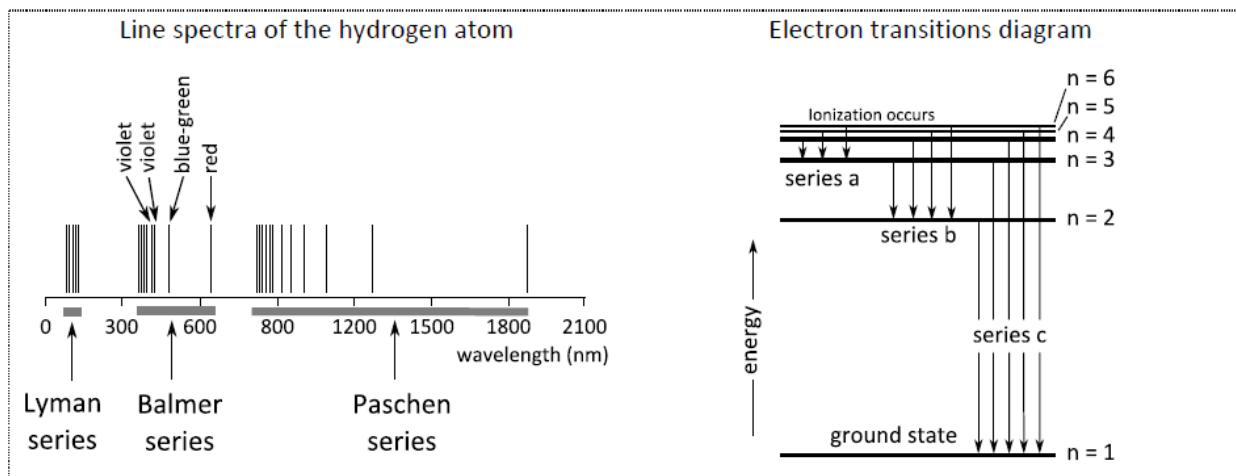
Solution:

Bohr's atom   or   Balmer-Rydberg equation

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

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_{in}^2} - \frac{1}{n_{out}^2} \right)$$

$$E_6 = -B \frac{1^2}{6^2}, \quad E_3 = -B \frac{1^2}{3^2}$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \, m^{-1} \left(\frac{1}{3^2} - \frac{1}{6^2} \right)$$

$$\Delta E_{atom} = E_3 - E_6 = \left(-B \frac{1}{9}\right) - \left(-B \frac{1}{36}\right)$$

$$\frac{1}{\lambda} = 9.145 \times 10^5 \, m^{-1}$$

$$\Delta E_{atom} = -2.178 \times 10^{-18} J \, (0.0833 \times 10^{-2})$$

$$\lambda = 1.094 \times 10^{-6} \, m \quad \text{or} \quad \textbf{1094 nm}$$

$$\Delta E_{atom} = -1.815 \times 10^{-19} J$$

$$|\Delta E_{atom}| = E_{photon} = h\nu$$

Since $c = \lambda \nu$ then $E_{photon} = hc/\lambda$

Finally, $\lambda = hc / E_{photon} = (6.626 \times 10^{-34} J.s)(2.998 \times 10^8 m.s)/(1.815 \times 10^{-19} J) = 1.094 \times 10^{-6} \, m$

The Periodic Table

- *The properties of elements are periodic functions of their atomic numbers*
- The vertical columns of elements represented in the periodic table are called groups, and the horizontal rows are called periods.
- There are seven periods in the periodic table. The groups are usually designated by roman numerals followed by the letter A or B as shown in the periodic table.

- The groups IA through VIIA are called the representative elements. These elements have either *s* or p orbital valence electrons. The last group in the periodic table is the noble gas group otherwise known as the zero group.
- The groups ranging from IB through VIIIB are called transition metals, and finally the metals from lanthanum through hafnium and metals from actinium onward are called the inner transition metals.

Period 1

Orbital Notation

	$1s$	Simplified Notation
$_1$H	↑	$1s^1$
$_2$He	↑↓	$1s^2$

Period 2

Orbital Notation

	$1s$	$2s$	$2p$			Simplified Notation		
$_3$Li	↑↓	↑				$1s^2 2s^1$	or	[He] $2s^1$
$_4$Be	↑↓	↑↓				$1s^2 2s^2$		[He] $2s^2$
$_5$B	↑↓	↑↓	↑	_	_	$1s^2 2s^2 2p^1$		[He] $2s^2 2p^1$
$_6$C	↑↓	↑↓	↑	↑	_	$1s^2 2s^2 2p^2$		[He] $2s^2 2p^2$
$_7$N	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$		[He] $2s^2 2p^3$
$_8$O	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$		[He] $2s^2 2p^4$
$_9$F	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$		[He] $2s^2 2p^5$
$_{10}$Ne	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$		[He] $2s^2 2p^6$

Period 3

Orbital Notation

		$3s$	$3p$			Simplified Notation
$_{11}$Na	[Ne]	↑				[Ne] $3s^1$
$_{12}$Mg	[Ne]	↑↓				[Ne] $3s^2$
$_{13}$Al	[Ne]	↑↓	↑	_	_	[Ne] $3s^2 3p^1$
$_{14}$Si	[Ne]	↑↓	↑	↑	_	[Ne] $3s^2 3p^2$
$_{15}$P	[Ne]	↑↓	↑	↑	↑	[Ne] $3s^2 3p^3$
$_{16}$S	[Ne]	↑↓	↑↓	↑	↑	[Ne] $3s^2 3p^4$
$_{17}$Cl	[Ne]	↑↓	↑↓	↑↓	↑	[Ne] $3s^2 3p^5$
$_{18}$Ar	[Ne]	↑↓	↑↓	↑↓	↑↓	[Ne] $3s^2 3p^6$

Period 4

Orbital Notation

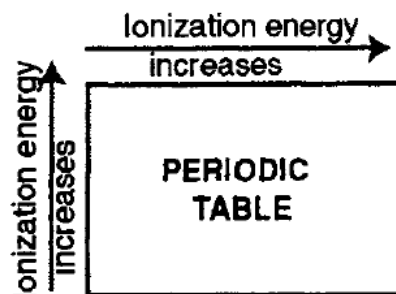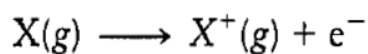|		3d	4s	4p	Simplified Notation
$_{19}$K	[Ar]		↑		[Ar] $4s^1$
$_{20}$Ca	[Ar]		↑↓		[Ar] $4s^2$
$_{21}$Sc	[Ar]	↑ _ _ _ _	↑↓		[Ar] $3d^14s^2$
$_{22}$Ti	[Ar]	↑ ↑ _ _ _	↑↓		[Ar] $3d^24s^2$
$_{23}$V	[Ar]	↑ ↑ ↑ _ _	↑↓		[Ar] $3d^34s^2$
$_{24}$Cr	[Ar]	↑ ↑ ↑ ↑ ↑	↑		[Ar] $3d^54s^1$
$_{25}$Mn	[Ar]	↑ ↑ ↑ ↑ ↑	↑↓		[Ar] $3d^54s^2$
$_{26}$Fe	[Ar]	↑↓ ↑ ↑ ↑ ↑	↑↓		[Ar] $3d^64s^2$
$_{27}$Co	[Ar]	↑↓ ↑↓ ↑ ↑ ↑	↑↓		[Ar] $3d^74s^2$
$_{28}$Ni	[Ar]	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓		[Ar] $3d^84s^2$
$_{29}$Cu	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑		[Ar] $3d^{10}4s^1$
$_{30}$Zn	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓		[Ar] $3d^{10}4s^2$
$_{31}$Ga	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑ _ _	[Ar] $3d^{10}4s^24p^1$
$_{32}$Ge	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑ ↑ _	[Ar] $3d^{10}4s^24p^2$
$_{33}$As	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑	[Ar] $3d^{10}4s^24p^3$
$_{34}$Se	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑	[Ar] $3d^{10}4s^24p^4$
$_{35}$Br	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑	[Ar] $3d^{10}4s^24p^5$
$_{36}$Kr	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	[Ar] $3d^{10}4s^24p^6$

Periodicity of Atomic Properties
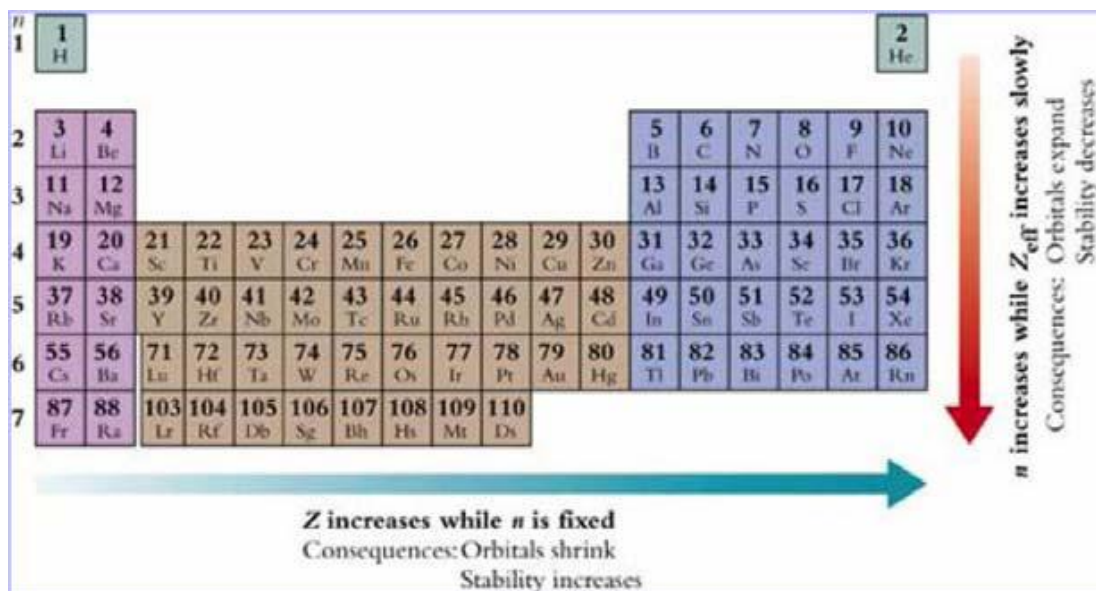
As principal quantum number n increases, atomic orbitals become larger and less stable. As atomic number Z increases, any given atomic orbital becomes smaller and more stable.
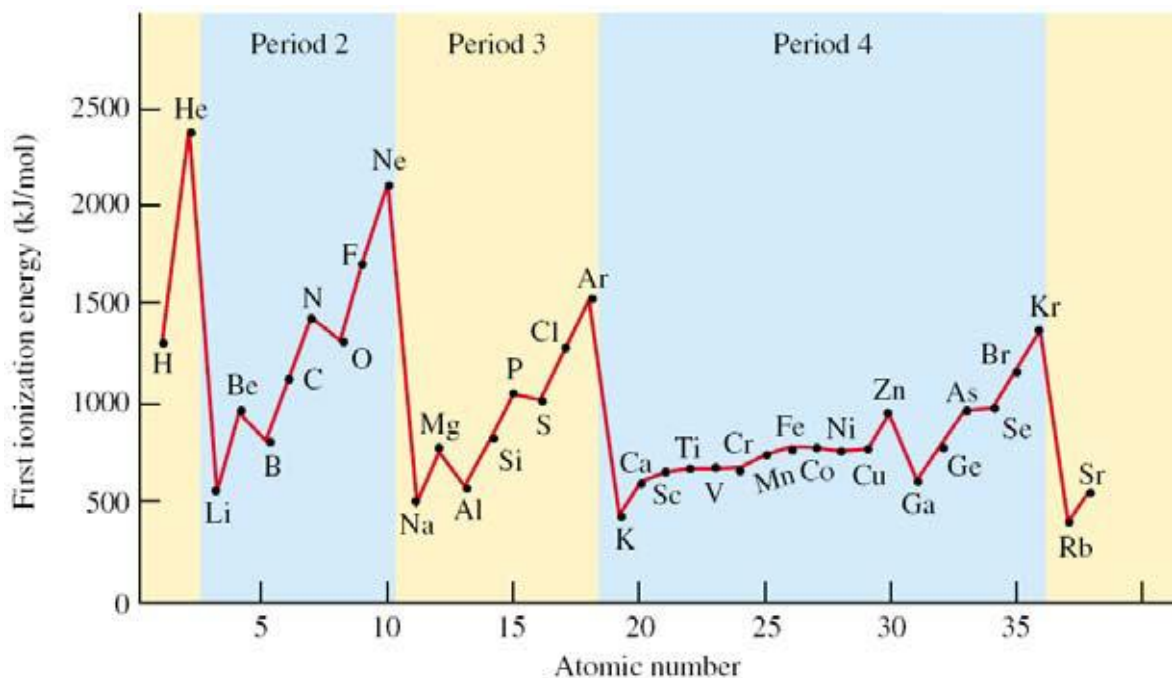
Atomic size

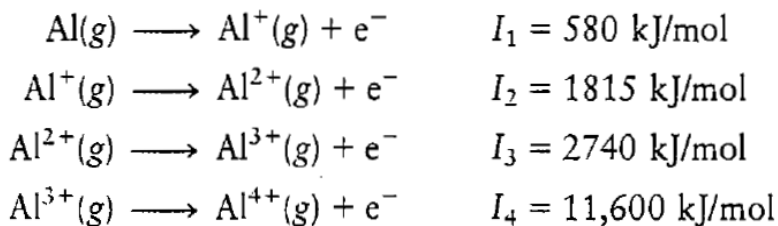| IA	IIA		IIIA	IVA	VA	VIA	VIIA	VIIIA
				Atomic radii				
H 0.37								He 0.31
Li 1.52	Be 1.12		B 0.85	C 0.77	N 0.75	O 0.73	F 0.72	Ne 0.71
Na 1.86	Mg 1.60		Al 1.43	Si 1.18	P 1.10	S 1.03	Cl 1.00	Ar 0.98
K 2.27	Ca 1.97		Ga 1.35	Ge 1.22	As 1.20	Se 1.19	Br 1.14	Kr 1.12
Rb 2.48	Sr 2.15		In 1.67	Sn 1.40	Sb 1.40	Te 1.42	I 1.33	Xe 1.31
Cs 2.65	Ba 2.22		Tl 1.70	Pb 1.46	Bi 1.50	Po 1.68	At 1.40	Rn 1.41

Exercise: Arrange the following elements in terms of increasing atomic radius: Mg, Cl, K and Cs.

Ionization energy (IE) is the minimum amount of energy required to remove an electron from an atom.

$$X(g) \longrightarrow X^+(g) + e^-$$

Ionization energy increases →

Ionization energy increases ↑

PERIODIC TABLE

First IE < Second IE < Third IE < Fourth IE < ...

$$Al(g) \longrightarrow Al^+(g) + e^- \qquad I_1 = 580 \text{ kJ/mol}$$
$$Al^+(g) \longrightarrow Al^{2+}(g) + e^- \qquad I_2 = 1815 \text{ kJ/mol}$$
$$Al^{2+}(g) \longrightarrow Al^{3+}(g) + e^- \qquad I_3 = 2740 \text{ kJ/mol}$$
$$Al^{3+}(g) \longrightarrow Al^{4+}(g) + e^- \qquad I_4 = 11,600 \text{ kJ/mol}$$

Electron affinity is the energy change associated with the addition of an electron to a gaseous atom.

$$X(g) + e^- \longrightarrow X^-(g)$$

H					Electron Affinity				He	
−73									0	
Li	Be			B	C	N	O	F	Ne	
−60	(~0)			−29	−122	0	−141	−328	0	
Na	Mg			Al	Si	P	S	Cl	Ar	
−53	(~0)	Cu		−43	−134	−72	−200	−349	0	
		−118								
K	Ca	Ag	Ga	Ge	As	Se	Br	Kr		
−48	(~0)	−125	−29	−119	−78	−195	−324	0		
Rb	Sr	Au	In	Sn	Sb	Te	I	Xe		
−47	(~0)	−282	−29	−107	−101	−190	−295	0		
Cs	Ba		Tl	Pb	Bi					
−45	(~0)		−19	−35	−91					

Electronegativity

The relative tendency of an atom to attract the bonding electrons to itself is called electronegativity. The popularly used electronegativity scale is based on a system called Pauling's scale, according to which fluorine (the most electronegative element) has an electronegativity value of 4.0. Nonmetals are the most electronegative elements.
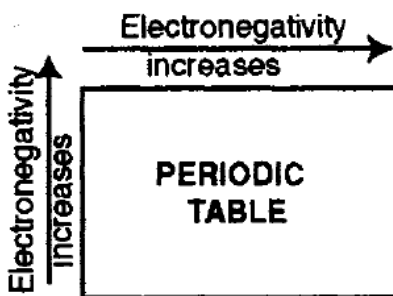
Electronegativity Values of the Elements:

Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	H 2.1																	He
2	Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
3	Na 1.0	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
4	K 0.9	Ca 1.0	Sc 1.3	Ti 1.4	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.6	Ga 1.7	Ge 1.9	As 2.1	Se 2.4	Br 2.8	Kr
5	Rb 0.9	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.5	Mo 1.8	Tc 1.7	Ru 1.8	Rh 1.8	Pd 1.8	Ag 1.6	Cd 1.6	In 1.6	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
6	Cs 0.8	Ba 1.0	La 1.1	Hf 1.3	Ta 1.4	W 1.5	Re 1.7	Os 1.9	Ir 1.9	Pt 1.8	Au 1.9	Hg 1.7	Tl 1.6	Pb 1.7	Bi 1.8	Po 1.9	At 2.1	Rn
7	Fr 0.8	Ra 1.0	Ac 1.1															

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.0	Lu 1.2

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th 1.2	Pa 1.3	U 1.5	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.5

Legend: Metals, Nonmetals, Metalloids

Atomic Number and Mass Number

The presence of positive charge on the nucleus is due to the protons in the nucleus. The number of protons present in the nucleus is equal to atomic number (Z). For example, the number of protons in the hydrogen nucleus is 1, in sodium atom it is 11. In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, Z). For example, number of electrons in hydrogen atom and sodium atom are 1 and 11 respectively.

$$Mass\ number \nearrow \quad ^{A}_{Z}X \longleftarrow Element$$
$$Atomic\ number \nearrow$$
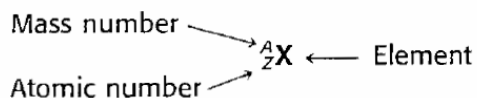
(Z) = number of protons in the nucleus = number of electrons in a nuetral atom

Mass number (A) = number of protons (Z) + number of neutrons (n)

Atomic mass unit (amu)

Atomic mass unit (amu) is defined as exactly 1/12 the mass of a ^{12}C atom. The mass of the ^{12}C atom is taken to be exactly 12 amu.

^{1}H	1.00783	^{12}C	12.00000	^{17}O	16.99913	^{35}Cl	34.96885
^{2}H	2.01410	^{13}C	13.00335	^{18}O	17.99916	^{37}Cl	36.96590
^{3}H	3.01605	^{14}C	14.00324	^{18}F	18.00094	^{36}Ar	35.96755
^{4}He	4.00260	^{16}C	16.01470	^{18}Ne	18.00571	^{38}Ar	37.96273
^{6}He	6.01889	^{14}N	14.00307	^{28}Si	27.97693	^{40}Ar	39.96238
^{6}Li	6.01512	^{15}N	15.00011	^{29}Si	28.97649	^{87}Rb	86.90919
^{7}Li	7.01600	^{16}N	16.00610	^{30}Si	29.97377		
^{7}Be	7.01693	^{16}O	15.99491	^{32}S	31.97207		

Isobars and Isotopes

- **Isobars**: atoms with same mass number but different atomic number e.g., $^{14}_{6}$C and $^{14}_{7}$N.
- **Isotopes**: atoms with identical atomic number but different atomic mass number. For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called protium ($^{1}_{1}$H). Rest of the percentage of hydrogen atom contains two other isotopes; deuterium ($^{2}_{1}$D, 0.015%) and tritium ($^{3}_{1}$T).
- The *atomic mass* of an element is the weighted average of the masses of the individual isotopes of the element.
  Example: Naturally occurring copper consists of 69.17% ^{63}Cu and 30.83% ^{65}Cu. The mass of ^{63}Cu is 62.939598 amu, and the mass of ^{65}Cu is 64.927793 amu. What is the atomic mass of copper?

  The *weighted average* is the sum of the mass of each isotope times its fraction present:

  $$62.939\ 598\ \text{amu}\left(\frac{69.17}{100}\right) + 64.927\ 793\ \text{amu}\left(\frac{30.83}{100}\right) = 63.55\ \text{amu}$$

  Chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus. Therefore, all the isotopes of a given element show same chemical behaviour.