BIOL 157: BIOLOGICAL CHEMISTRY

Lecture 3:

Atomic Structure and Periodic Chemistry

Lecturer:

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LECTURE OBJECTIVES

- In this lecture, the following would be learnt:
  - Various ideas about the atom
  - Models of atomic structure
    - plum pudding model of Thomson
    - nuclear atom of Rutherford
    - planetary atom of Bohr
    - wave mechanics model of Schrodinger
  - the various quantum numbers
  - electronic configuration
  - periods, groups and blocks of the periodic table
  - periodic properties of atoms

Early theories about the atom

- Atoms are the basic units of elements.
- In about 400 BC, the Greek philosopher, Democritus suggested the world was made up of two things;
  - empty space and
  - tiny particles which he called ‘atoms’.
- He considered atoms as the smallest particle of matter.
- Aristotle came in to propose that matter was continuous and was not composed of smaller particles.
- Aristotle named the continuous substance, ‘hyle’.

- It was an English chemist, John Dalton who made logical deduction about the nature of the atom.

- His proposals have become accepted as the Dalton's atomic theory.

- He made his proposals based on the experimental work of Joseph Proust and Antoine Lavoisier.
  - The French chemist, Lavoisier from his experimentation had come out with the law of conservation of mass: for a reaction taking place in a closed system, mass remained unchanged.
  - Proust, another Frenchman, worked on the law of definite proportion: a chemical compound always contains exactly yje same proportion of elements by mass.

Dalton's atomic theory

- Each element is made up of unique type of atoms which are indivisible.
- Atoms can neither be created nor destroyed.
- Atoms of the same element are identical: they have identical mass and show the same physical and chemical properties.
- When elements combine to form compounds, their atoms join together in fixed proportions.

- Dalton’s ideas helped in the explanation of some observations in chemical reactions.
  - They paved the way for understanding some quantitative aspects of chemistry.

- However, some of his postulates have been found to be incorrect.
  - Indivisibility of atoms
  - Impossibility of creating atom
  - Atoms of same element having identical mass e.g. isotopes of H have different physical properties

Various models of atomic structure

The following will be considered:

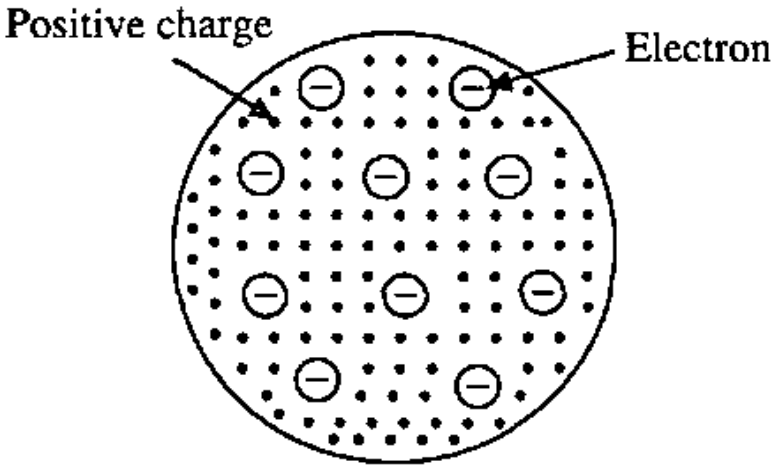
- The plum pudding (water melon) model of J.J. Thomson.
- The nuclear atom model of Rutherford
- The planetary model of Bohr.
- The wave mechanics model of Schrodinger.

The plum-pudding model

- The positive charges (protons) of an atom are uniformly distributed in a sphere

- The electrons are also embedded in the sphere in such a way that the attraction of the electrons for the positive charge just overcome the repulsion among the electrons.

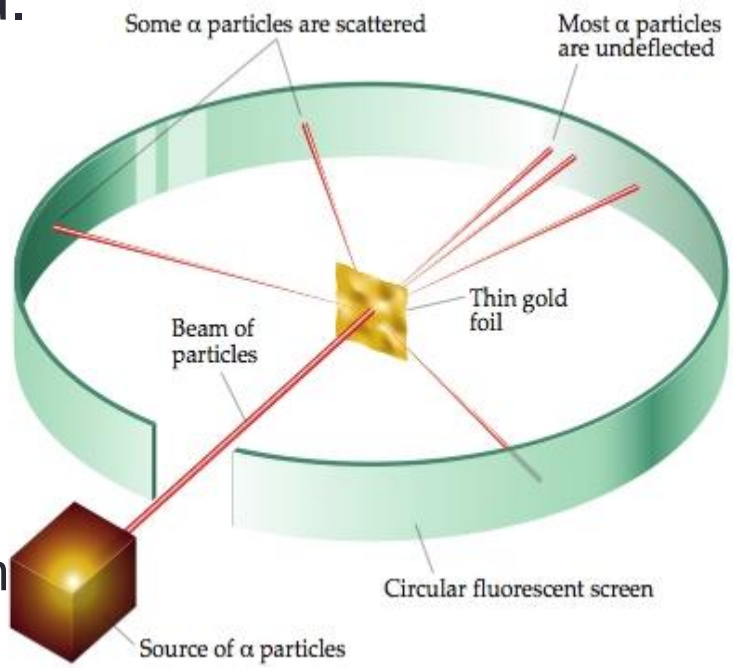
- The Thomson's model of an atom had no nucleus.



Rutherford's α-scattering experiment

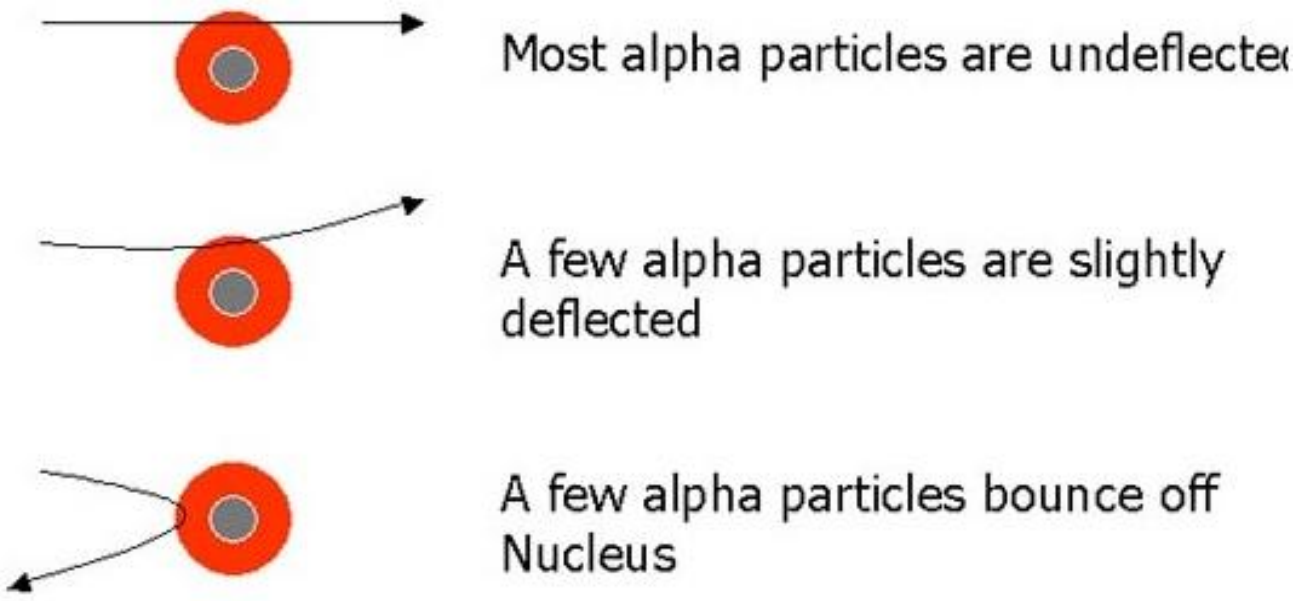
- Rutherford, a student of Thomson set out to prove the plum pudding model of the atom his mentor had proposed.

- Rutherford assigned the experiment to his assistant, Hans Geiger and undergraduate student, Ernest Marsden.
  - The experiment is also called the gold foil experiment.
  - A particle gun (containing radon) which could emit α-particle was put before a thin sheet of gold.
  - Then a detector was placed beyond the gold toil.
  - The detector was a zinc sulphide screen which could fluoresce as the alpha-particles hit it.



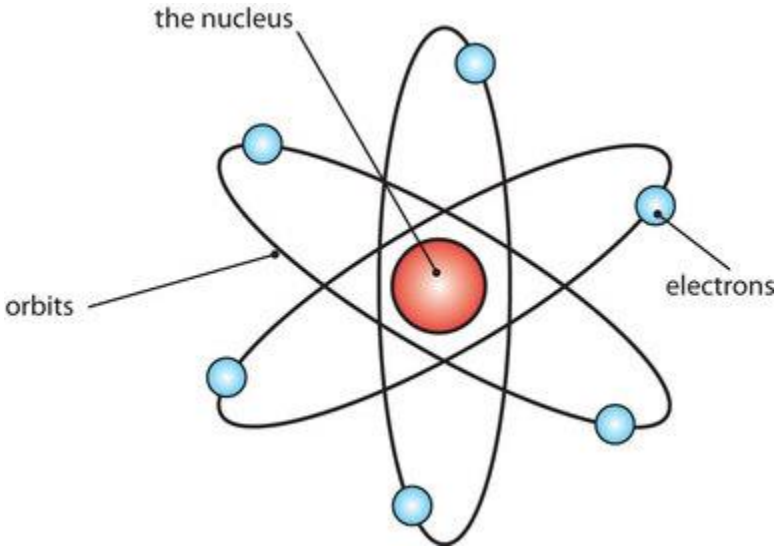
Observations from Rutherford's experiment

- Most of the α-particles went through the gold foil undeflected.
- A small percentage of the α-particles were deflected through some small angles.
- Very few of the particles bounced back or were deflected through large angles.



Rutherford's nuclear atom

- From the α-scattering experiment, Rutherford could deduce the structure of an atom.
  - That an atom has a central nucleus containing the positively charged protons.
  - The mass of the atom is concentrated in the nucleus, but the volume of the nucleus was relatively small as compared to the volume occupied by the electrons.
  - It was also held that electrons move speedily around the nucleus in circular orbits.

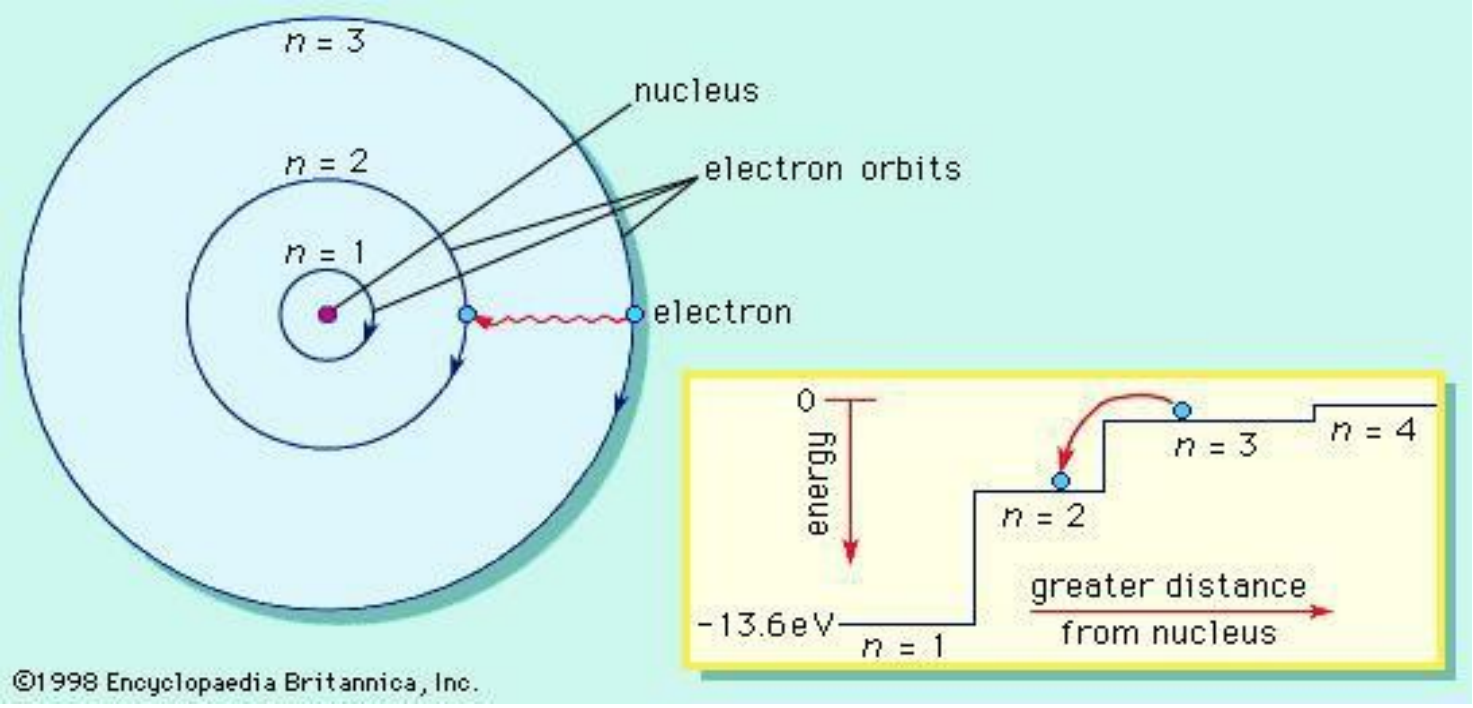


Bohr's model of an atom

- From Rutherford's model of the atom it was thought that electrons orbit around the nucleus at high speed.
  - However, scientists wondered why the negative electrons did not lose energy and spiral into the nucleus.

- Why nothing like that happened was taken care of by the quantum theory, of which Niels Bohr, a Danish physicist was a chief exponent.
  - Using the hydrogen atom for his study, Bohr suggested that the electron in hydrogen could not just have any energy, but that the electron was restricted to some permissible energy levels.
  - Thus he talked of the fact that the electrons were in discrete energy levels.

- What facilitated Bohr's study of hydrogen atom was his examination of spectra.
  - When hydrogen atoms are given energy by passing an electric current through it at low pressure, or when it is heated in a flame, a line spectrum was observed.



- A spectroscope is a device for producing and observing spectra.
  - It is made up of an energy source (heat or electric), a prism or diffracting grating to separate the light and an eyepiece.
  - When different elements are heated in a flame, they glow, and upon viewing the glowing light in a spectroscope, depending on the type of element, some series of brightly coloured lines are seen separated by dark lines.

- The spectra of different elements are different.
  - The spectrum of sodium has two closely-spaced yellow lines at 590 and 589 nm.
  - The spectrum of hydrogen is made up of red, green and purple lines at 656, 486 and 434 nm respectively.

- Contrast to the line spectrum of elements with a continuous spectrum, which is obtained when sunlight is passed through a prism.
  - In the latter case, light is separated into a rainbow of colours.
  - This is a continuous spectrum in which one colour of light fuses into another. Such a spectrum contains light of all wavelengths.

- Niels Bohr explained that electrons were responsible for the line spectrum of hydrogen of the way electrons are arranged in energy levels around the nucleus.
  - The electrons were said to revolve around the nucleus in definite orbits or energy levels like planets revolve around the sun. Each of the orbits has a certain energy associated with it.
  - Only certain energy values were permissible for these orbits.
  - Therefore, the energy or the electron was quantised.

- In Bohr's model, each orbit was assigned a number called the principal quantum number.
- This could be a whole number from 1 to infinity.
- When the electron is in the lowest energy level or orbit, it is said to be in the ground state.
- Electrons can move from a lower energy state to a-higher one if energy is supplied to it.
  - By this the electrons become excited.
  - The electron will not remain in the excited state indefinitely.
  - It can lose some or all the energy absorbed, and this lost energy is emitted as photon of light which could be visible or invisible.

- The decrease in energy can he designated as ΔE, where

  $\Delta E = h\nu$ or $\Delta E = nh\nu$,

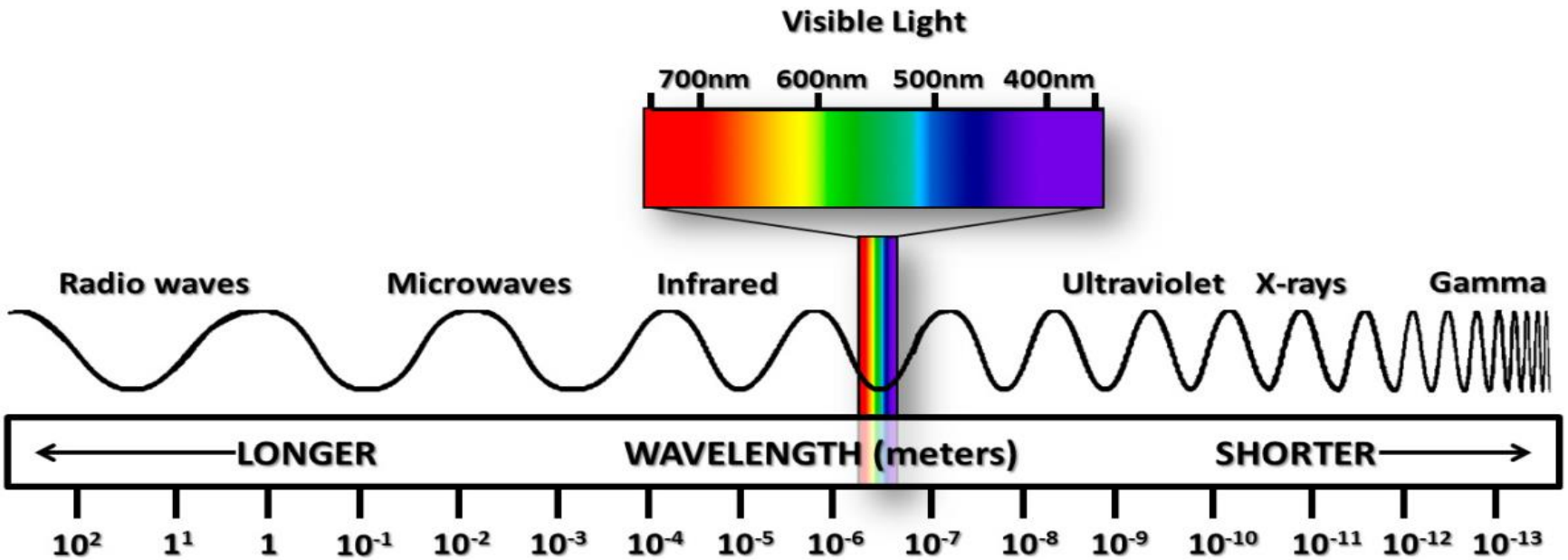
  - h = Planck's constant
  - v = frequency of the radiation
  - n= integer

- If the decrease in energy of the atom is large then a photon of light of high frequency will be emitted which may be in the blue or UV region.

- On the other hand, if the decrease in energy is low, then a photon of light of low frequency would he emitted, maybe in the red or infra-red region of the electro-magnetic spectrum.

- Each spectral line in the spectrum for an element corresponds to a certain energy change.
  - The red line at 656 nm results from an electron n =3 to n =2.
  - The green line at 486 nm results from an electron from n =4 to n=2.

- The greater the difference in energy between two levels, the higher the energy of the electromagnetic radiation given off and the shorter its wavelength



Quantum or wave mechanics model of an atom

- The Bohr's atomic model could not account for the line spectra of elements bigger than hydrogen.
  - The appearance of the spectra of such bigger atoms had more complicated pattern of lines, which could not be accounted for.

- The Bohr model considered an electron to be particle but Louis de Broglie, a French graduate student suggested in 1924 that apart from having a particle nature, electrons also had wave properties.
  - He formulated an equation which took account of this wave-particle dual nature of electron.

- As a particle, it would have a momentum associated with it, while as a wave, it would have a wavelength.

- The relationship between the mass of the electrons, its wavelength and velocity (v) was shown as:

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

- As soon as scientists began to consider an electron as behaving as waves, a problem arose:
  - for a subatomic particle, would it be possible to know its position and momentum or speed?

- In answer to this, a German physicist, Werner Heisenberg postulated the ‘uncertainty principle’.
  - It is difficult to define the position and momentum of an electron at the same time.

- The Bohr’s idea of an atom violated this principle because both the position of the electron and its energy was known.
  - The line spectrum indicated that electrons were in definite orbits with definite energies.
  - To be in consonance with the uncertainty principle, the fact that electrons have definite energies is upheld.
  - It is rather the position of the electron that cannot be known with any degree of certainty.

- Erwin Schrodinger was to combine de Broglie's equation with other equations for wave motion to derive a new wave equation or Schrodinger equation to describe the behaviour of an electron in a hydrogen atom.
  - For atoms with more than one electron, the calculations were even more complicated.

- Solutions of the Schrodinger equation are functions called wave functions psi (Ψ).
  - The square of the wave function (Ψ^2) is a mathematical expression of how the probability of finding an electron in a small volume varies from place to place.
  - In atoms the wave functions are called orbitals.
  - An orbital can be defined as a volume of space around the nucleus within which there is 95% probability of finding an electron.

- The Bohr model also considered only one quantum number, but in the wave mechanics model, two other quantum numbers,
  - the orbital or azimuthal or shape quantum number (ℓ) and
  - magnetic quantum numbers (m_t),
- in addition to the principal quantum number (n) are considered.

The Principal quantum number (n)

- It has integral values from 1 to infinity.
  - It can also be represented by the letters, K, L, M, N...

- The value of ***n*** gives an indication of how close an electron is to the nucleus.
  - The higher the value of n, the farther away the electron is from the nucleus.

- The value of **n** also determines the energy of the electron.
  - The higher the value, the higher the energy of the electron.

- For a principal quantum number ***n***, the maximum number of electrons it can accommodate is given by $\boldsymbol{2n^2}$.

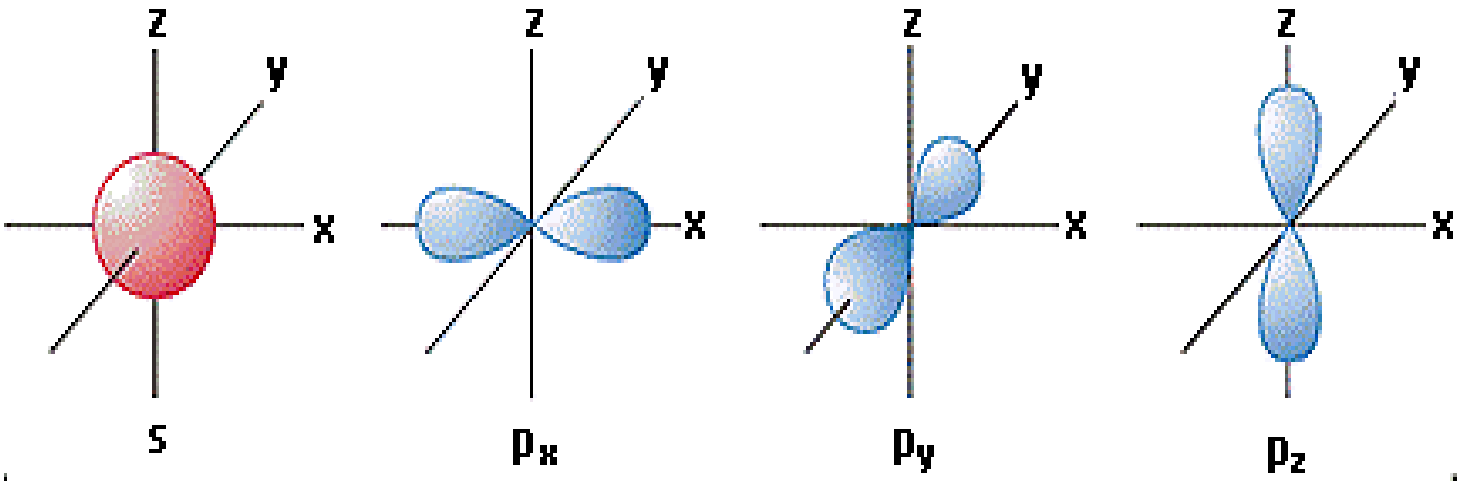
- The table below shows the maximum number of electrons in the first four shells,

n	Max. no. of electrons
1	2
2	8
3	18
4	32

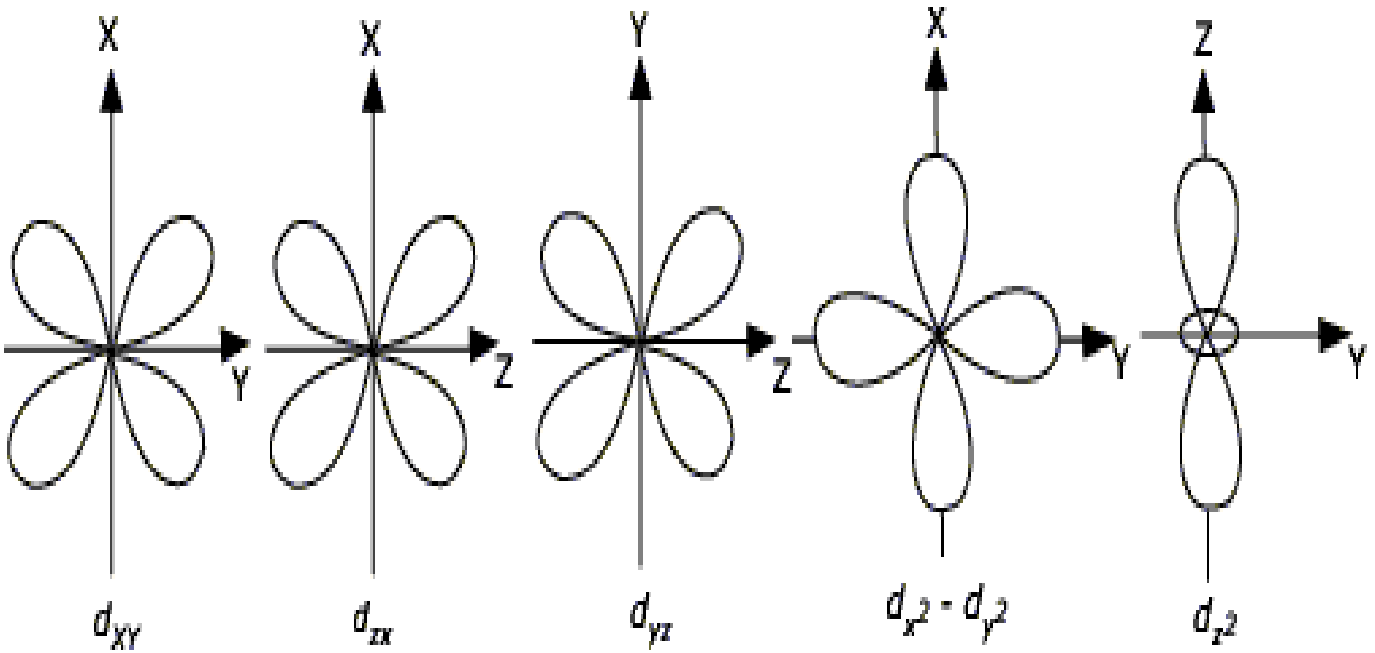
The orbital or azimuthal or angular momentum quantum number (l)

- It can have values from zero to n_{-1}.
- This quantum number defines the shape of an orbital.
  - Thus there is only one orbital or subshell in the first shell of n=1.
- This orbital with ***l***=0 is also called the s-orbital.
  - The shape of an s-orbital is symmetrically spherical.
  - All s-orbitals have the same shape, and each orbital can take two electrons.

- When n = 2; ***l*** = 0, 1 or s and p-orbitals.
- Thus the shell of principal quantum number 2 has two orbitals or subshells, 2s and 2p.
- The shape of a p-orbital is different from that of an s-orbital.
- Whereas the s-orbital is spherical, the p-orbital is dumb-bell in shape.



- So the shell with principal quantum number 3 will have three orbitals; s, p and d.
- There will be 3s, 3p and 3d orbitals.
- The shapes of the d-orbitals are more complex.



The magnetic quantum number (m_l)

- It can have whole number values of -***l*** to +***l***, including zero.
- It describes the orientation of the orbitals in space.
- When n = 1, ***l*** = 0.
  - Thus, the s-orbital has no directions of orientation.
- When n = 2, ***l*** =0,1 m_l = -1,0,+1.
  - Thus there are three p-orbitals of the same shape but differ with respect to their orientation in space.
  - Each of the three can be arbitrarily assigned to one of the Cartesian x, y and z.
  - So the three are mutually perpendicular.

- When n=3, l = 0,1,2; m_l = -2, -1, 0, 1, +2
  - The d-subshell is made up of five orbitals. So in all, ten electrons can be accommodated in the d-subshell while the p-subshell takes six electrons.

- The p-subshell has three orbitals of the same energy or degenerate orbitals while the d-subshell has five degenerate orbitals.

Spin quantum number

- This is the fourth type of quantum number.
- It arises from the ability of electrons to spin about their axes either in the clockwise or anti-clockwise direction.
- The spin quantum numbers have values of $+\frac{1}{2}$, $-\frac{1}{2}$.

Electronic configuration

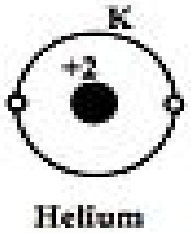
- This is the arrangement of electrons in atoms.
  - It is the specific pattern of arrangement that will make every element unique.
- In a way the electronic configuration of an element will serve as the ‘face’ for the identification of the elements.
- There can be two approaches for arranging electrons in elements.
  - The first is simple in that the electrons are arranged in shells, taking into account only the principal quantum number, ***n***.
  - The second approach which is rather more involving requires the consideration of all the four quantum numbers.

- Whichever of the two approaches is used, there is one rule that has to be adhered to - the ‘aufbau rule’.
  - According to this rule, electronic energy levels have to be filled starting from the low energy level.
  - Thus, we have to start from n = l before proceeding to n =2, and so on.

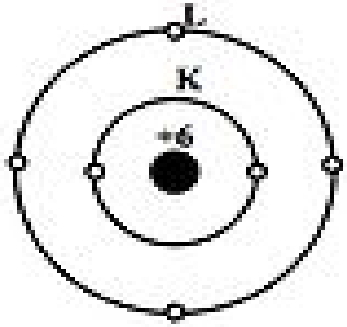
- For the simplest approach, we could either draw the energy levels as concentric circles around the nucleus or we could just represent the energy levels by the letters, K, L, M, N

- Bear in mind that each shell has the maximum number of electrons it can take.

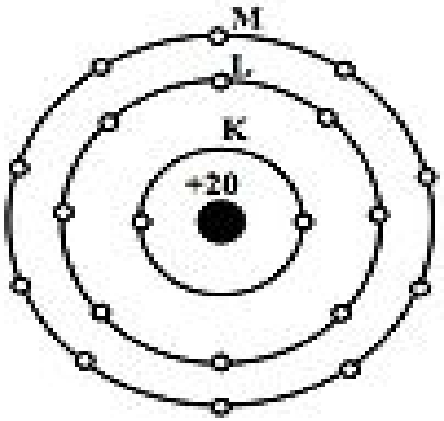
Hydrogen



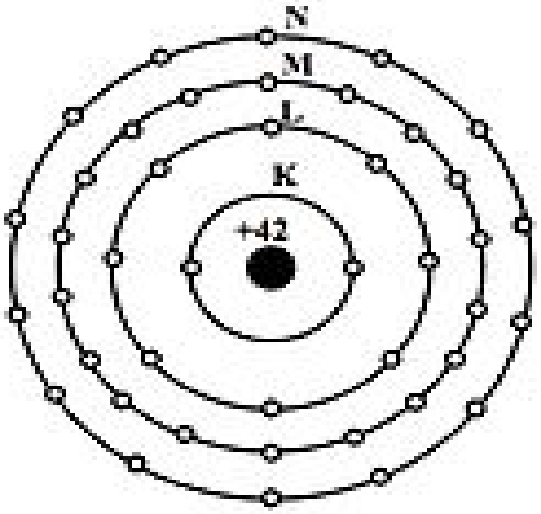
Helium



Carbon



Calcium



Molybdenum

Atomic no.	Symbol	K	L	M	N
1	H	1			
2	He	2			
3	Li	2	1		
4	Be	2	2		
11	Na	2	8	1	
12	Mg	2	8	2	
13	Al	2	8	3	
14	Si	2	8	4	
19	K	2	8	8	1
20	Ca	2	8	8	2
21	Sc	2	8	9	2
28	Ni	2	8	16	2
29	Cu	2	8	18	1
30	Zn	2	8	18	2

- In the other way of arrangement of electrons, atomic orbitals in the various shells are used.
  - According to the aufbau rule, the order of filling of the orbitals is as follows:
  - 1s 2s 2p 3s 3p 4s 3d 4p

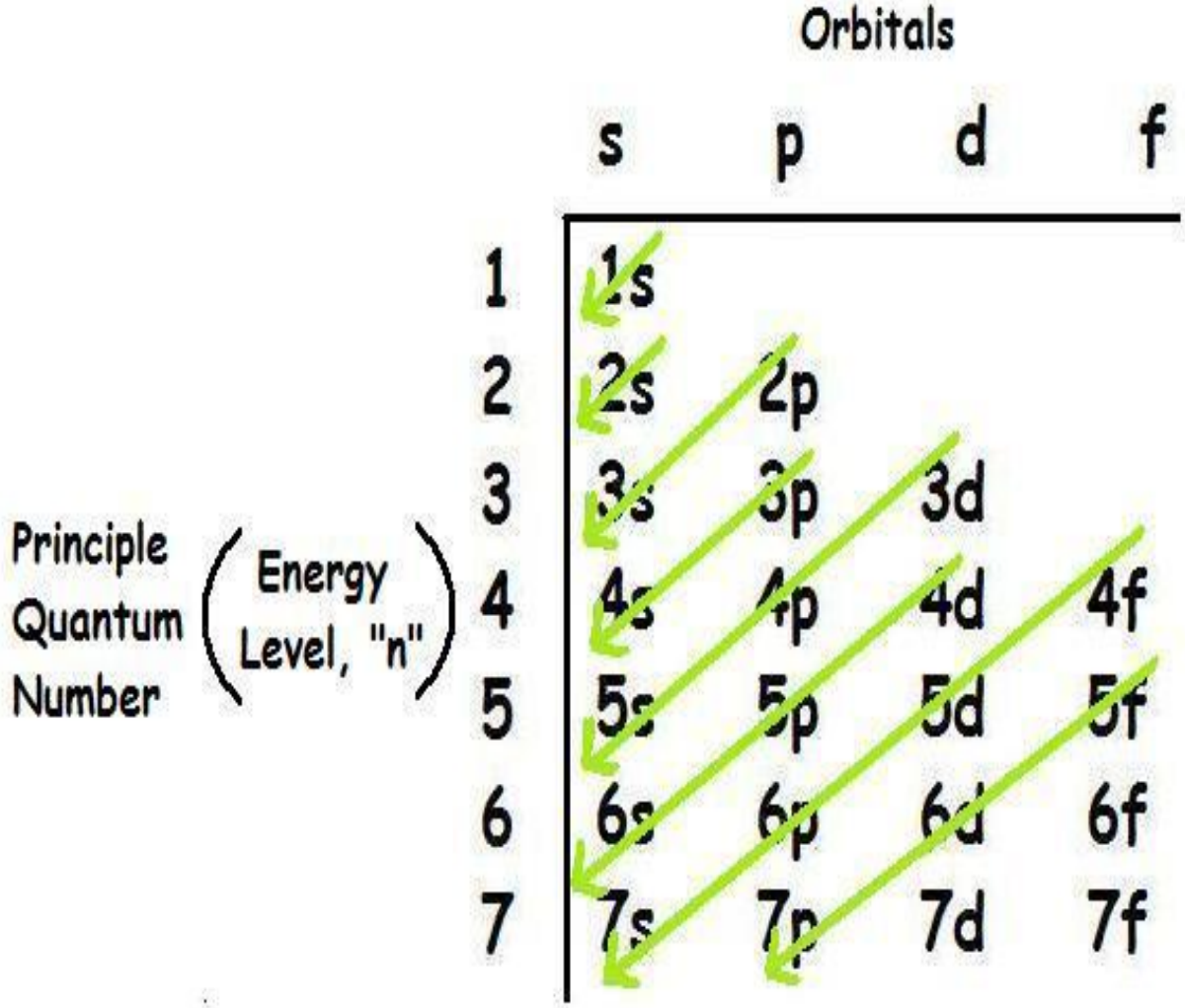
- Two other rules are condisered;

Hunds rule

- In filling degenerate orbitals, they are filled singly with electrons to maximum before pairing up the electrons in the orbitals.

Pauli' s exclusion principle

- Pauli's exclusion principle states that no two electrons in an orbital would have all the four numbers being the same.



Order: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p

Atomic number	Symbol	Electron configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	[He]$2s^1$
4	Be	[He]$2s^2$
5	B	[He]$2s^2 2p^1$
6	C	[He]$2s^2 2p^2$
7	N	[He]$2s^2 2p^3$
8	O	[He]$2s^2 2p^4$
9	F	[He]$2s^2 2p^5$
10	Ne	[He]$2s^2 2p^6$
11	Na	[Ne]$3s^1$
12	Mg	[Ne]$3s^2$
13	Al	[Ne]$3s^2 3p^1$
14	Si	[Ne]$3s^2 3p^2$
15	P	[Ne]$3s^2 3p^3$
16	S	[Ne]$3s^2 3p^4$
17	Cl	[Ne]$3s^2 3p^5$
18	Ar	[Ne]$3s^2 3p^6$
19	K	[Ar]$4s^1$
20	Ca	[Ar]$4s^2$
21	Sc	[Ar]$4s^2 3d^1$
22	Ti	[Ar]$4s^2 3d^2$
23	V	[Ar]$4s^2 3d^3$
24	Cr	[Ar]$4s^2 3d^5$
25	Mn	[Ar]$4s^2 3d^5$
26	Fe	[Ar]$4s^2 3d^6$
27	Co	[Ar]$4s^2 3d^7$
28	Ni	[Ar]$4s^2 3d^8$
29	Cu	[Ar]$4s^2 3d^{10}$
30	Zn	[Ar]$4s^2 3d^{10}$
31	Ga	[Ar]$4s^2 3d^{10} 4p^1$
32	Ge	[Ar]$4s^2 3d^{10} 4p^2$
33	As	[Ar]$4s^2 3d^{10} 4p^3$
34	Se	[Ar]$4s^2 3d^{10} 4p^4$
35	Br	[Ar]$4s^2 3d^{10} 4p^5$
36	Kr	[Ar]$4s^2 3d^{10} 4p^6$

Atomic number	Symbol	Electron configuration
37	Rb	[Kr]$5s^1$
38	Sr	[Kr]$5s^2$
39	Y	[Kr]$5s^2 4d^1$
40	Zr	[Kr]$5s^2 4d^2$
41	Nb	[Kr]$5s^1 4d^4$
42	Mo	[Kr]$5s^1 4d^5$
43	Tc	[Kr]$5s^2 4d^5$
44	Ru	[Kr]$5s^1 4d^7$
45	Rh	[Kr]$5s^1 4d^8$
46	Pd	[Kr]$4d^{10}$
47	Ag	[Kr]$5s^1 4d^{10}$
48	Cd	[Kr]$5s^2 4d^{10}$
49	In	[Kr]$5s^1 4d^{10} 5p^1$
50	Sn	[Kr]$5s^1 4d^{10} 5p^2$
51	Sb	[Kr]$5s^1 4d^{10} 5p^3$
52	Te	[Kr]$5s^1 4d^{10} 5p^4$
53	I	[Kr]$5s^1 4d^{10} 5p^5$
54	Xe	[Kr]$5s^1 4d^{10} 5p^6$
55	Cs	[Xe]$6s^1$
56	Ba	[Xe]$6s^2$
57	La	[Xe]$6s^2 5d^1$
58	Ce	[Xe]$6s^2 4f^1 5d^1$
59	Pr	[Xe]$6s^2 4f^3$
60	Nd	[Xe]$6s^2 4f^4$
61	Pm	[Xe]$6s^2 4f^5$
62	Sm	[Xe]$6s^2 4f^6$
63	Eu	[Xe]$6s^2 4f^7$
64	Gd	[Xe]$6s^2 4f^7 5d^1$
65	Tb	[Xe]$6s^2 4f^9$
66	Dy	[Xe]$6s^2 4f^{10}$
67	Ho	[Xe]$6s^2 4f^{11}$
68	Er	[Xe]$6s^2 4f^{12}$
69	Tm	[Xe]$6s^2 4f^{13}$
70	Yb	[Xe]$6s^2 4f^{14}$
71	Lu	[Xe]$6s^2 4f^{14} 5d^1$
72	Hf	[Xe]$6s^2 4f^{14} 5d^2$

Atomic number	Symbol	Electron configuration
73	Ta	[Xe]$6s^2 4f^{14} 5d^3$
74	W	[Xe]$6s^2 4f^{14} 5d^4$
75	Re	[Xe]$6s^2 4f^{14} 5d^5$
76	Os	[Xe]$6s^2 4f^{14} 5d^6$
77	Ir	[Xe]$6s^2 4f^{14} 5d^7$
78	Pt	[Xe]$6s^1 4f^{14} 5d^9$
79	Au	[Xe]$6s^1 4f^{14} 5d^{10}$
80	Hg	[Xe]$6s^2 4f^{14} 5d^{10}$
81	Tl	[Xe]$6s^2 4f^{14} 5d^{10} 6p^1$
82	Pb	[Xe]$6s^2 4f^{14} 5d^{10} 6p^2$
83	Bi	[Xe]$6s^2 4f^{14} 5d^{10} 6p^3$
84	Po	[Xe]$6s^2 4f^{14} 5d^{10} 6p^4$
85	At	[Xe]$6s^2 4f^{14} 5d^{10} 6p^5$
86	Rn	[Xe]$6s^2 4f^{14} 5d^{10} 6p^6$
87	Fr	[Rn]$7s^1$
88	Ra	[Rn]$7s^2$
89	Ac	[Rn]$7s^2 6d^1$
90	Th	[Rn]$7s^2 6d^2$
91	Pa	[Rn]$7s^2 5f^2 6d^1$
92	U	[Rn]$7s^2 5f^3 6d^1$
93	Np	[Rn]$7s^2 5f^4 6d^1$
94	Pu	[Rn]$7s^2 5f^6$
95	Am	[Rn]$7s^2 5f^7$
96	Cm	[Rn]$7s^2 5f^7 6d^1$
97	Bk	[Rn]$7s^2 5f^9$
98	Cf	[Rn]$7s^2 5f^{10}$
99	Es	[Rn]$7s^2 5f^{11}$
100	Fm	[Rn]$7s^2 5f^{12}$
101	Md	[Rn]$7s^2 5f^{13}$
102	No	[Rn]$7s^2 5f^{14}$
103	Lr	[Rn]$7s^2 5f^{14} 6d^1$
104	Rf	[Rn]$7s^2 5f^{14} 6d^2$
105	Db	[Rn]$7s^2 5f^{14} 6d^3$
106	Sg	[Rn]$7s^2 5f^{14} 6d^4$
107	Bh	[Rn]$7s^2 5f^{14} 6d^5$
108	Hs	[Rn]$7s^2 5f^{14} 6d^6$
109	Mt	[Rn]$7s^2 5f^{14} 6d^7$
110	Ds	[Rn]$7s^1 5f^{14} 6d^9$
111	Rg	[Rn]$7s^1 5f^{14} 6d^{10}$

Periodic table and periodic properties of elements

- All elements are arranged on the periodic table.
  - The modem form of the periodic table was put forward by Mendeleev, a Russian chemist.
- The arrangement is based on the periodicity of the electronic structure of the atoms.
  - Such a pattern has been made possible because elements the table have been arranged according to their atomic numbers.
- The elements of the periodic table can be divided into **groups**, **periods** and **blocks**.

Groups of a periodic table

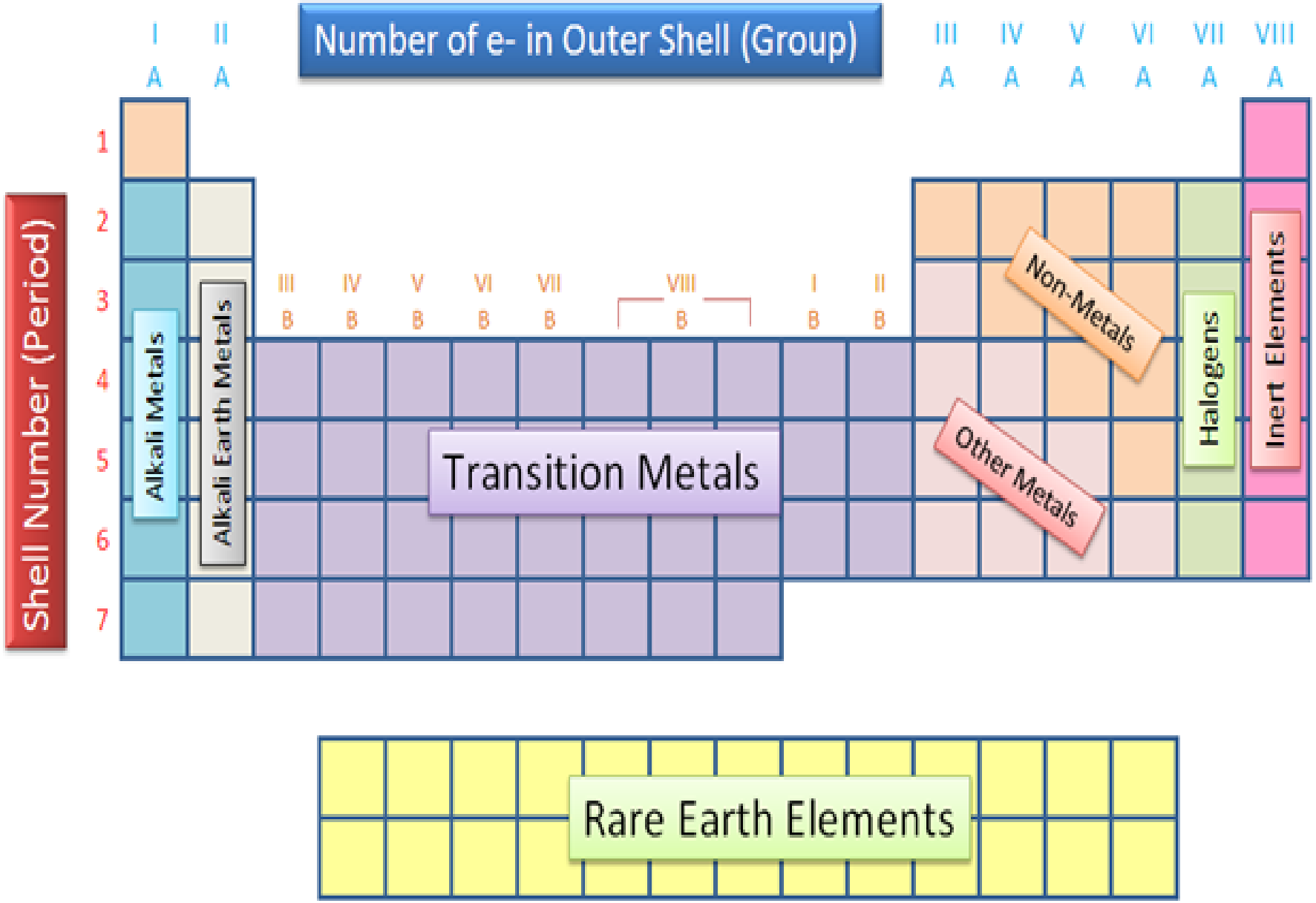
- A group is a vertical arrangement on the periodic table.
-
- The elements in a group have the same valence electrons or they have similar electronic configuration.
-
- Consider the electronic configuration of the elements; Li, Na, K, Rb, Cs and Fr.

Atomic number	Symbol	Electronic configuration
3	Li	$1s^2 2s^1$ **(or)** [He]$2s^1$
11	Na	$1s^2 2s^2 2p^6 3s^1$ **(or)** [Ne]$3s^1$
19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ **(or)** [Ar]$4s^1$
37	Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ **(or)** [Kr]$5s^1$
55	Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ **(or)** [Xe]$6s^1$
87	Fr	[Rn]$7s^1$

- Where group members share similar physical and chemical properties, they could be considered as a ‘family’.
  - For example, the alkali metals made up of Li, Na, K, Rb, Cs as well as the halogens or group VII elements form families.

- Where similarity of elements in the same group (congeners) is not marked, the tag ‘family’ should be avoided.
  - An example is group IV made up of C, Si, Ge, Sn and Pb.

- Elements in the same group have different n values.


Number of e- in Outer Shell (Group)
I A
II A
III A
IV A
V A
VI A
VII A
VIII A
Shell Number (Period)
1
2
3
4
5
6
7
III B
IV B
V B
VI B
VII B
VIII B
I B
II B
Alkali Metals
Alkali Earth Metals
Transition Metals
Non-Metals
Other Metals
Halogens
Inert Elements
Rare Earth Elements

Periods

- A period is a row or horizontal arrangement of elements on the periodic table.
- In a period, from one element to the next, the atomic number increases by one.
- In all, there are seven periods.
  - The length of the periods is not uniform, but varies.
  - The short period has two elements, and the longest should have thirty two elements.
  - The periods are numbered from 1 to 7.

- The period number refers to the main energy level that the valence electrons of the elements of a period occupy.
  - In period 1, the valence electrons of the elements occupy n= 1.
  - There are only two elements in period 1; hydrogen and helium.

- The valence electrons of elements of the second period enter n=2 (or 2s 2p).
  - The maximum number of electrons in 2s and 2p subshells is two and six respectively, giving a total of eight.
  - So the total number of elements in period 2 is eight.

- Next is the third period in which the valence electrons enter the main shell of principal quantum number, n=3. This has three orbitals 3s, 3p and 3d.
  - We would have expected the third period to have eighteen elements, but this period, like the second one, has eight elements.

- This is because the 3d-orbitals are not filled.
- The reason for the non-filling of the 3d is that they have higher energy.
- So the next electrons rather enter the 4s orbital which is of lower energy than 3d.
- However, 4s is of a higher quantum number, so it is considered a new shell, and the first element whose valence electron enters the 4s is not considered to be period 3 element

- Rather, a period 4 element in the fourth period therefore, the orbitals that are filled by the valence electrons of the elements of the period are 4s, 3d and 4p, corresponding to eighteen elements.

- Similarly the valence electrons of the fifth period elements fill 5s, 4d and 5 p orbitals: this also gives eighteen elements

- The sixth period is made up of elements in which the valence electron fill 6s, 4f, 5d and 6p orbitals, giving the size of the period as 32 elements.
  - But then, accommodating such a large number of elements in one row would make the period unduly wide.
  - As a way of avoiding this clumsy arrangement, the elements with their valence electrons filling the 4f orbitals are placed in a separate row at the bottom of the periodic table.
  - This row of elements forms the lanthanide series.The lanthanides start from $_{58}$Ce to $_{71}$Lu .
- In the seventh period, a similar modification is made whereby elements with their valence electrons filling 5f orbitals are placed below the lanthanides.
  - These are the Actinides; the actinides start from $_{90}$Th to $_{103}$Lr.
- *It is worthy of note that a new period begins after a noble gas configuration with a duplet or octet*

Blocks of the periodic table

- The last subshell or orbital that contains the valence electrons is the s-orbital in both groups I and II elements.

- Therefore, these two groups of elements are also called s-block elements.

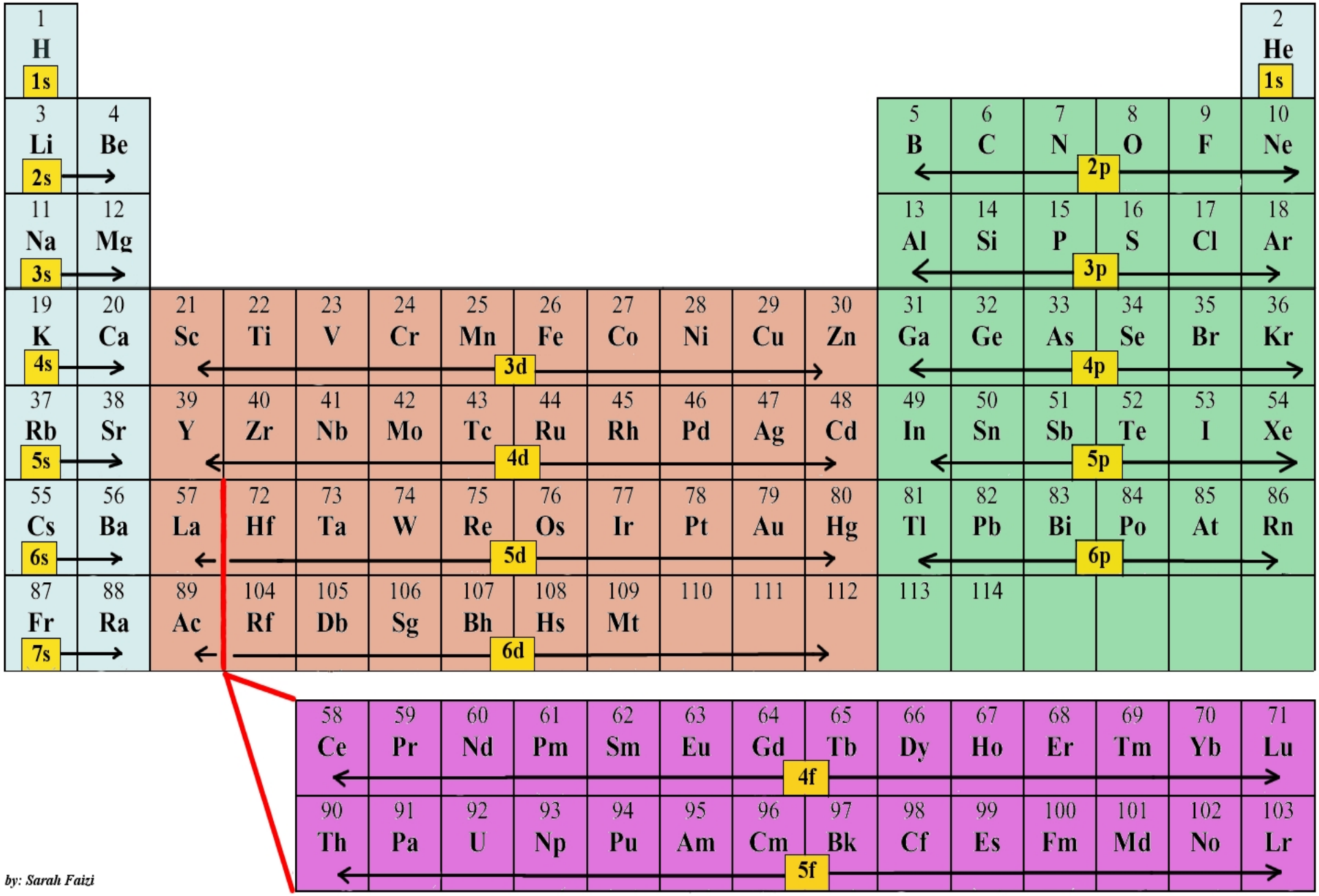
- We can also look at the electronic configuration of the second period elements from boron to Neon.
  - It is clear that the valence electrons of the above-listed second period elements are in s- and p-orbitals.
  - However, the last orbital occupied by the valence electrons is p-orbital.
  - It is for this reason that group IIIA to group O or VIIIB elements are called p-block elements.

- The d-block elements form the transition metals in which the valence electrons fill d- orbitals.
  - Such d-block elements in the fourth period (Sc-Zn) form the first transition series.
  - The d-block elements in the fifth period (Y-Cd) form the second transition series.
  - There is also the third transition series from Lu-Hg.

- Finally, there are the f-block elements: these are the lanthanides and actinides.
  - All the f-block elements in a period have the same outer electron configuration; either $6s^2$ or $7s^2$.
  - The properties of the lanthanides, for example are similar.
  - This is probably due to their having the same outer electronic configuration $6s^2$ (but the 4 f electrons differ).
  - The f-block elements are sometimes called the inner transition elements.

- Those elements with their valence electrons in s- and p-orbitals are referred to as A group of elements.
  - The group number refers to the number of electrons in the outermost orbital or orbitals.

- There are groups IA to VIIIA.
  - The group VIIIA is sometimes designated as group O.
  - The s-block and p-block elements are the representative or main-group elements.



by: Sarah Faizi

Periodic properties

- The physical and chemical properties of atoms which do recur on the periodic table are called periodic properties.

- The recurrence of these properties is due to some common features of the electronic structures.

- Some of the atomic properties which do recur are
  - Atomic / ionic radius
  - ionization energy
  - electron affinity
  - electronegativity

- In order to follow how these properties change on the periodic table, some terms have to be introduced and explained.

- These include
  - *Valence electrons*: Valence electrons or the outermost electrons are those electrons that are involved in bond formation. They have high energy.
  - *Core electrons*: The core electrons are the innermost electrons. They are between the nucleus and the valence electrons. Unlike the valence electrons, they are not involved in bond formation.
  - *Effective nuclear charge*: The effective nuclear charge refers to the net attraction of the nucleus for the outermost or valence electrons.

- *Shielding/screening effect*: The screening effect is the reduced attraction of the protons for the valence electrons due to the core electrons. These core electrons, using their negative charge, reduce the full effect of the nuclear attraction for the valence electrons. The core electrons, thus shield or screen the valence electrons from the full attraction of the protons in the nucleus.

- Across a period, electrons enter the same shell
  - Screening amongst electrons in the same shell is not much so effective nuclear charge increases.
  - On the other hand, as a group is descended new shells are added, the screening effect increases, and the effective nuclear charge virtually does not change even though the number of protons increases as the group is descended.

Atomic radius

- For covalently bonded atoms in a molecule, the atomic radius can be taken as half the distance between the two bonded nuclei.

- Metallic radius is also half the distance between the two nuclei of adjacent metal atoms.

- The size of an atom is dependent on how strongly the protons in the nucleus attract the valence electrons.
  - Across a period, electrons enter the same shell.
  - The screening effect due to electrons in the same shell is not much, almost constant.
  - However, the positive charge on the nucleus increases by one proton from one element to the next in a period.

- As a result, there is greater attraction for the valence electrons, and leads to a decrease in the size of the atom.

- But from the halogens to the rare gases, there is an increase.
  - This is attributed to the fact that the repulsion amongst electrons in a complete outer shell is marked.

Ionic radius

- Ions are charged atoms which are formed either by the loss or gain of electrons.

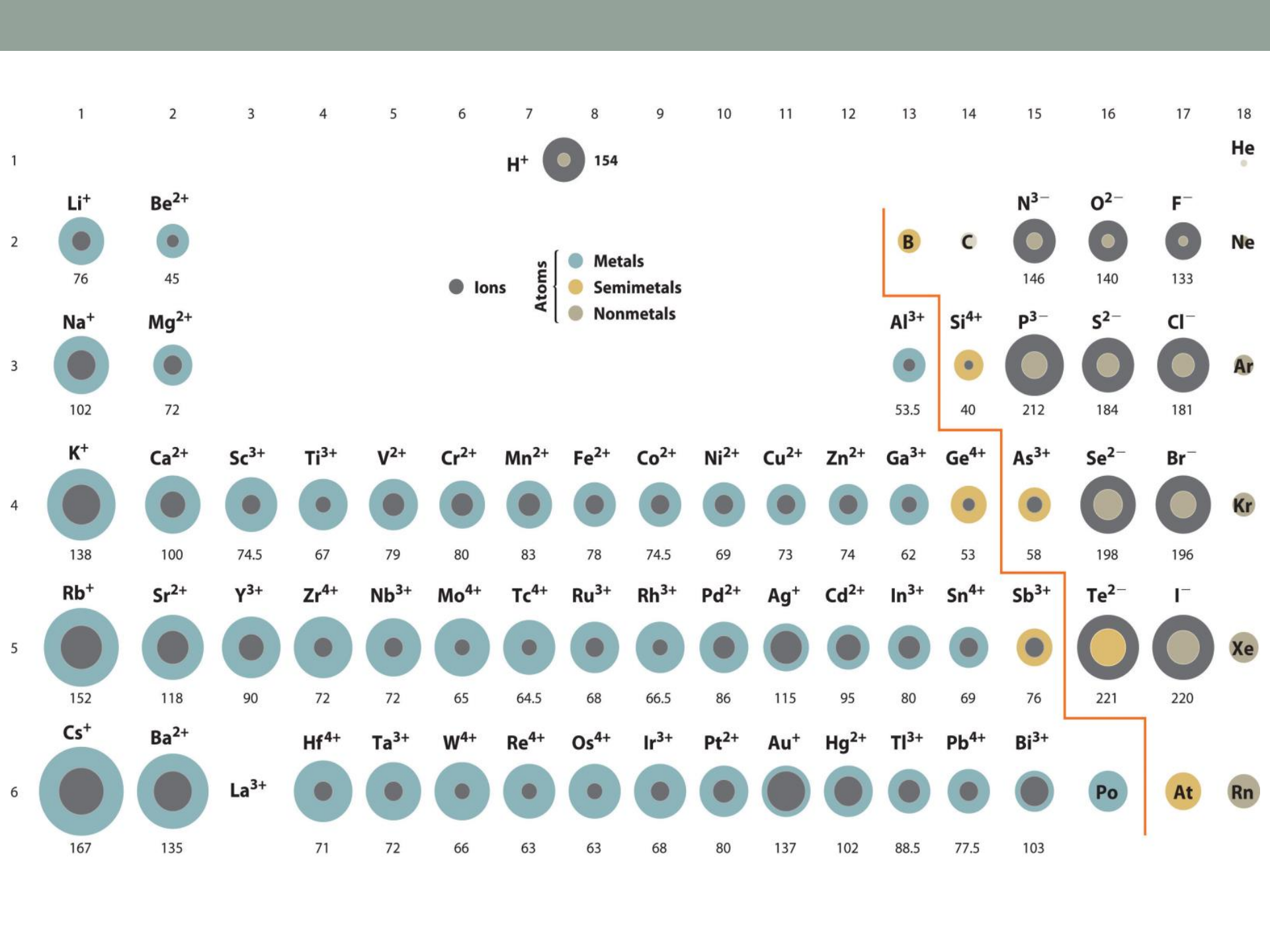
- There are two types of ions;
  - Cations
  - Anions.

- A cation is formed when an element loses an electron.
  - For example Li and Na can each lose an electron to form Li^+ and Na^+ respectively.
  - Li^+, now has the electronic configuration of its preceding noble gas, He, while Na^+ has the electronic configuration of Ne.
  - They are said to be isoelectronic with the noble gases.

- A cation is smaller than its parent atom.
  - A cation has fewer number of electrons than the neutral atom.
  - So the fewer electrons are attracted more strongly, hence the size decreases.
  - The more the number of electrons lost, the greater the attraction and hence the smaller the size of the cation.

- We expect Mg^{2+} to be smaller in size than Na^{+} due to the greater nuclear attraction in Mg^{+} ion with a double positive charge.

- Anions are formed when atoms gain electrons.
  - An anion is isoelectronic with the noble gas which is immediately ahead of its atom.
- Anions are bigger than their parent atoms for two reasons.
  - Firstly, in the anions there are more electrons than protons, so the attraction for the outer electronic shells is less.
  - Secondly, the gaining of electrons increases the repulsive forces amongst the electrons.
- Just like atomic radius, cationic radius decreases across a period, but down a group, there is an increase.
  - In a series of ions with the same number of electrons (isoelectronic series) cationic radius decreases with increase in atomic number.
  - The ionic radius of the following isoelectronic series will be in the order; $Na^{+}>Mg^{2+}>Al^{3+}$.


1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
1
2
3
4
5
6
H+ 154
He
Li+ 76
Be2+ 45
B
C
N3− 146
O2− 140
F− 133
Ne
Ions
Atoms
Metals
Semimetals
Nonmetals
Na+ 102
Mg2+ 72
Al3+ 53.5
Si4+ 40
P3− 212
S2− 184
Cl− 181
Ar
K+ 138
Ca2+ 100
Sc3+ 74.5
Ti3+ 67
V2+ 79
Cr2+ 80
Mn2+ 83
Fe2+ 78
Co2+ 74.5
Ni2+ 69
Cu2+ 73
Zn2+ 74
Ga3+ 62
Ge4+ 53
As3+ 58
Se2− 198
Br− 196
Kr
Rb+ 152
Sr2+ 118
Y3+ 90
Zr4+ 72
Nb3+ 72
Mo4+ 65
Tc4+ 64.5
Ru3+ 68
Rh3+ 66.5
Pd2+ 86
Ag+ 115
Cd2+ 95
In3+ 80
Sn4+ 69
Sb3+ 76
Te2− 221
I− 220
Xe
Cs+ 167
Ba2+ 135
La3+
Hf4+ 71
Ta3+ 72
W4+ 66
Re4+ 63
Os4+ 63
Ir3+ 68
Pt2+ 80
Au+ 137
Hg2+ 102
Tl3+ 88.5
Pb4+ 77.5
Bi3+ 103
Po
At
Rn

- The more the number of electrons gained, the larger the size of the anion.
- Of the three ions, Al^{3+} is the smallest. Some values of atomic and ionic radius (in nm) are shown below

Atom	Li	Be	B	C	N	O	F	Ne
Atomic radius	156	112	85	77	71	60	69	131
Ionic radius	90	59	41	260	132	126	119	

Ionisation energy

- This is the energy required to expel the most loosely bound electron from a gaseous atom.

- Alternatively, it could be defined as the energy required to remove an electron from a gaseous atom to form one mole of gaseous cation with a single charge.

- The following factors determine ionization energy;
  - atomic radius
  - shielding effect
  - stability of electronic configuration
  - penetration effects

- As a group is descended, the increasing size of the atom, coupled with the screening effect make the attraction of the nucleus for the outermost electrons less.
  - Therefore, less energy is required to expel the outermost electrons.

- Across a period, there is a general increase in the ionization energy.
  - The effective nuclear charge increases, and atomic radius decreases.
  - Attraction for the outermost electrons increases, accounting for the increase in the ionization energy.

- However, there are some discrepancies in this trend across the period.
  - In the second period for instance, the ionization energy of Be ($1s^2$ $2s^2$) is higher than that of B (ls^2 $2s^2$ $2p^1$) while that N is higher than O.
  - The 2p electron of B of higher energy than 2s electron of Be.

- The higher energy implies less stability, making the loss of an electron from 2p easier, and thus requiring less energy.
- It could also be said that the ***s*** electron has greater penetrating power than the 2p electron
- This makes the loss of a p-electron easier.
- It is because the s electron may be found closer to the nucleus than the p-electron that the former is said to have greater penetrating power (a p-electron will have greater penetrating effect than a d-electron).

- Another explanation that could be given is that there is greater stability associated with an outermost orbital which is fully filled as found in Be.

- One other irregular feature in the trend of ionization energies across the second period is the higher ionization energy of nitrogen ($ls^2\ 2s^2\ 2p^3$) as against that of oxygen ($ls^2\ 2s^2\ 2p^4$).

- In N, the 2p orbitals are half-filled, and there is stability associated with the half-filled orbitals as the single electrons in the p-orbitals are spread out, minimizing repulsion.

- Alternatively, we could ascribe the lower ionization energy of oxygen to its instability due to repulsion between the two electrons which become paired up in a p-orbital.

- To remove the second, third. . . . electrons in an atom (ion) requires the input of second, third... .etc.
  - Ionization energies which will be increasing.
  - The net positive charge makes it increasingly difficult to lose electrons in the successive steps.
  - Fewer electrons are being attracted by the same number of protons: in addition, the remaining electrons are more close to the nucleus.
  - Where a noble gas electronic configuration is involved, an unusually high ionization energy is required owing to the stability of the noble gas configuration.

Electron affinity

- This is the energy change when an electron is added to a gaseous atom.
- For a halogen, we could define electron affinity as the energy released when an electron is added to a gaseous atom to form a gaseous anion.

$$Cl_{(g)} + e^- \rightarrow Cl^- \qquad -349 \text{ kJ/mol}$$

- The halogens have highly negative electron affinities.

- The electron which is being add faces repulsion from the shell it has filled, but there is also the attraction between the add electron and the protons

- It is this attraction that accounts for the release of energy.
- A caution should be taken here: it is not in all cases that electron affinity is a negative energy value.
- Take the case of oxygen which can step wisely gain two electrons.

$$O_{(g)} + e^- \rightarrow O^- \qquad -141 \text{ kJ/mol}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-} \qquad +798 \text{ kJ/mol}$$

- The second electron is added against the repulsive force of the negatively charged oxygen.

- The repulsive force must be overcome by an energy input, hence the positive value of electron affinity.

- The way the electron affinity varies in more complex than the variation of ionization energy.

- All the same, electron affinity depends on
  - atomic radius
  - stability of electronic configuration
  - for anions, the charge carried on them

- Down a group the electron affinity decreases because atomic radius increases and attraction for the added electron gets less.

- Across the same period, electron affinity increases, effective nuclear charge increases, resulting in the increased attraction for the add electron.

- The incoming electron is attracted more strongly by the decreasing atomic size as well as the increasing positive charge on the nucleus.

Electron Affinities (kJ/mol)

1A	2A	3A	4A	5A	6A	7A	8A
H −73							He >0
Li −60	Be >0	B −27	C −122	N >0	O −141	F −328	Ne >0
Na −53	Mg >0	Al −43	Si −134	P −72	S −200	Cl −349	Ar >0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr >0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe >0

- The electron affinities of B, C and N are as shown below

$B + e^- \rightarrow B^-$ EA = - 27 kJ/mol

$1s^2\ 2s^2\ 2p^1$ $1s^2\ 2s^2\ 2p^2$

$C + e^- \rightarrow C^-$ EA = -122 kJ/mol

$1s^2\ 2s^2\ 2p^2$ $1s^2\ 2s^2\ 2p^3$

$N + e^- \rightarrow N^-$ EA = 0 kJ/mol

$1s^2\ 2s^2\ 2p^3$ $1s^2\ 2s^2\ 2p^4$

Electronegativity

- Electronegativity is the ability of an atom in a molecule to attract shared electrons.

- A distinction should be made between electronegativity and electron affinity.
  - In defining electron affinity, we consider gaseous isolated atoms whereas in electronegativity we consider atoms in molecules.

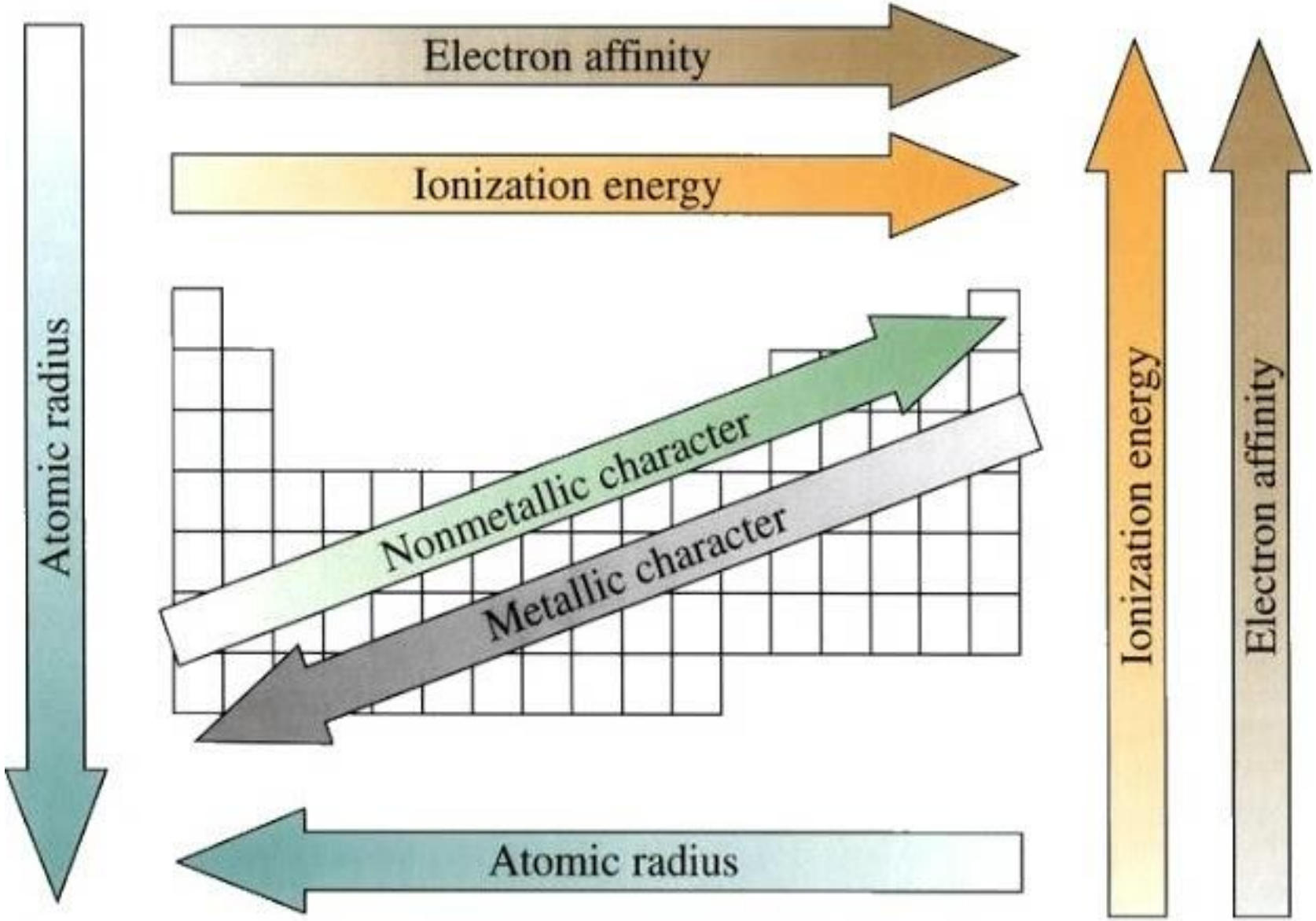
- Electron affinity is an energy input or output, having units of kJ/mol; it could be positive or negative.

- Electronegativity is a comparative scale, giving a quantitative measure of atom's ability to attract electrons.
  - It has no units or it is a dimensionless number. Its values are always positive.

- Values of electronegativity are given according to the Pauling's scale.
- The highest value of 4.0 is given to fluorine in group VIIA while the lowest value of 0.7 is assigned to Francium in group IA.
- Another difference between electron affinity and electronegativity is that the former can be directly measured whereas the latter is measured indirectly.
- Like electron affinity, electronegativity increases across a period but decreases down a group.
- The most electronegative atoms are the reactive non-metals, the halogens which are on the right side of the periodic table.

- On the other hand, the least electronegative atoms are the reactive metals, group IA on the left of the periodic table.

- We will come to see later that the electronegativity difference between atoms in compounds can be used to predict the type of bonding in compounds.

H 2.20																He n.a.
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne n.a.
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar n.a.
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	La 1.10	Hf 1.30	Ta 1.50	W 2.36	Re 1.90	Os 2.20	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.00	At 2.20	Rn n.a.
Fr 0.70	Ra 0.89	Ac 1.10	Rf n.a.	Db n.a.	Sg n.a.	Bh n.a.	Hs n.a.	Mt n.a.	Ds n.a.	Rg n.a.	Uub n.a.	—	Uuq n.a.	—	—	—	—

Summary of periodic properties