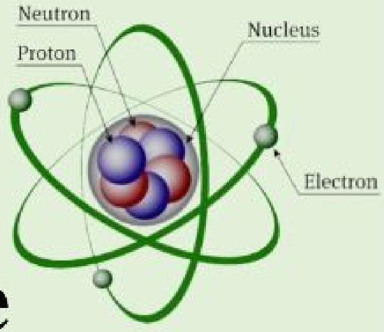

1.Atomic Structure

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Introduction

Chemistry is the study of the properties and behaviour of matter. **Matter** is the physical material of the universe; it is anything that has mass and occupies space.

Although the materials in our world vary greatly in their properties, everything is formed from only about 100 elements and, therefore, from only about 100 chemically different kinds of atoms. (118 elements have been discovered so far but the heavier atoms are short lived and not found naturally.)

1.1 The atomic theory of matter

Philosophers from the earliest times speculated about the nature of the fundamental components from which the world is made. **Empedocles** (~ 440 BC) believed that the four elements-earth, fire, air and water made up all things. The Hindus believed that the four elements stated above makeup the world and space. However, **Democritus** (460–370 BC) and other early Greek philosophers described the material world as being made up of tiny, invisible, indivisible particles that they called ‘atomos’, meaning “indivisible” or “uncuttable.”

Later, however, **Plato** and **Aristotle** formulated the notion that there can be no ultimately indivisible particles, and the “atomic” view of matter faded for many centuries during which Aristotelean philosophy dominated the Western culture.

It was in 1808 that an English scientist and school teacher, **John Dalton** (1766-1844), formulated a precise definition of the indivisible building blocks of matter that we call atoms. Dalton’s atomic theory was based on four postulates.

1. Elements are made out of extremely small, indivisible particles called atoms.
2. All atoms of a given element are identical in mass and size, but the atoms of one element are different from the atoms of all other elements.
3. Atoms of one element cannot be changed into atoms of a different element by chemical reactions; atoms are neither created nor destroyed in chemical reactions.
4. Compounds are formed by union of two or more atoms of different elements in a simple numerical ratio.

Dalton’s atomic model is called the "Golf ball model".

(a) (b)

Figure1.1 (a) John Dalton and (b) the golf ball model

Johnstone G. Stoney (1826-1911) named the fundamental unit carrying electricity as "electrons" in 1891 but did not have any experimental evidence of its existence. During the mid-1800s, scientists began to study electrical discharge through a glass tube pumped almost empty of air. This device was an invention of the British chemist and physicist **Sir William Crookes** (1832-1919) and is called **Crookes tube** or **cathode ray tube**.

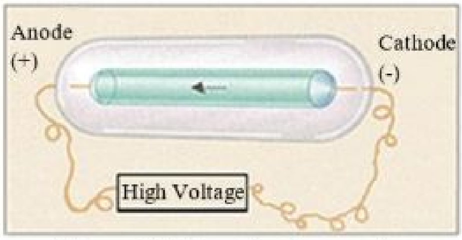


Figure 1.2 A cathode ray tube

The experiment of Crookes and the others showed that when two electrodes are connected to a high-voltage source, the heated negatively charged plate, called the cathode, produced a stream of invisible radiation. Although the rays could not be seen, their presence was detected because they cause gases at low pressure to glow and which made other substances to fluoresce, or to give off light. The radiation emitted from the cathode was given the name '**cathode rays**'.

Later it was known that these rays could be deflected by a magnetic field and they carried a negative electrical charge. Some scientists felt that these rays were waves and others were inclined to think they were particles.

The British scientist **J. J. Thomson** (1856–1940) observed that cathode rays are the same regardless of the identity of the cathode material or the gas in the tube. In 1897 he described cathode rays as streams of negatively charged particles. He used a cathode tube with an anode that had a hole at the centre. Using experimental measurements obtained from that cathode tube he then calculated a value of 1.76 x 10^8 coulombs per gram (C g^{-1}) for the ratio of the electron's electrical charge to its mass.

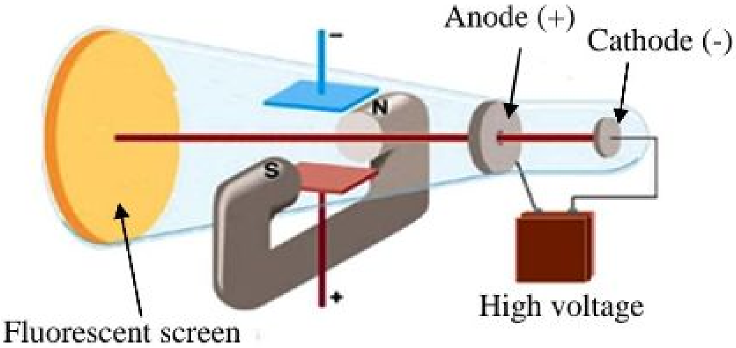


Figure 1.3 Thomson's cathode ray tube

1.1.1 Properties of cathode rays (Experimental observations)

- Cathode rays travel in straight lines. When an opaque object like a metal cross is placed in the path of cathode rays in a discharge tube, a shadow with sharp edges of the metal cross is formed at the end opposite to the cathode. The placement of the shadow proves that cathode rays emit from the cathode and they travel in a straight line.

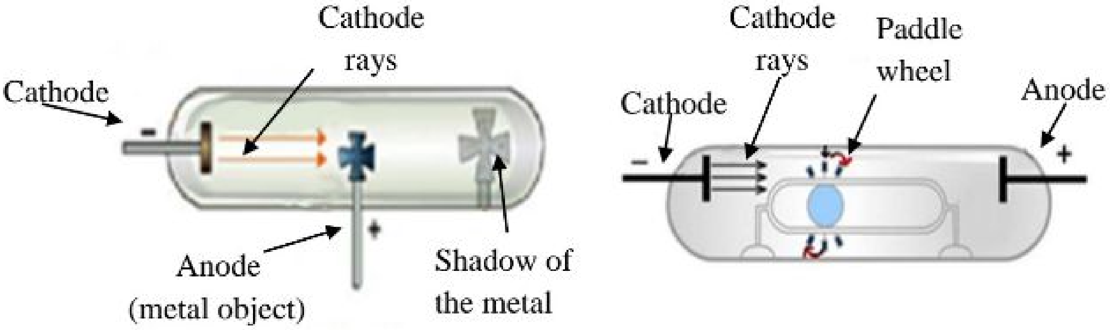


Figure 1.4 Cathode ray properties

- Cathode rays are a beam of particles having mass and possess kinetic energy. On placing a light paddle wheel in the path of cathode rays in a discharge tube, the blades of the paddle wheel rotate. This was considered evidence that electrons (cathode rays) have momentum.

  (However there is doubt on this conclusion as heating of the tube can also make the paddles move.)

- When an electric field is applied in the path of cathode rays, they are deflected towards the positively charged plate. Hence the cathode rays are composed of negatively charged particles. They are affected by magnetic fields showing a deflection perpendicular to the magnetic field. The direction of deflection is similar to the deflection of any other negatively charged particles. Therefore electron can be concluded as a negatively charged particle too.

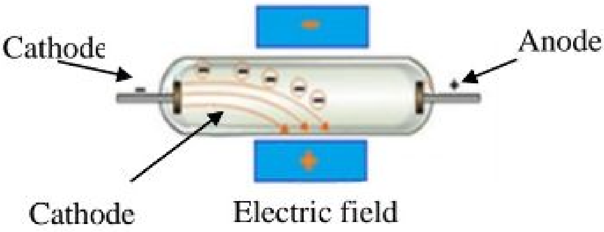


Figure 1.5 Interaction of cathode rays with external electrical fields

- The nature of the cathode rays does not depend on the nature of the gas taken in the discharge tube or the material of the cathode.
- The ratio of the charge to mass (e/m ratio) of cathode ray particles obtained from different gases was found to be exactly the same.

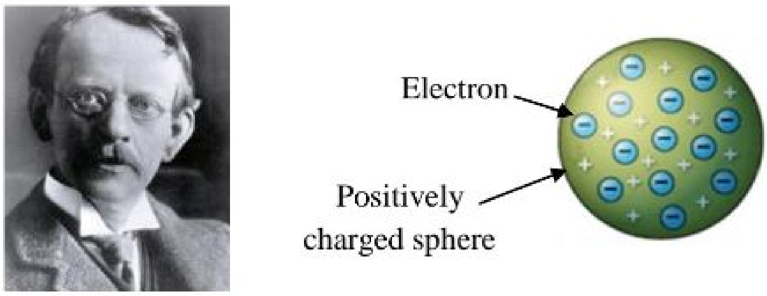
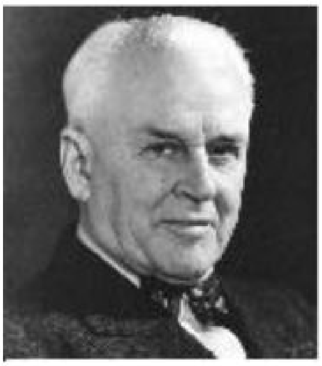


Figure 1.6 J. J. Thomson and his model

Using his findings in 1899 **J.J. Thomson** postulated the "plum-pudding" model of atomic structure. In 1909, **Robert Millikan** (1868–1953) succeeded in measuring the **charge of an electron as 1.602 x 10^{-19} C** by performing the oil drop experiment. The mass of the electron could be calculated by using the experimental values for the charge of electron and Thomson's charge-to-mass ratio.



$$\text{Electron mass} = \frac{1.602 \times 10^{-19}\ \text{C}}{1.76 \times 10^{8}\ \text{C g}^{-1}} = 9.10 \times 10^{-28}\ \text{g}$$

Figure 1.7 Robert Millikan and mass of an electron

This mass is about 1/1837 of a hydrogen atom which is the lightest atom. The **relative charge of an electron is -1**.

1.1.2 The nucleus of the atom

The German physicist, Eugen Goldstein experimentally proved the existence of positive charges in matter. In his experiments, a perforated cathode was used in a discharge tube along with air at very low pressure. When a high voltage of about 10,000 volts was applied across the electrodes, a faint red glow was observed behind the perforated cathode. When the high voltage is applied, its electric field accelerates the small number of ions present in the gas. These collide with atoms of the gas, knocking electrons off of them and creating more positive ions. These ions and electrons in turn strike more atoms, creating more positive ions. The positive ions are all attracted to the cathode, and some pass through the holes in the cathode. Goldstein called these positive rays "canal rays", because they were produced by the holes or channels in the cathode. Although the rays are not exactly formed at the positive electrode or anode, since they are formed away from the cathode close to the anode, they were also known as anode rays or positive rays.

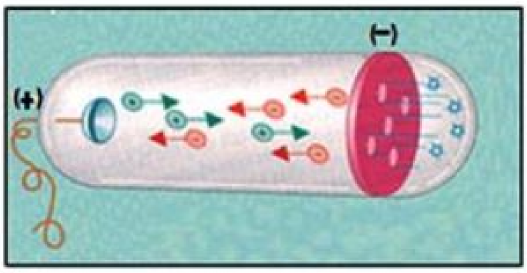


Figure 1.8 A cathode ray tube with a perforated cathode

1.1.3 Properties of positive rays (Experimental observations)

- They travel in straight lines and cast a shadow of the objects placed in their way.
- They can move a paddle wheel placed in their path.
- These rays are positively charged and when an electric field is applied in the path of the rays, they are deflected towards the negative plate of an electric field.
- The nature of the positive rays depends upon the gas taken in the discharge tube. Different gases give different types of positive rays, which contain particles having different masses and different charges. Therefore the e/m ratio is not constant for positive ray particles obtained from different gases.

In 1907 a study of how this "ray" was deflected in a magnetic field, revealed that the particle making up the ray were not all the same mass. The lightest ones, formed when there was some hydrogen gas in the tube, were calculated to be about 1840 times heavier than an electron. The mass of any other positive particle is a multiplication of the mass of the lightest positive particle. Therefore it should be a subatomic particle. They were named as protons. The relative mass of a proton is 1, hence, the **mass of a proton is 1.6 x 10^{-24} g** or **1.007276 u (atomic mass units) or Da (Daltons)**. (The unit was earlier given the name amu.)

The proton has a charge equal and opposite to that of an electron. Hence the absolute charge of a proton is 1.6 x 10^{-19} coulomb and its charge is positive. Proton is the smallest positive charge carrying particle in an atom and the **relative charge of proton is +1.**

Following the discovery of radioactivity in 1896 by the French scientist **Henri Becquerel (1852–1908),** the British physicist **Lord Ernest Rutherford (1871-1937)** showed that radioactive materials produce three types of emissions alpha (α), beta (β) and gamma (γ). The paths of α and β radiation are bent by an electric field.

Alpha (α) **rays** consist of positively charged particles, called **α particles,** and therefore are deflected towards the positively charged plate. **Beta (β) rays** or **β particles** have the identity of electrons and are deflected towards the negatively charged plate. The third type of radioactive radiation consists of high–energy rays called **gamma (γ) rays**. Like X rays, γ rays have no charge and are not affected by an external electric or magnetic field.

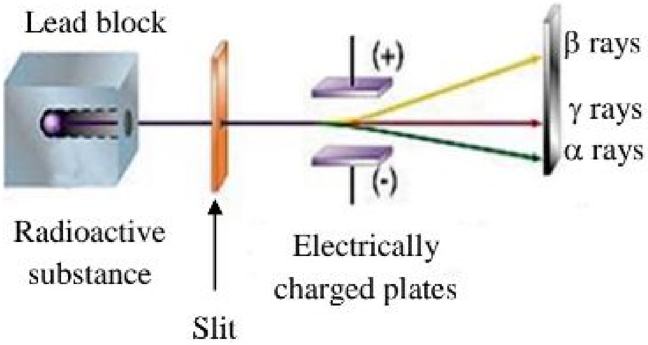


Figure 1.9 Behaviour of alpha (α), beta (β) and gamma (γ) rays in an electric field

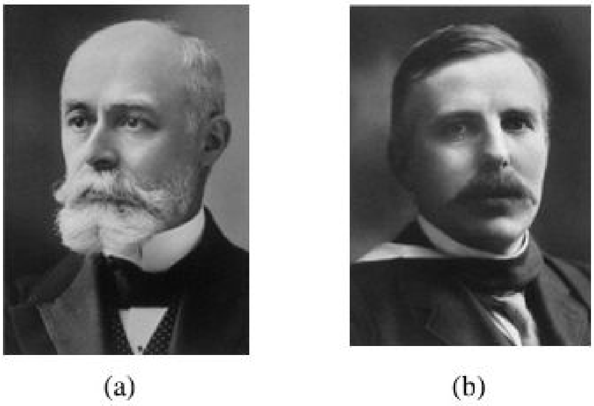

(a) (b)

Figure 1.10 (a) Henri Becquerel and (b) Lord Ernest Rutherford

1.1.4 Rutherford's gold foil experiment

In **1908-09,** Rutherford together with his associate **Johannes Hans Wilhelm Geiger (1882-1945)** a German physicist and an undergraduate named **Ernest Marsden**, carried out a series of experiments using very thin foils of gold and other metals as targets for α particles from a radioactive source.

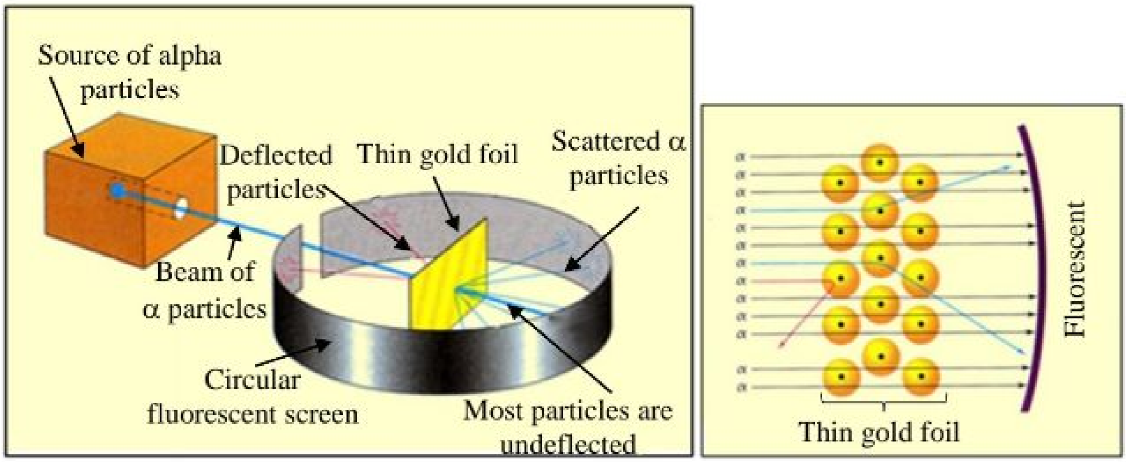


Figure 1.11 Rutherford's gold foil experiment

They observed that the majority of particles penetrated the foil either unreflected or only with a slight deflection. They also noticed that a few α particles were scattered (or deflected) at a large angle. Very few α particles bounced back in the direction from which it came.

To explain the results of the experiment, Rutherford devised a new model of atomic structure, suggesting that most of the atom must be empty. This structure would allow most of the α particles to pass through the gold foil with little or no deflection. The atom's positive charges, Rutherford proposed, are all concentrated in the **nucleus,** a dense central core within the atom. Whenever an α particle came close to a nucleus in the scattering experiment, it experienced a large repulsive force and therefore a large deflection. Moreover, an α particle traveling directly toward a nucleus would experience an enormous repulsion that could completely reverse the direction of the moving particle.

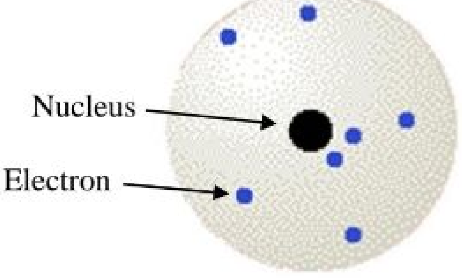
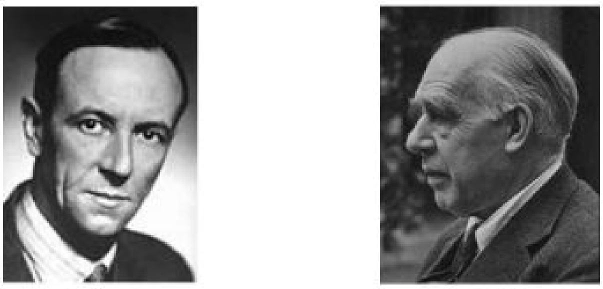


Figure 1.12 Rutherford's model (1911)

Subsequent studies, mainly based on mass spectroscopy revealed that the masses of atoms were much greater than the masses of protons and electrons present. Therefore another subatomic particle should be present to contribute towards the mass of the atom. In1932 **Sir James Chadwick (1891-1972)** a British scientist discovered the 'neutron'. The charge of a neutron is 0 (zero) and its mass is 1.6749×10^{-24}g or 1.008665 amu.



(a) (b)

Figure 1.13 (a) James Chadwick and (b) Niels Bohr

Since Rutherford's time, physicists have learned more and more about atomic nuclei. In 1913 **Niels Henrik David Bohr** (1885-1962) a Danish physicist, combined the ideas at that time and suggested that the atomic nucleus was surrounded by electrons moving in orbit, like planets around the sun. He postulated that the electrons in order to remain in orbit, the electrostatic attraction between the nucleus and electron must be equal to the centrifugal force. In other words, the electrons have to travel in a constant speed around the nucleus keeping the distance from the nucleus constant. The model he introduced is known as the **Rutherford–Bohr model** or the **Bohr model.** Particles found in the nucleus are called **nucleons**, including the protons and neutrons in to the atom. A **nuclide** is the nucleus of an atom that has specific numbers of protons and neutrons (all **nucleons**). Therefore, nuclides are **composite particles of nucleons**.

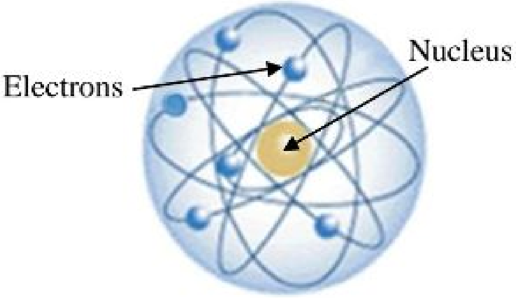


Figure 1.14 The Bohr model

1.1.5 Atomic number, isotopes and mass number

Henry Gwynn Jeffrey Moseley (1887-1915), an English physicist and a co-worker of Rutherford, found that the number of positive charges on the nucleus increases in atoms by single electron units. The atoms of each element have a characteristic number of protons. The number of protons in an atom of any particular element is called that element's **atomic number.**

Atomic number (Z) = Number of protons in the nucleus = Number of electrons in an atom

Since an atom has no net electrical charge, the number of electrons it contains is equal to the number of protons found in its nucleus. All atoms of carbon, for example, have six protons and six electrons, whereas all atoms of oxygen have eight protons and eight electrons. Thus, carbon has atomic number 6 and oxygen has atomic number 8.

British scientists **J. J. Thomson** and **Francis William Aston (1877-1945)** perfected the 'mass spectrometer' which they used in 1912-13 to discover the first isotopes (of neon).

Atoms of a given element can differ in the number of neutrons they contain and therefore their mass can also vary. The number of protons plus neutrons (nuclide) in an atom is called its **mass number.**

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

In the atomic symbol used to represent a particular atom the mass number is given at the top left of the element symbol and the atomic number may be given at the bottom left. However, since the symbol also gives the same information, the atomic number usually may not be shown in the symbol.

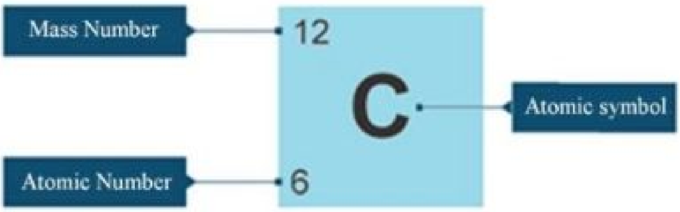


Figure 1.15 Atomic symbol of carbon

Example 1.1

How many protons, neutrons and electron are there in an atom of ^{197}Au?

Answer:

The superscript 197 is the mass number (protons + neutrons). According to the periodic table gold has atomic number 79. Hence, an atom of 197 Au has 79 protons, 79 electrons and 197-79 = 118 neutrons.

Atoms with identical atomic numbers but different mass numbers (that is, same number of protons but different numbers of neutrons) are called **isotopes** of one another.

For example, while most atoms of carbon have six neutrons, some have more. The carbon atoms containing six protons and six neutrons have a mass number 12 and are depicted as ^{12}C, while atoms that contain six protons and seven neutrons have mass number 13 and are depicted as ^{13}C. The atoms with six protons and eight neutrons have mass number 14 and are depicted as ^{14}C. Isotopes of an element that are stable in nature are called stable isotopes and those that are not stable called radioisotopes.

1.1.6 The atomic mass scale

Atoms are very small pieces of matter, however they have a mass. However, it is convenient to use the **unified atomic mass unit (u)** when dealing with these extremely small masses, where;

1 u or **1Da** (earlier **amu**) $= \frac{12\text{ g}}{6.02214 \times 10^{23}} \times \frac{1}{12} = 1.66054 \times 10^{-24}\text{g}$

$$\mathbf{1\ u = 1.66054 \times 10^{-24}\ g \quad and \quad 1\ g = 6.02214 \times 10^{23}\ u}\ \text{or}\ \mathbf{Da}$$

The unified atomic mass unit is defined as a mass of exactly 1/12 of a chemically unbound atom of the ^{12}C isotope of carbon. In these units, a ^{1}H atom has a mass of 1.0078 u or Da and a ^{16}O atom has a mass of 15.9949 u or Da.

1.1.7 Average atomic mass and relative atomic mass of an element

Most elements occur in nature as mixtures of isotopes. The mass of an atom can be given as **relative atomic mass or atomic mass**. It can be obtained by summing over the masses of its isotopes multiplied by their relative abundances:

Average atomic mass = Σ [(isotope mass) x (fractional isotope abundance)]

Example 1.2

Naturally occurring carbon is composed of 98.93% ^{12}C, 1.07% ^{13}C and a negligible amount of ^{14}C. The relative masses of two initial isotopes are 12 u (exactly) and 13.00335 u, respectively. Calculate the average atomic mass of carbon.

Answer:

$(0.9893 \times 12.00\ u) + (0.0107 \times 13.00335\ u) = 12.01\ u$

Relative atomic mass = 12.01

When the atomic mass is given as mass per mole of atoms (in units of **g mol^{-1}**), it is known as the **molar mass** of the element or atom.

Since 1 g = 6.02214×10^{23} u and 1 mole of atoms = 6.02214×10^{23} atoms, the molar mass of carbon will be 12.01 g mol^{-1}.

Relative atomic mass (**A_r**) is a dimensionless physical quantity. It is the ratio of the average mass of atoms of an element to $^1/_{12}$ the mass of an atom of carbon-12 (known as the unified atomic mass unit). Hence the relative atomic mass of carbon will be 12.01.

In periodic tables the relative atomic mass of the element is usually given below the symbol of the element.

1.1.8 Ions

The nucleus of an atom is unchanged by chemical processes, but some atoms can readily gain or lose electrons. If electrons are removed from or added to an atom, a charged particle called an **ion** is formed. An ion with a positive charge is a **cation** and a negatively charged ion is an **anion**.

e.g.: The sodium atom, which has11 protons and 11 electrons can easily lose one electron. The resulting cation has 11 protons and 10 electrons, which means it has a net charge of +1.

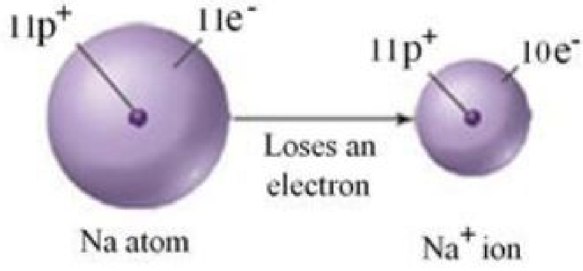


Figure 1.16 Ionization of sodium atom

e.g.: Chlorine, with 17 protons and 17 electrons, can gain an electron in chemical reactions, producing the Cl^- ion.

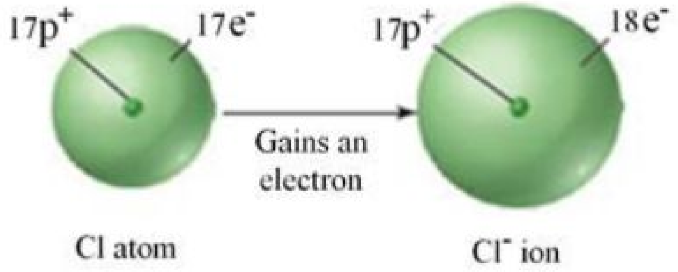


Figure 1.17 Formation of chloride ion

The net charge on an ion is represented by a superscript right to the atomic symbol. Hence the symbol for the ferric ion (an iron atom that has lost 3 electrons) will be:

$$^{58}_{26}\mathrm{Fe}^{3+}$$

In addition to simple ions such as Na^+ and Cl^-, there are **polyatomic ions**, given as NH_4^+ (ammonium ion) and SO_4^{2-}(sulfate ion), which consist of joined atoms to form molecules carrying a net positive or negative charge.

1.2 Electromagnetic radiation and wave like properties of matter

Much of our present understanding of the electronic structure of atoms has come from analysis of the light either emitted or absorbed by substances. Electromagnetic radiation (EMR) consists of **electromagnetic waves**, which are synchronized oscillations of electric and magnetic fields that propagate at the speed of light through a vacuum. The oscillations of the two fields are perpendicular to each other and perpendicular to the direction of wave propagation.

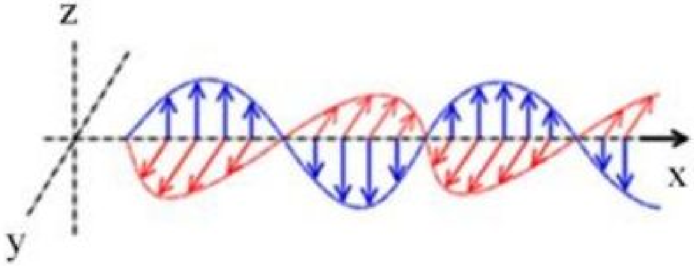


Figure 1.18 Electro-magnetic radiation

The light we see with our eyes, visible light, is one type of electromagnetic radiation. All types of electromagnetic radiation move through a vacuum at a speed of 2.998 x10^8 m s^{-1}, the speed of light **(c)** and have wave-like characteristics.

Waves are periodic, which means that the pattern of peaks and troughs repeats itself at regular intervals. The distance between two adjacent peaks or between two adjacent troughs (distance between a cycle) is called the **wavelength (λ)**. The number of complete wavelengths, or cycles, that pass a given point each second is the **frequency (ν)** of the wave. Frequency is expressed in cycles per second using a unit called **hertz** (Hz). Since it is understood that cycles are involved, it may also be simply called "per second," which is denoted by s^{-1}. Hence,

$$\boxed{c = \lambda\nu}$$

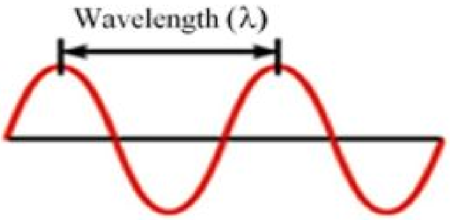


Figure 1.19 An electromagnetic wave

Example 1.3

The yellow light given off by a sodium vapour lamp used for public lighting has a wavelength of 589 nm. Calculate the frequency of this radiation.

Answer:

$$\nu = \frac{c}{\lambda} = \left(\frac{3.00 \times 10^{8}\ \text{m/s}}{589\ \text{nm}}\right)\left(\frac{1\ \text{nm}}{10^{-9}\ \text{m}}\right) = 5.09 \times 10^{14}\ \text{s}^{-1}$$

Different types of electromagnetic radiations have different properties due to their different wavelengths. The display of electromagnetic radiation arranged in order of increasing wavelength is called the **electromagnetic spectrum**.

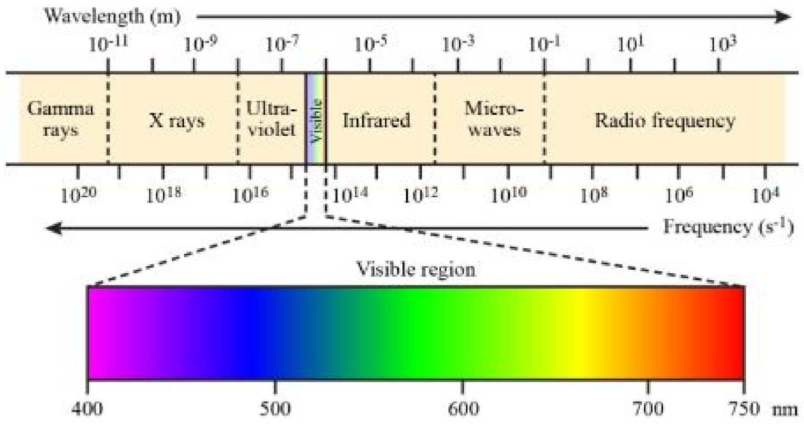


Figure 1.20 The electromagnetic spectrum

1.2.1 Quantization of energy

In 1900 a German physicist named **Max Planck (1858–1947)** proposed that energy is quantized; that is the energy can be either released or absorbed by atoms only in discrete quantities of some minimum size. Planck gave the name **quantum** (meaning "fixed amount") to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation. He proposed that the energy E, of a single quantum equals a constant time the frequency of the radiation:

$$\boxed{E = h\nu}$$

The constant h is called **Planck constant** and has a value of 6.626×10^{-34} J s.

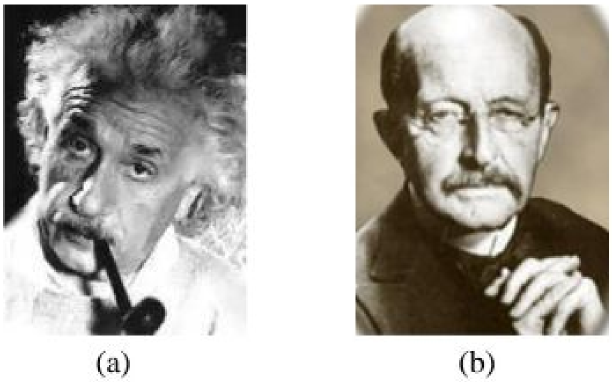

(a) (b)

Figure 1.21 (a) Albert Einstein and (b) Max Planck

In 1905, **Albert Einstein (1879–1955)** extending Planck's quantum theory, deduced that the radiant from a metal surface behaves like a stream of tiny energy packets. Each packet, which is like a "particle" of energy, is called a **photon** and each photon must have an energy equal to Planck constant times the frequency of the light:

Energy of a photon $= E = h\nu$

Example 1.4

Calculate the energy of one photon of yellow light that has a wavelength of 589 nm.

Answer:

$$\nu = \frac{c}{\lambda} = 5.09 \times 10^{14}\ s^{-1}$$

$$E = h\nu = (6.626 \times 10^{-34}\ J\ s \times 5.09 \times 10^{14}\ s^{-1}) = 3.37 \times 10^{-19}\ J$$

If one photon of radiant energy supplies 3.37×10^{-19} J,

Energy of one mole of photons $= (6.02 \times 10^{23}\ mol^{-1})\ (3.37 \times 10^{-19}\ J)$
$= 2.03 \times 10^{5}\ J\ mol^{-1}$ of energy.

In the years following the development of Bohr's model for the hydrogen atom, scientists established that depending on the experimental circumstances, radiation appears to have a wave-like and a particle-like (photon) character.

Louis de Broglie (1892–1987), extended the idea that if radiant energy could, under appropriate conditions, behave as though it were a stream of particles (photons), matter under appropriate conditions, possibly would show the properties of a wave.

De Broglie suggested that an electron moving about the nucleus of an atom behaves like a wave and therefore has a wavelength. He proposed that the wavelength of the electron, or of any other particle, depends on its mass, m, and on its velocity, v:

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

where h is the Planck constant. The quantity mv for any object is called its **momentum** (***p***).

Because de Broglie's hypothesis is applicable to all matter, any object of mass (m) and velocity(v) would give rise to a characteristic matter wave. However, the wavelength associated with an object of ordinary size, such as a golf ball, is so tiny as to be completely unobservable. This is not so for an electron because its mass is so small.

1.3 Electronic energy levels of atoms

The **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion. The magnitude of the ionization energy tells us how much energy is required to remove an electron; the greater the ionization energy, the more difficult it is to remove an electron.

The ionization energies for a given element increase as successive electrons are removed. This trend is because with each successive removal, an electron is being pulled from an increasingly more positive ion, requiring increasingly more energy.

The sharp increase in ionization energy that occurs when an inner-shell electron is removed is a clear evidence for the fact that electrons are in discrete energy levels.

Table 1.1 Successive values of ionization energies I, for the elements from sodium to argon (kJ mol^{-1})

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562					
Mg	738	1451	7733		(Inner-shell electrons)		
Al	578	1817	2745	11577			
Si	786	1577	3232	4356	16091		
P	1012	1907	2914	4964	6274	21267	
S	1000	2252	3357	4556	7004	8496	27107
Cl	1251	2298	3822	5159	6542	9362	11018
Ar	1521	2666	3931	5771	7238	8781	11995

1.3.1 The hydrogen spectrum

Most common radiation sources, including light bulbs and stars, produce radiation containing many different wavelengths. A **spectrum** is produced when radiation from such sources is separated into its component wavelengths. This range of colours, containing light of all wavelengths, is called a **continuous spectrum**. Not all radiation sources produce a continuous spectrum. When a high voltage is applied to tubes that contain different gases under reduced pressure, the gases emit different colours of light. For example the light emitted by neon gas is the familiar red-orange glow of many "neon" lights. When light emitted from such tubes is passed through a prism, only a few wavelengths are present in the resultant spectrum. A spectrum containing radiation of only specific wavelengths is called a **line spectrum.**

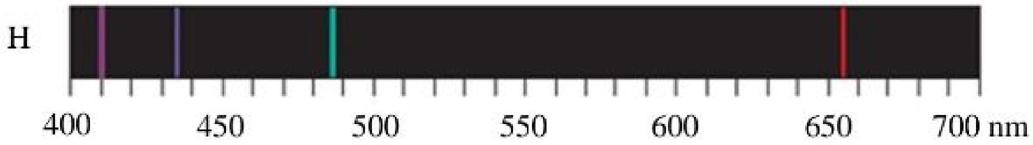


Figure 1.22 Line spectrum of hydrogen

Scientists studied the line spectrum of hydrogen thoroughly in the mid-1800s. At that time, only four lines at wavelengths of 410 nm (violet), 434 nm (blue) 486 nm (blue-green) and 656 nm (red) were observed in the spectrum.

Bohr's atomic model together with Planck's idea that energies are quantized was capable of explaining the line spectrum of hydrogen.

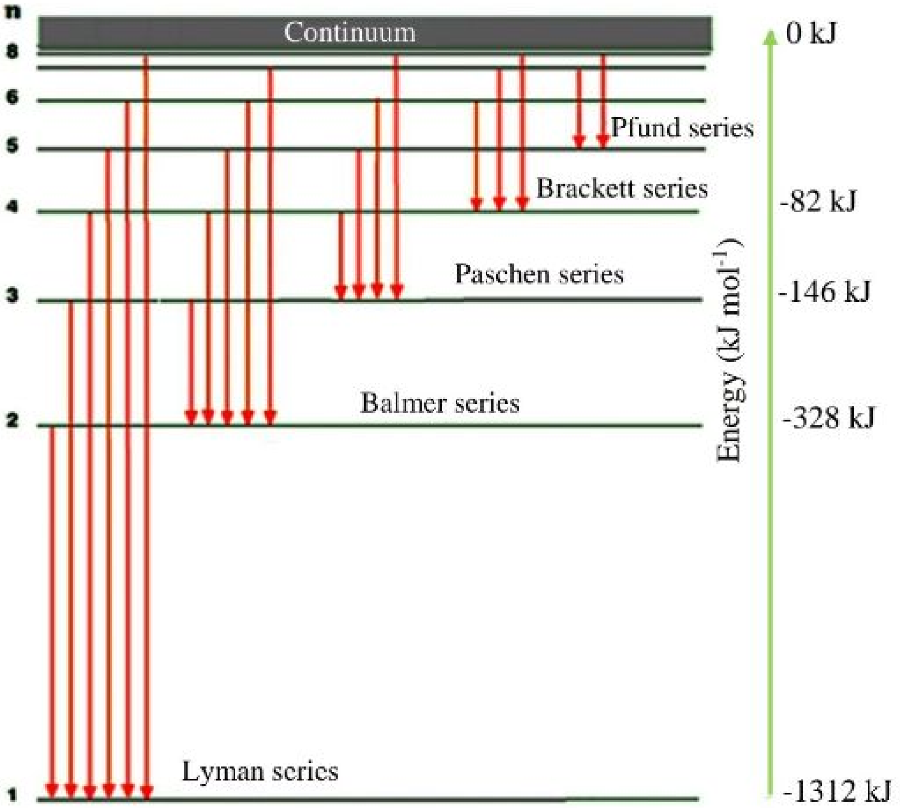


Figure 1.23 Possible electron emissions in hydrogen

Each allowed orbit around the atom corresponds to a different value of *n* (*n* is a whole number). The radius of the orbit gets larger as *n* increases. Thus, the first allowed orbit (the one closest to the nucleus) has $n = 1$, the next allowed orbit (the one second closest to the nucleus) has $n = 2$, and so forth.

The line spectra are the result of emission when electrons fall from an initial energy level (n_i) to a final energy level (n_f), so $\boldsymbol{E_{photon} = h\nu = hc/\lambda = -\Delta E = (E_f - E_i)}$ for these transitions. ΔE is negative for emission as n_f is less than n_i; the electron is falling in energy to a lower-energy orbit. The possible emissions results in the line spectra seen in hydrogen.

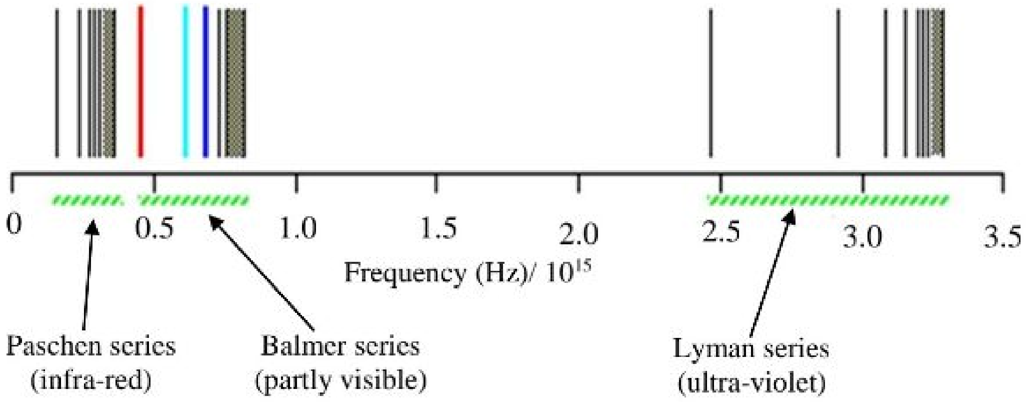


Figure 1.24 (a) The line spectrum of hydrogen

Figure 1.24(a) shows the spectrum as it varies with frequency. However, the variation of wavelength has shown in Figure 1.24(b).

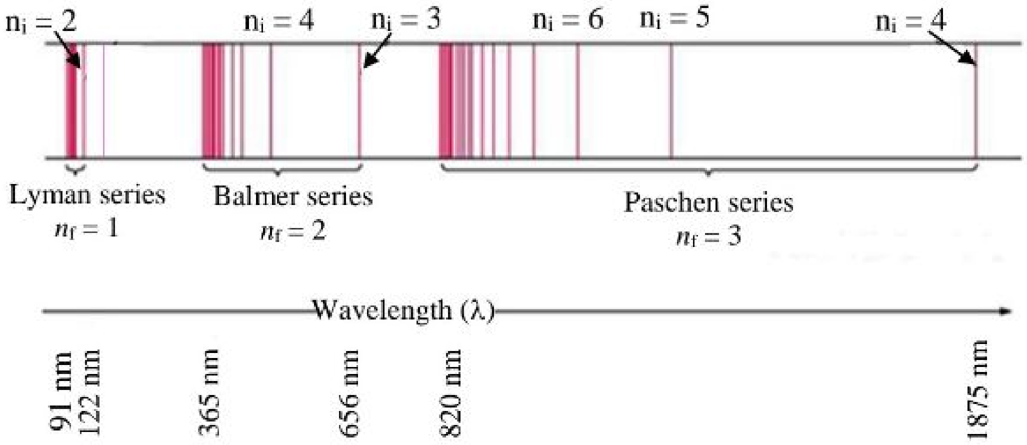


Figure 1.24 (b) The line spectrum of hydrogen

1.3.2 Shapes of orbitals

An electron's probable location in space around an atom (shapes of orbitals) shows us how the electron density is distributed around the nucleus.

The electron density for an *s* orbital is spherically symmetric and centered on the nucleus or in other words the *s* orbitals are spherical in shape.

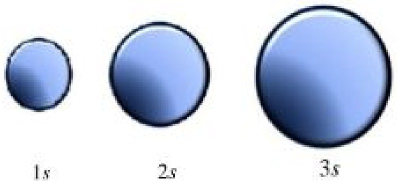


Figure 1.25 Shapes of the *s* orbitals

Each *p* subshell has three orbitals, corresponding to the three allowed values of m_l: -1, 0 and +1. The electron density is not distributed spherically as in an *s* orbital. Instead, the density is concentrated in two regions on either side of the nucleus, separated by a node at the nucleus. This dumbbell-shaped orbital has two lobes.

For each value of *n,* the three *p* orbitals have the same size and shape but differ from one another in spatial orientation. It is convenient to label these as p_x, p_y, and p_z orbitals where the letter subscript indicates the Cartesian axis along which the orbital is oriented.

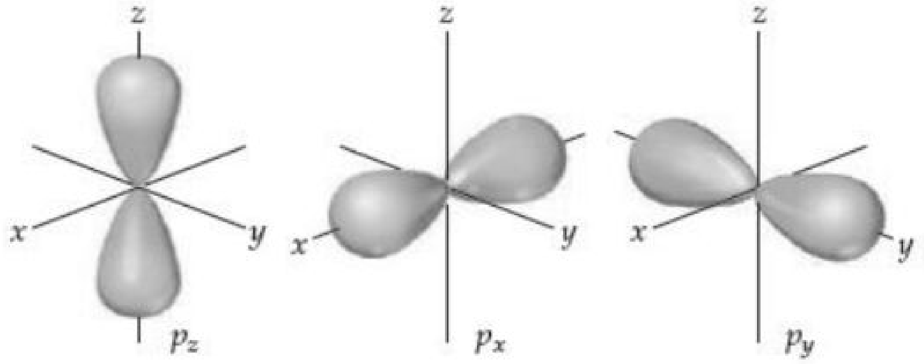


Figure 1.26 Shapes of the *p* orbitals

The different *d* orbitals in a given shell have different shapes and orientations in space. The shapes of the *f* orbitals are even more complicated than those of the *d* orbitals.

1.3.3 Orbitals and Quantum Numbers

The Bohr model introduced a single quantum number, *n*, to describe an orbit. The quantum mechanical model uses three quantum numbers, *n*, *l* and m_l, which result naturally from the mathematics used to describe an orbital that electrons occupy in an atom and m_s that describes the spin of the electron.

1. **The principal quantum number *n*,** can have positive integral values 1, 2, 3, ... This quantum number defines the main energy level (electron shell) that the electron occupies in the atom. As *n* increases, the orbital becomes larger, and the electron spends more time further from the nucleus.

2. **The angular momentum (or azimuthal) quantum number *l*,** can have integral values from 0 to (*n* - 1) for each value of *n*. This quantum number defines the shape of the orbital. The value of ***l*** for a particular orbital is generally designated by the letters *s*, *p*, *d* and *f* corresponding to *l* values of 0, 1, 2 and 3 respectively.

   The set of orbitals that have the same *n* and *l* values is called a **subshell**. Each subshell is designated by a number (the value of *n*) and a letter (*s*, *p*, *d* or *f* corresponding to the value of *l*). For example, the orbitals that have $n = 3$ and $l = 2$ are called 3*d* orbitals and are in the 3*d* sub shell.

3. **The magnetic quantum number m_l,** can have integral values between $-l$ and l, including zero. This quantum number describes the orientation of the orbital in space and the number of possible values for *l* denotes the number of orbitals in the subshell. For example for $l = 2$ the values possible will be 2, 1, 0, -1 and -2 denoting that *a d* subshell has five orbitals.

4. **The spin quantum number m_s.** Two possible values are allowed for m_s, + ½ or -1/2, which indicate the two opposite directions in which the electron can spin. A spinning charge produces a magnetic field. The two opposite directions of spin therefore produce oppositely directed magnetic fields.

Table 1.2 Relationship between values *n, l,* and m_l

n	Possible values of *l*	Subshell designation	Possible values of m_l	Number of orbitals in subshell	Total number of orbitals in shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	-1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	-1, 0, 1	3	
	2	3*d*	-2, -1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	-1, 0, 1	3	
	2	4*d*	-2, -1, 0, 1, 2	5	
	3	4*f*	-3, -2, -1, 0, 1, 2, 3	7	

The restrictions on possible values for quantum numbers give rise to the following very important observations:

1. The shell with principal quantum number *n* consists of exactly *n* subshells. Each subshell corresponds to a different allowed value of *l* from 0 to $(n - 1)$. Thus, the first shell $(n = 1)$ consists of only one subshell, the 1*s* $(l = 0)$; the second shell $(n = 2)$ consists of two subshells, the 2*s* $(l = 0)$ and 2*p* $(l = 1)$; the third shell consists of three subshells, 3*s*, 3*p*, and 3*d*, and so forth.

2. Each subshell consists of a specific number of orbitals. Each orbital corresponds to a different allowed value of m_l. For a given value of *l*, there are $(2l + 1)$ allowed values

of m_l, ranging from $-l$ to $+l$. Thus, each s ($l = 0$) subshell consists of one orbital; each p ($l = 1$) subshell consists of three orbitals; each d ($l = 2$) subshell consists of five orbitals, and so forth.

3. The total number of orbitals in a shell is n^2, where n is the principal quantum number of the shell. The resulting number of orbitals for the shells 1, 4, 9 and 16 is related to a pattern seen in the periodic table: We see that the number of elements in the rows of the periodic table 2, 8, 18 and 32 equals twice these numbers.

1.4 Electron configuration

When considering the electronic structures of atoms: In a many-electron atom, for a given value of n, the energy of an orbital increases with increasing value of l. For example, $n = 3$ orbitals increase in energy in the order $3s < 3p < 3d$ and all orbitals of a given subshell (such as the five $3d$ orbitals) have the same energy, just as they do in the hydrogen atom. Orbitals with the same energy are said to be **degenerate**.

1.4.1 The Aufbau principle

The filling of electrons in an atom begins with the subshell lowest energy and continues upwards according to the "Aufbau principle" (The German word 'Aufbau' means 'building up').

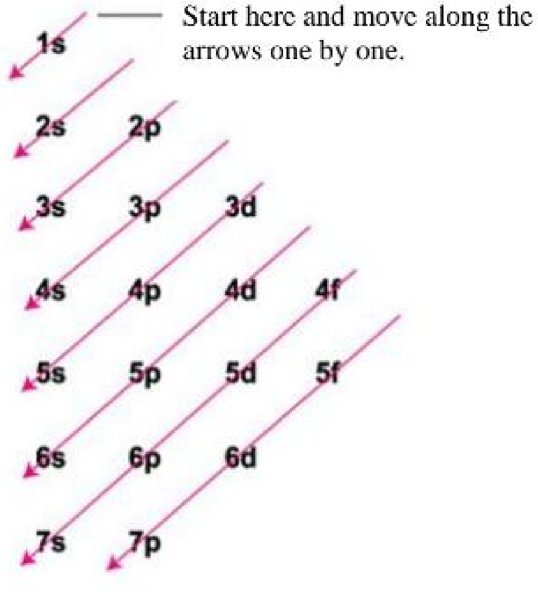


Figure 1.27 Sequence of filling of electrons

Thus the general order of energies of energy levels and sub energy levels are shown in Figure 1.28.

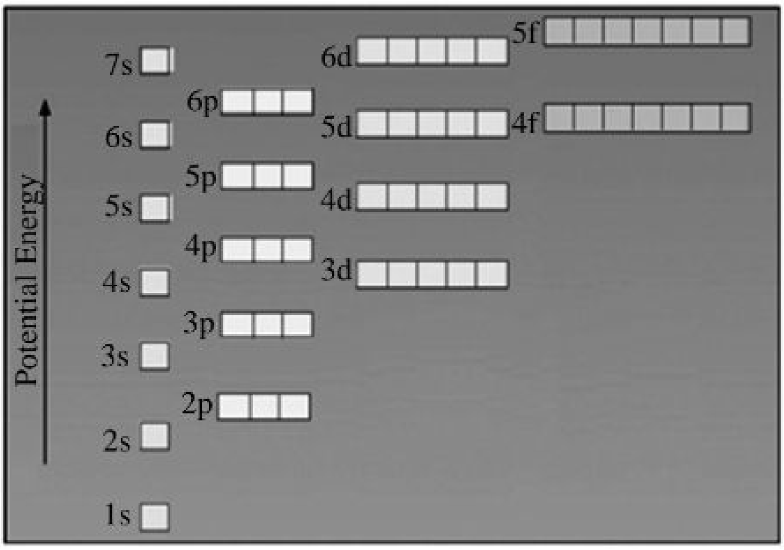


Figure 1.28 Order of the energy levels in an atom

1.4.2 The Pauli exclusion principle

The **Pauli Exclusion Principle,** which was postulated by **Wolfgang Pauli** in 1925, states that *no* two electrons in an atom can have the same set of four quantum numbers n, l, m_l, and m_s.

For a given orbital, the values of n, l, and m_l are fixed. Thus, if we want to put more than one electron in an orbital and satisfy the Pauli Exclusion Principle, our only choice is to assign different m_s values to the electrons. This indicates that an orbital can hold a maximum of two electrons and they must have opposite spins. This restriction allows us to index the electrons in an atom by giving their quantum numbers.

Thus, each *s* subshell which consists of one orbital can hold a maximum of two electrons; each *p* subshell that consists of three orbitals can hold a maximum of six electrons; each *d* subshell which consists of five orbitals can hold a maximum of ten electrons, and so forth.

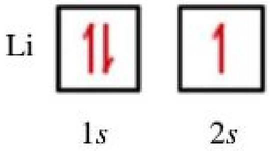
Electrons are distributed among the various orbitals of an atom based on the relative energies of orbitals and the Pauli Exclusion Principle and this distribution is called the **electron configuration** of the atom. The most stable electron configuration, known as the ground state, is that in which the electrons are in the lowest possible energy states.

According to the Pauli Exclusion Principle however, there can be only two electrons in any single orbital. Thus, the orbitals are filled in the order of increasing energy, with no more than two electrons per orbital.

For example, in the lithium atom, which has three electrons, the 1*s* orbital can accommodate two electrons. The third one goes into the next lowest-energy orbital, the 2*s*.

Any electron configuration can be represented by writing the symbol for the occupied subshell and adding a superscript to indicate the number of electrons in that subshell. For example, for lithium we write $1s^22s^1$ and for sodium $1s^22s^22p^63s^1$.

In another representation, called an **orbital diagram**, each orbital is denoted by a box or circle and each electron by a half arrow/ full arrow. A half/ full arrow pointing up represents an electron with a positive spin magnetic quantum number ($m_s = +1/2$) and a half/ full arrow pointing down represents an electron with a negative spin magnetic quantum number ($m_s = -1/2$).



Electrons having opposite spins are said to be paired when they are in the same orbital. An unpaired electron is one not accompanied by a partner of opposite spin.

In the lithium atom the two electrons in the 1*s* orbital are paired and the electron in the 2*s* orbital is unpaired.

1.4.3 Hund's rule

The Hund's rule states that for degenerate orbitals, the lowest energy is attained when the number of electrons having the same spin is maximized.

This means that electrons occupy orbitals singly to the maximum extent possible and that these single electrons in a given subshell all have the same spin magnetic quantum number. Electrons arranged in this way are said to have parallel spins.

e.g. Carbon atom; the two 2*p* electrons singly occupy two of the three 2*p* orbitals and they will be parallel to each other so that they can have the same spin.

Table 1.3 Electron distribution of some elements in second and third period

Element	Total electrons	Orbital diagram				Electron configuration
		1*s*	2*s*	2*p*	3*s*	
Li	3	⇅	↑	☐☐☐	☐	$1s^2\ 2s^1$
Be	4	⇅	⇅	☐☐☐	☐	$1s^2\ 2s^2$
B	5	⇅	⇅	↑☐☐	☐	$1s^2\ 2s^2\ 2p^1$
C	6	⇅	⇅	↑↑☐	☐	$1s^2\ 2s^2\ 2p^2$
N	7	⇅	⇅	↑↑↑	☐	$1s^2\ 2s^2\ 2p^3$
Ne	10	⇅	⇅	⇅⇅⇅	☐	$1s^2\ 2s^2\ 2p^6$
Na	11	⇅	⇅	⇅⇅⇅	↑	$1s^2\ 2s^2\ 2p^6\ 3s^1$

1.4.4 Condensed electron configurations

The electron configuration (also known as the electron distribution) of sodium, atomic number 11, is written as $1s^22s^22p^63s^1$. However, the filling of the 2*p* subshell is complete at neon, which has a stable configuration with eight electrons (an *octet*) in the outermost occupied shell. The next element, sodium, marks the beginning of a new row of the periodic table. Sodium has a single 3*s* electron beyond the stable configuration of neon. The configuration of sodium can therefore be abbreviated as $[\mathrm{Ne}]3s^1$.

The part represented by the bracketed symbol is the noble-gas core of the atom. More usually, these inner-shell electrons are referred to as the **core electrons**.

The electrons given after the noble-gas core are called the **outer-shell electrons** or valence shell electrons. The outer-shell electrons include the electrons involved in chemical bonding, as they are called the **valence electrons**.

Similarly, phosphorous, which has 15 electrons can be represented as $1s^22s^22p^63s^23p^3$ or $[\mathrm{Ne}]3s^23p^3$.

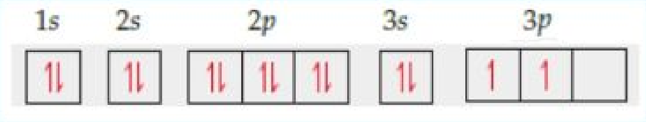
Example 1.5

(a) Write the electron configuration for silicon, element 14, in its ground state.
(b) How many unpaired electrons does a ground-state silicon atom possess?

Answer:

(a) $1s^22s^22p^63s^23p^2$ or $[Ne]3s^23p^2$

(b)



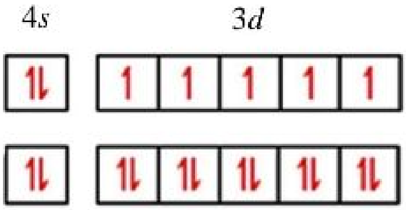
two unpaired electrons.

After the noble-gas element argon ($1s^22s^22p^63s^23p^6$), according to Aufbau principle, it is not the 3*d* but 4*s* orbital that the next electron goes to. Hence, the element that follows Argon, which is potassium (K) has the electronic configuration of $1s^22s^22p^63s^23p^64s^1$ or $[Ar]4s^1$. Calcium, with 20 electrons hence is written as $1s^22s^22p^63s^23p^6 4s^2$ or $[Ar]4s^2$.

Following the complete filling of the 4*s* orbital (this occurs in the calcium atom), the next set of orbitals to be filled is the 3*d*.

Mn: $[Ar]\ 3d^5 4s^2$ or [Ar]

Zn: $[Ar]\ 3d^{10} 4s^2$ or [Ar]



Once all the 3*d* orbitals have been filled with two electrons each, the 4*p* orbitals begin to be occupied until the completed octet of outer electrons ($4s^24p^6$) is reached with krypton (Kr), atomic number 36, another of the noble gases.

Elements with completely filled or precisely half-filled sub energy levels appear to be relatively more stable than elements with other electron configurations. Thus elements with configurations ending with s^2, p^6 and d^{10} will be more stable.

e.g.: Zn: $[Ar]3d^{10}4s^2$, Mg: $[Ne]3s^2$, Ar: $[Ne]3s^23p^6$, N: $[He]2s^22p^3$ and Mn: $[Ar]3d^54s^2$ will be relatively stable atoms.

The electron configurations of certain elements appear to deviate from the rules of configuration discussed. For an example, the electron configuration of chromium (element 24) is $[Ar]3d^5 4s^1$ rather than $[Ar]3d^4 4s^2$ which we might expect. Similarly, the configuration of copper (element 29) is $[Ar]3d^{10} 4s^1$ instead of $[Ar]3d^9 4s^2$.This anomalous behaviour is largely a consequence of the closeness of the $3d$ and $4s$ orbital energies. It frequently occurs when there are enough electrons to form precisely half-filled sub energy levels (as in chromium) or a completely filled sub energy levels (as in copper), that would result in relatively stable configurations. (Note that the filling of the $3d$ orbitals occurs after filling of $4s$. However, the electronic configuration is commonly written as $3d$ first and then $4s$).

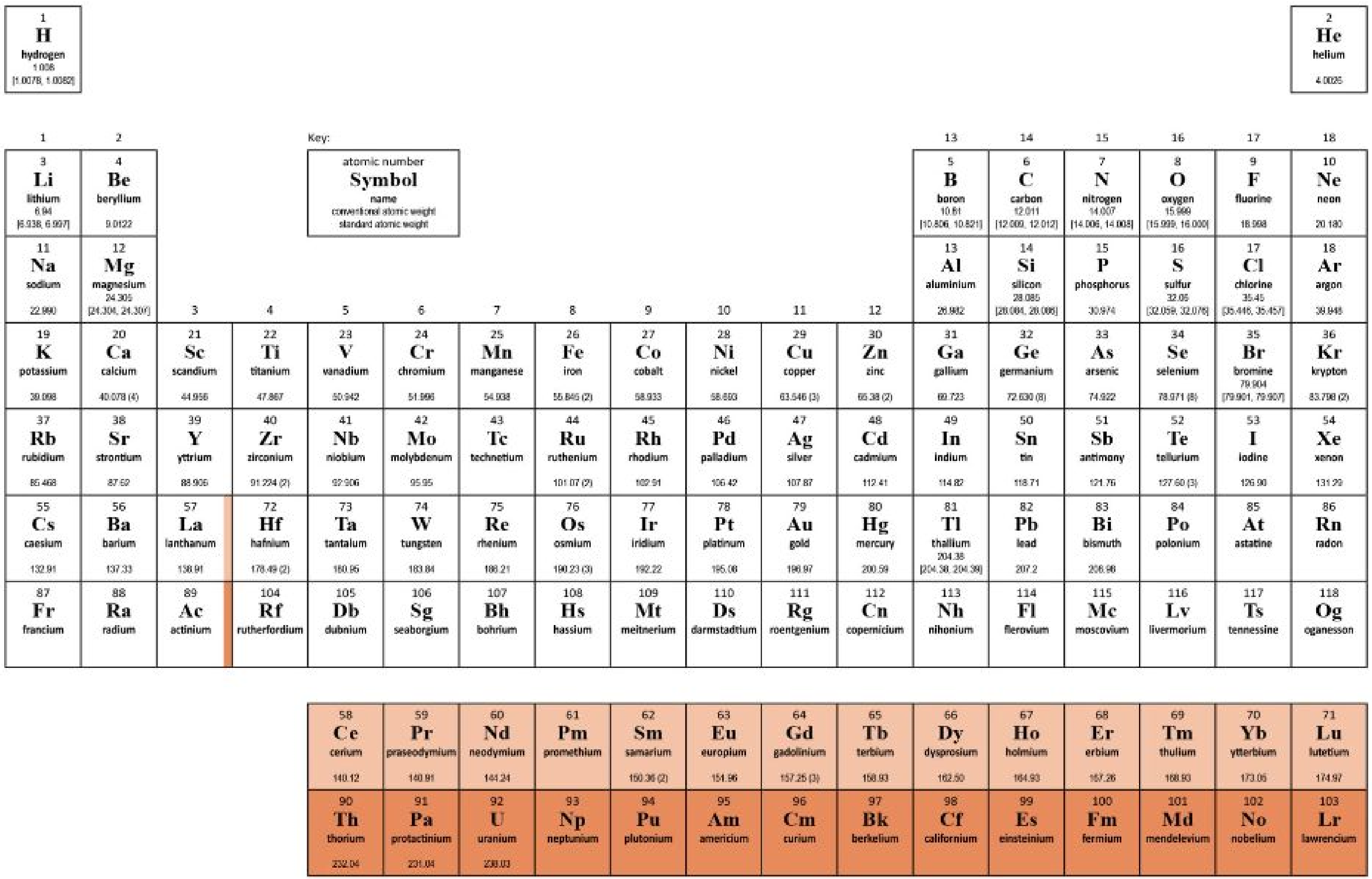
1.5 Building of the periodic table

The discovery of chemical elements has been ongoing since ancient times. Certain elements, such as gold (Au), appear in nature in elemental form and were thus discovered thousands of years ago. In contrast, some elements, such as technetium (Tc), are radioactive and intrinsically unstable and were discovered after the development of technology during the twentieth century.

As the number of known elements increased, scientists began classifying them. In 1869, **Dmitri Ivanovich Mendeleev** in Russia and **Lothar Meyer** in Germany published nearly identical classification schemes. Both noted that similar chemical and physical properties occur periodically when the elements are arranged in order of increasing atomic mass. Scientists at that time had no knowledge of atomic numbers. However with the introduction of the concept of atomic number the modern periodic table was constructed.

(a) (b)

Figure 1.29 (a) Dmitri Mendeleev and (b) Lothar Meyer



Key:

atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.948
19 **K** potassium 39.098	20 **Ca** calcium 40.078 (4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845 (2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546 (3)	30 **Zn** zinc 65.38 (2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630 (8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971 (8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798 (2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224 (2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07 (2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60 (3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57 **La** lanthanum 138.91	72 **Hf** hafnium 178.49 (2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23 (3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89 **Ac** actinium	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson

58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36 (2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25 (3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.06	71 **Lu** lutetium 174.97
90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

Figure 1.30 The periodic table of elements

The way in which the columns (groups) are labeled is somewhat arbitrary. The labeling scheme widely used in the past had Arabic numerals and A and B designations. Thus the numbers ran from 1A-8A and 1B-8B. The group headed by fluorine (F) hence was group 7A.

In a similar convention, the columns are numbered using Roman numerals rather than Arabic numerals together with the letters A and B.

In an effort to eliminate this confusion, the International Union of Pure and Applied Chemistry (IUPAC) has proposed a convention that numbers the groups from 1 to18 with no A or B designations, as shown in the Figure 1.30.

The electron configurations of the elements correspond to their locations in the periodic table. The rows of the table are called periods and elements of the same row show trends in some of their properties.

Elements in the same column of the table, which are called groups, have related outer-shell (valence) electron configurations. For example, all group 2 elements have an ns^2 outer configuration, and all group 3 elements have an ns^2np^1 outer configuration, with the value of 'n' increasing as we move down each column.

Table 1.4 Electron configurations of Group 2 and 13 elements

Group 2		Group 13	
Be	[He]2s^2	B	[He]2s^2 2p^1
Mg	[Ne]3s^2	Al	[Ne]3$s^2$3p^1
Ca	[Ar]4s^2	Ga	[Ar]4$s^2$4p^1
Sr	[Kr]5s^2	In	[Kr]5$s^2$5p^1
Ba	[Xe]6s^2	Tl	[Xe]6$s^2$6p^1
Ra	[Rn]7s^2		

Elements in a group in the periodic table, often exhibit similarities in physical and chemical properties.

Table 1.5 Names of some groups in the periodic table

Group	Name	Elements
1	Alkali metals	Li, Na, K, Rb, Cs, Fr
2	Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
16	Chalcogens	O, S, Se, Te, Po
17	Halogens	F, Cl, Br, I, At
18	Noble gases (rare gases)	Ne, Ar, Kr, Xe, Rn

Since the total number of orbitals in each shell equals n^2: 1, 4, 9 and 16 respectively and because two electrons can be placed in each orbital, each shell accommodates up to $2n^2$ electrons: 2, 8, 18, or 32. The overall structure of the periodic table too reflects these electron numbers: Each row of the table has 2, 8, 18 or 32 elements in it.

The periodic table can be further divided into four blocks based on the filling order of orbitals.

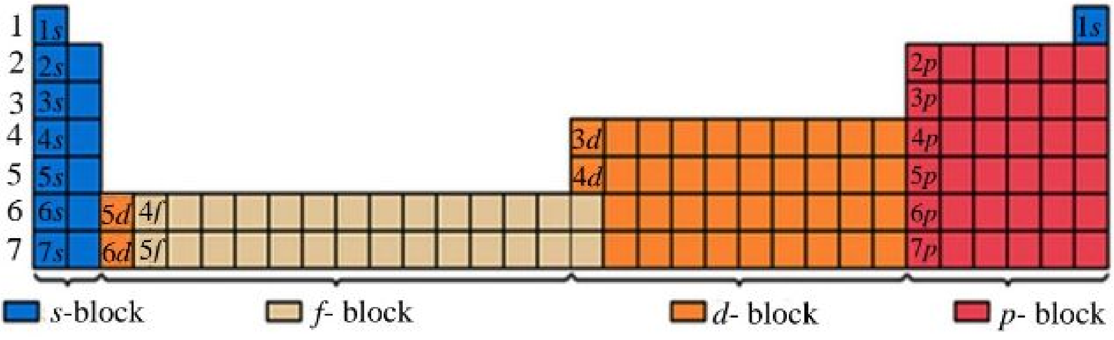


Figure1.31 Regions of the periodic table

The two columns of elements on the left known as the alkali metals (group 1) and alkaline earth metals (group 2), are those in which the valence *s* orbitals are being filled. These two columns make up the ***s* block** of the periodic table.

The block on the far right with *six* columns (group 13 to group 18) comprises the ***p* block**, where the valence *p* orbitals are being filled. The *s* block and the *p* block elements together are the **representative elements**, sometimes called the **main-group elements**.

The block before the *p*-block in the Figure 1.31 has *ten* columns containing the **transition metals**. However in general practice group 1 and 10 elements are not considered as transition metals. These are the elements in which the valence *d* orbitals are being filled and make up the ***d* block.**

The elements in the two rows between and *s* block and *d* block, containing 14 columns are the ones in which the valence *f* orbitals are being filled and make up the ***f* block**. (However filling of electrons and hence their electron configurations are complicated). These elements are often referred to as the ***f* block metals** or **inner transition elements**.

The number of columns in each block corresponds to the maximum number of electrons that can occupy each kind of subshell. Since that 2, 6, 10, and 14 are the numbers of electrons that can fill the *s*, *p*, *d* and *f* subshells, respectively, the *s* block has 2 columns, the *p* block has 6, the *d* block has 10 and the *f* block has 14.

1.6 Periodic trends shown by *s* and *p* block elements

Many properties of atoms depend on their electron configuration and on how strongly the outer electrons in the atoms are attracted to the nucleus. Coulomb's law tells us that the strength of the interaction between two electrical charges depends on the magnitudes of the charges and on the distance between them. Therefore, the attractive force between an electron and the nucleus depends on the magnitude of the nuclear charge and on the average distance between the nucleus and the electron. The force increases as the nuclear charge increases and decreases as the electron moves further from the nucleus.

In an atom that containing a large number of electrons, in addition to the attraction of each electron to the nucleus, each electron experiences a repulsion due to the proximity of other electrons. These electron–electron repulsions cancel some of the attraction of the electron to the nucleus so that the electron experiences less attraction than it would if the other electrons were not there. The outer electrons are said to be screened or shielded from the nucleus by the inner electrons close to the nucleus and this phenomenon is hence termed the **screening effect** or **shielding effect** of electrons.

An electron, therefore, experiences a net attraction by the nucleus that is less than it would be in the absence of other electrons. This partially screened nuclear charge is termed the **effective nuclear charge**, $\mathbf{Z_{eff}}$. The effective nuclear charge is always less than the actual nuclear charge ($Z_{eff} < Z$).

For a valence electron, most of the shielding is due to the core electrons, which are much closer to the nucleus. As a result, the greater the number of core electrons and the higher the number of core shells, the greater will be the screening effect.

The effective nuclear charge increases from left to right across any period of the periodic table. Although the number of core electrons stays the same across the period, the number of protons increases. The valence electrons added to counterbalance the increasing nuclear charge thus it screens ineffectively. Thus, Z_{eff} increases steadily across the period.

1.6.1 Sizes of atoms and ions

Atoms are not hard, spherical objects as many of us think. According to the quantum mechanical model, atoms do not have sharply defined boundaries. We can define atomic size in several ways, based on the distances between atoms in various situations.

van der Waals radius

The van der Waals radius (nonbonding atomic radius) refers to one half the distance between two equivalent non-bonded atoms in their most stable arrangement, that is, where attractive forces are maximum.

Covalent radius

A chemical bond is the attractive interaction between any two adjacent atoms in a molecule. The two bonded atoms are closer together than they would be in a nonbonding collision. The bonding atomic radius for any atom in a molecule is equal to half of the bond distance (the distance between two bonded atoms). The bonding atomic radius (also known as the covalent radius) is smaller than the nonbonding atomic radius.

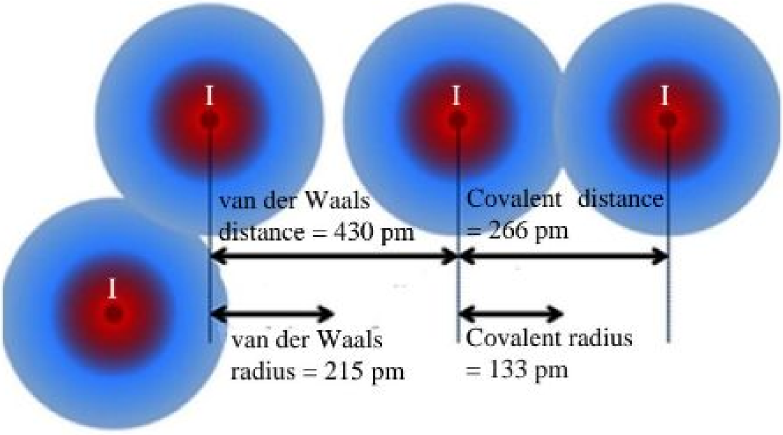


Figure 1.32 Covalent and van der Waals radius for Iodine (I_2)

Metallic radius

Metal atoms in a metallic structure are bonded to each other by metallic bonds. Half of the bond distance between the nuclei of two adjacent metal atoms in a metallic structure is called the **metallic radius**.

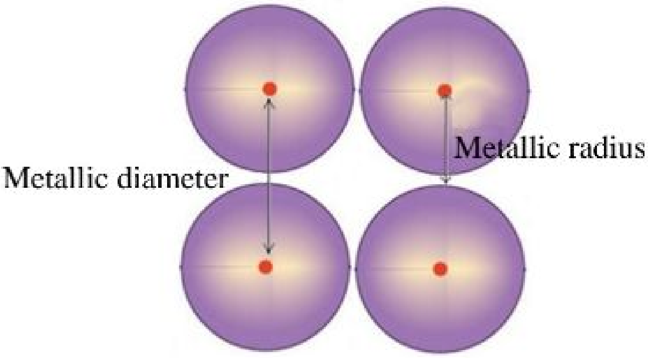


Figure 1.33 The metallic radius

Periodic trends in atomic radii

The atomic sizes within the periodic table show two interesting trends:

Within each group, the atomic radius tends to increase from top to bottom. This trend results primarily from the increase in the principal quantum number *(n)* of the outer electrons. As we go down a column, the outer electrons have a greater probability of being further away from the nucleus, causing the atomic radius to increase.

Within each period, the atomic radius generally tends to decrease from left to right. The major factor influencing this trend is the increase in effective nuclear charge across a period. The increasing effective nuclear charge steadily draws the valence electrons closer to the nucleus, causing the atomic radius to decrease.

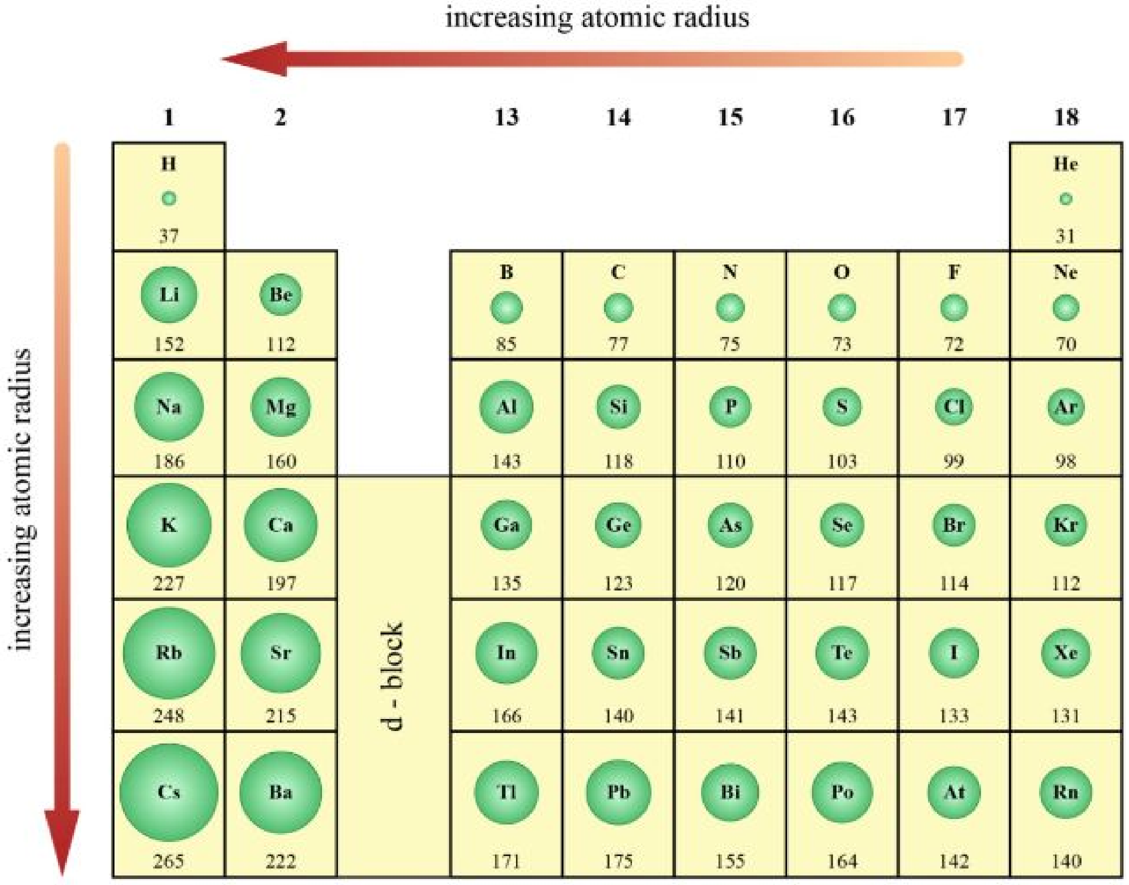


Figure 1.34 (a) Trends in atomic radii in the periodic table in pm

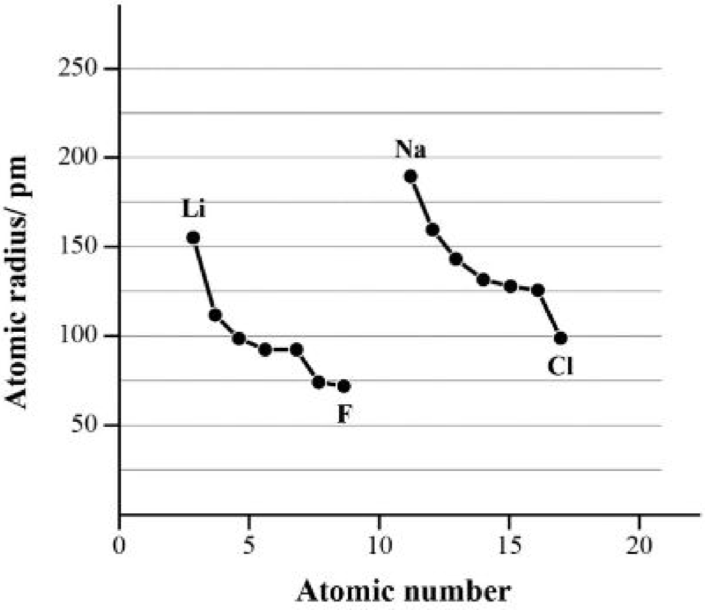


Figure 1.34 (b) Trends in atomic radii in the periodic table

Electron configurations of ions

When electrons are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the highest principal quantum number, n.

For example, when one electron is removed from a sodium atom ($1s^22s^22p^63s^1$), it is the $3s^1$ electron that is removed.

$$\mathrm{Na}(1s^22s^22p^63s^1 \text{or } [\mathrm{Ne}]3s^1) \longrightarrow \mathrm{Na}^+(1s^22s^22p^6 \text{ or } [\mathrm{Ne}]) \; + \; \mathrm{e}$$

If there is more than one occupied subshell for a given value of n, the electrons are first removed from the orbital with the highest value of l. For example, a boron atom loses its $2p$ electron before it loses its $2s$ electrons.

$$\mathrm{B}(1s^22s^22p^1) \longrightarrow \mathrm{B}^+(1s^22s^2) \; + \; \mathrm{e}$$

$$\mathrm{B}^+(1s^22s^2) \longrightarrow \mathrm{B}^{3+}(1s^2) \; + \; 2\mathrm{e}$$

When two electrons are removed from Fe ($[\mathrm{Ar}]3d^64s^2$), the $4s^2$ electrons are the ones that are removed even though in filling the $4s$ fills before the $3d$.

$$\mathrm{Fe}([\mathrm{Ar}]\, 3d^64s^2) \longrightarrow \mathrm{Fe}^{2+}([\mathrm{Ar}]3d^6) \; + \; 2\mathrm{e}$$

If an additional electron is removed, forming Fe^{3+}, it comes from a $3d$ orbital because

all the orbitals with $n = 4$ are empty.

$$Fe^{2+}([Ar]3d^6) \longrightarrow Fe^{3+}([Ar]3d^5) \ + \ e$$

Electrons added to an atom to form an anion are added to the empty or partially filled orbital having the highest value of *n*, which is the valence shell. For example, an electron added to a fluorine atom to form the F^- ion goes into the one remaining vacancy in the 2*p* subshell.

$$F(1s^2 2s^2 2p^5) \ + \ e \longrightarrow F^-(1s^2 2s^2 2p^6)$$

Periodic Trends in Ionic Radii

Like the size of an atom, the size of an ion depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the valence electrons reside. When a cation is formed from a neutral atom, electrons are removed from the occupied atomic orbitals that are the most spatially extended from the nucleus. Also, when a cation is formed the number of electron–electron repulsions is reduced. Therefore, cations are smaller than their parent atoms.

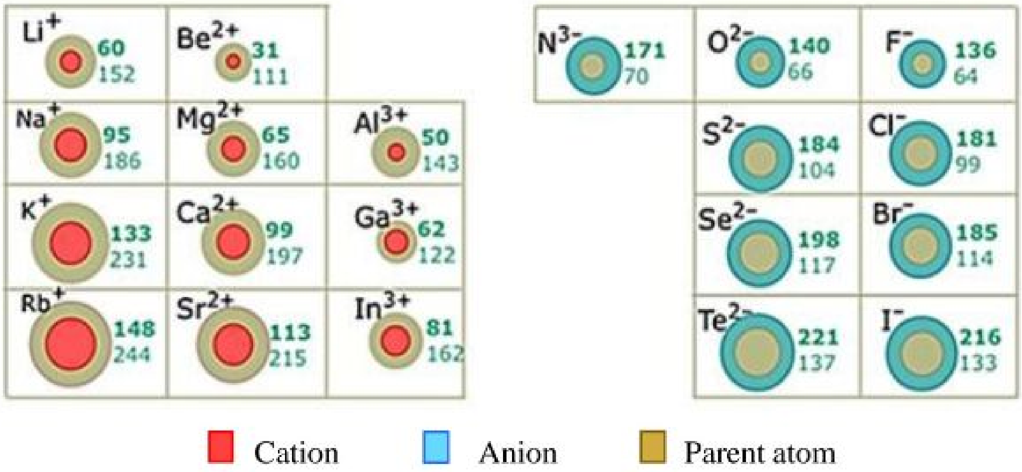


Figure 1.35 Radii of cations and anions compared to parent atoms in pm

The opposite is true of anions. When electrons are added to an atom to form an anion, the increased electron–electron repulsions cause the electrons to spread out more in space. Thus, anions are larger than their parent atoms.

For ions carrying the same charge (both positively or negatively charged ions), ionic radius increases as we move down a column in the periodic table. In other words, as the principal quantum number of the outermost occupied orbital of an ion increases, the radius of the ion increases.

An **isoelectronic series** is a group of ions/ atoms containing the same number of electrons. For example, each ion/ atom in the isoelectronic series O^{2-}, F^-, Ne, Na^+ and Mg^{2+} has a total number of 10 electrons. In any isoelectronic series the nuclear charge increases with increasing atomic number in the series. Because the number of electrons remains constant, ionic radius decreases with increasing nuclear charge as the electrons are more strongly attracted to the nucleus.

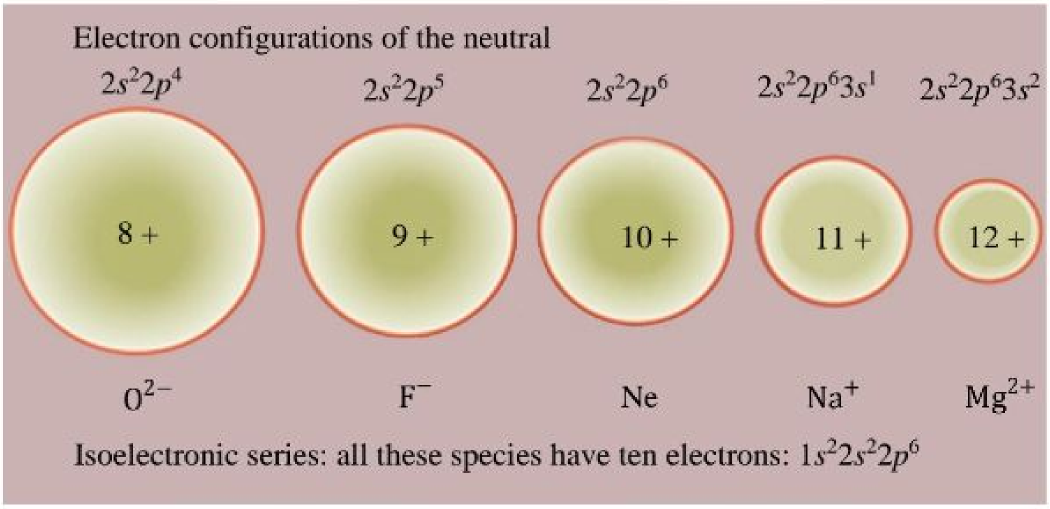


Figure 1.36 Radii in an isoelectronic series

1.6.2 Ionization energy

As explained at the beginning of section 1.3, the **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion.

In general, the first ionization energy (I_1) is the energy needed to remove the most loosely bound electron from a neutral gaseous atom. For example, the first ionization energy for the lithium atom is the energy required for the process; $Li(g) \longrightarrow Li^+(g) + e$

The second ionization energy (I_2) is the energy needed to remove the second loosely bound electron of an atom from a gaseous monovalent cation to form a gaseous divalent cation, and so forth, for successive removals of additional electrons. Thus, second ionisation energy for the lithium atom is the energy associated with the process; $Li^+(g) \longrightarrow Li^{2+}(g) + e$

The ionization energies for a given element increase as successive electrons are removed; $I_1 < I_2 < I_3$, and so forth. This trend is because with each successive removal, an electron is being pulled away from an increasingly more positive ion, requiring increasingly more energy. Furthermore, a sharp increase in ionization energy occurs when an inner-shell electron is removed compared to the removal of outer shell electrons. This is because the electrons of the inner shell are closer to the nucleus and hence are attracted to it more strongly.

Frequently ionization energy is expressed in kJ mol^{-1} by considering one mole of atom/ ion.

Periodic trends in the first ionization energies

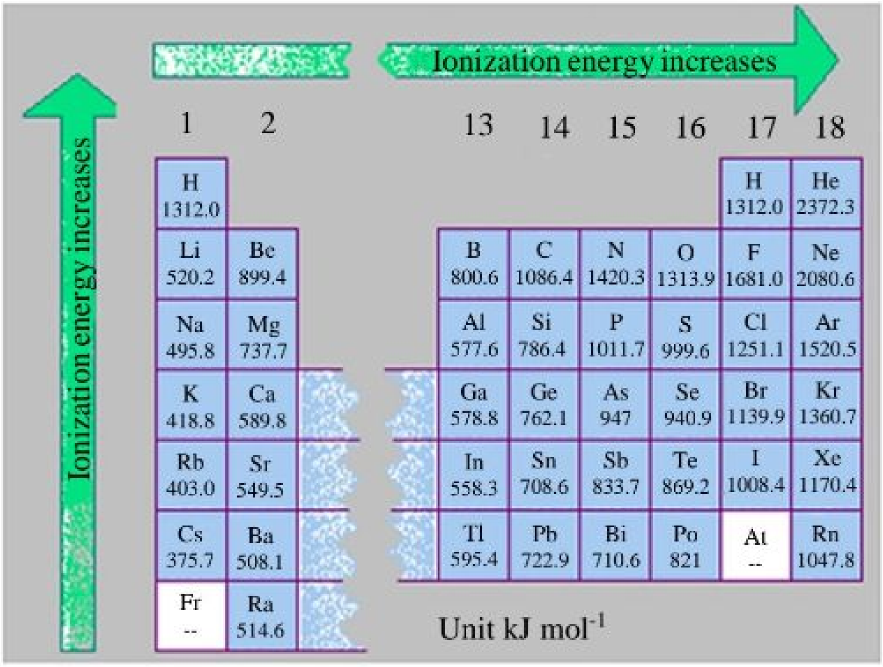
The first ionization energy generally increases as we move across a period. The alkali metals show the lowest ionization energy in each period, and the noble gases show the highest.

Generally, the first ionization energy decreases as we move down any column in the periodic table. For example, the ionization energies of the group 1 elements (alkali metals) follow the following order

Li >Na > K > Rb > Cs > Fr.

The *s* and *p* block elements show a larger range of I_1 values than do the transition metal elements. Generally, the ionization energies of the transition metals increases slightly from left to right in a period.

The same factors that influence atomic size also influence ionization energies. The energy needed to remove an electron from the outermost occupied shell depends on both the effective nuclear charge and the average distance of the electron from the nucleus. Either increasing the effective nuclear charge or decreasing the distance from the nucleus increases the attraction between the electron and the nucleus. As this attraction increases, it becomes more difficult to remove the electron, and thus the ionization energy increases.



1	2	13	14	15	16	17	18
H 1312.0						H 1312.0	He 2372.3
Li 520.2	Be 899.4	B 800.6	C 1086.4	N 1420.3	O 1313.9	F 1681.0	Ne 2080.6
Na 495.8	Mg 737.7	Al 577.6	Si 786.4	P 1011.7	S 999.6	Cl 1251.1	Ar 1520.5
K 418.8	Ca 589.8	Ga 578.8	Ge 762.1	As 947	Se 940.9	Br 1139.9	Kr 1360.7
Rb 403.0	Sr 549.5	In 558.3	Sn 708.6	Sb 833.7	Te 869.2	I 1008.4	Xe 1170.4
Cs 375.7	Ba 508.1	Tl 595.4	Pb 722.9	Bi 710.6	Po 821	At --	Rn 1047.8
Fr --	Ra 514.6						

Unit kJ mol^{-1}

Figure 1.37 Trends in the first ionization energies in the periodic table

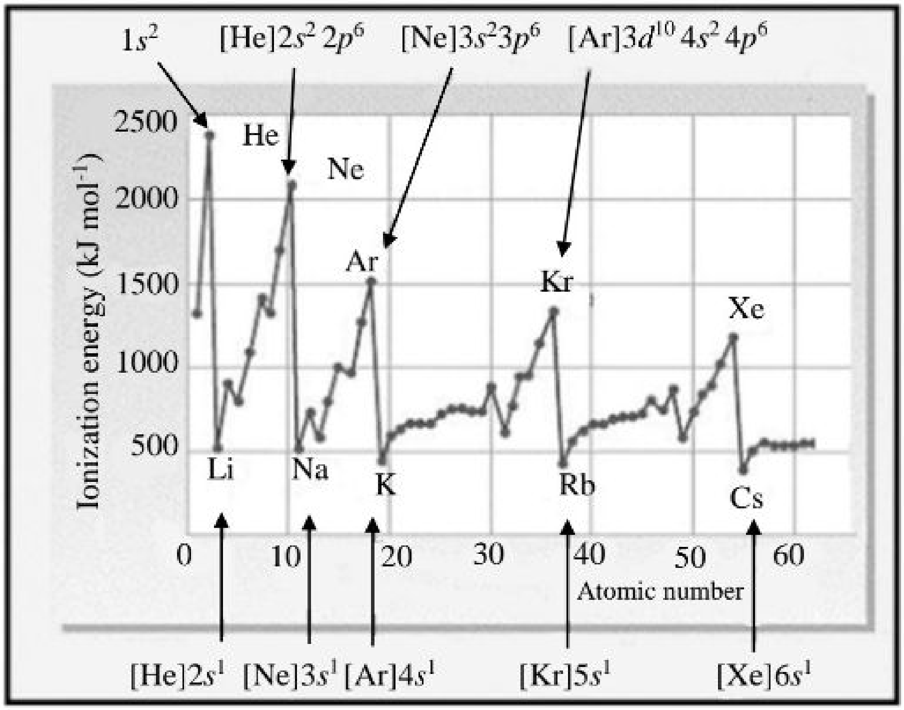


Figure 1.38 Variation of the first ionization energies with atomic number of elements

The irregularities in the trend of the first ionization energy in a given period are small but still readily explained. Removal of electrons from a completely filled subshell (e.g. group 2, group 12 and group 18) or a half filled subshell (e.g. group 7 and group 15), which are generally stable, will require more energy and thus the ionization energy will be higher than is expected from the common trend.

For example, in the second period neon with a completely filled shell has the highest first ionization energy. Beryllium with a complete *s* sub shell shows the first ionization energy greater than expected and it even exceeds the I_1 of boron. Similarly nitrogen with an exactly half filled *p* subshell shows an I_1 higher than what the common trend predicts.

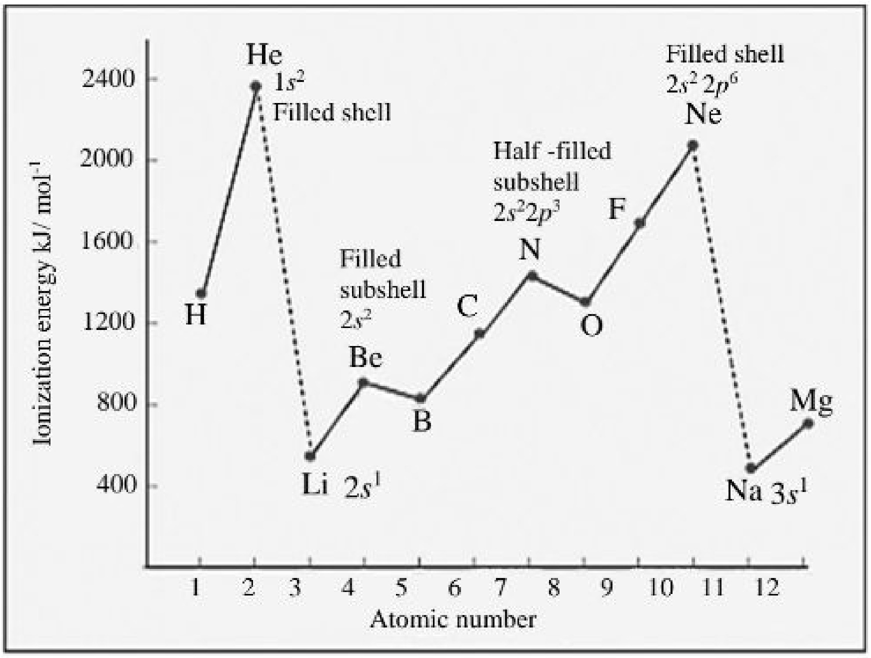


Figure 1.39 Variation of the first ionization energies along the first and second periods

1.6.3 Electron gain energy

The energy change that occurs when an electron is added to a gaseous atom is called the **electron gain energy.** For most atoms, energy is released when an electron is added.

For example, electron gain energy for the chlorine atom shown in the process below is -349 kJ mol^{-1}. The negative sign indicates that energy is released during the process.

$$Cl(g) \ + \ e \longrightarrow Cl^{-}(g) \qquad \Delta E_{EG} = -349 \text{ kJ mol}^{-1}$$

(ΔE_{EG} = Electron gain energy)

However, there are few atoms with positive electron gain energy. E.g.: Be, N. This is because they possess relatively stable configuration Be (s^2) and N (p^3) and as a result adding of an electron would be somewhat difficult with electron – electron repulsion is the dominating factor.

$$N(g) \ + \ e \longrightarrow N^{-}(g) \qquad \Delta E_{EG} = +134 \text{ kJ mol}^{-1}$$

$$Be(g) \ + \ e \longrightarrow Be^{-}(g) \qquad \Delta E_{EG} = +231 \text{ kJ mol}^{-1}$$

The electron gain energy become less positive across a period and more positive down a group.

As accepted internationally, ΔE_{EG} is used as a quantitative physical quantity to measure the attraction of an electron by an atom and related to electron affinity as follows.

$$\text{Electron gain energy } (\Delta E_{EG}) = -\text{ Electron affinity } (E_A)$$

Thus the electron affinity of an atom can be closely related to ΔE_{EG} and defined as the change in energy when the anion of the element loses an electron in the gaseous phase ($A^-(g) \longrightarrow A(g) + e$; $\Delta E = E_A$ which is equal in magnitude and opposite in sign to ΔE_{EG}) become more positive across a period and less positive down a group.

1.6.4 Electronegativity

It is defined as the ability of an atom in a molecule to attract electrons to itself. The greater an atom's electronegativity, the greater its ability to attract electrons.

The American chemist Linus Pauling (1901–1994) developed the first and most widely used electronegativity scale, which is known as the Pauling scale. Generally there is an increase in electronegativity from left to right across a period in the periodic table. With some exceptions (especially in the transition metals), electronegativity decreases with increasing atomic number in a group. Noble gases too have very small but non zero electronegativity according to the Pauling scale. In molecules, the difference between electronegativities of two atoms forming a bond will determine the ionic or covalent nature of the bond.

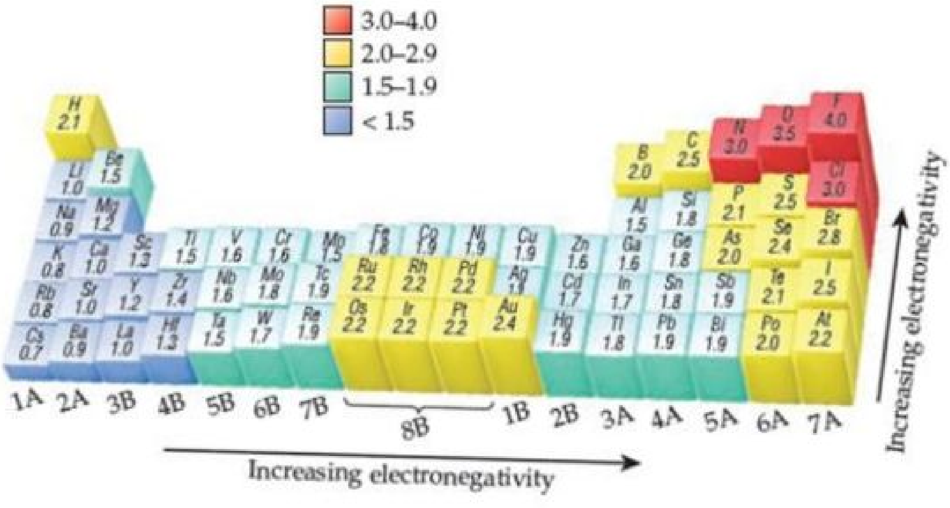


Figure 1.40 Pauling electronegativity values and the trends in the periodic table

Table 1.6 A summary of equations

Equation
Atomic number (Z) = Number of protons = Number of electrons in a atom
Mass number (A) = Number of protons (Z) + Number of neutrons
1 u or Da = 1.66054×10^{-24} g and 1 g = 6.02214×10^{23} u or Da
Atomic mass = Σ [(isotope mass) x (fractional isotope abundance)]
Speed of light = $c = \lambda\nu = 3.00 \times 10^{8}\ \text{m s}^{-1}$
Energy of a photon = $E = h\nu$ constant h is called Planck constant and has a value of 6.626×10^{-34} J s