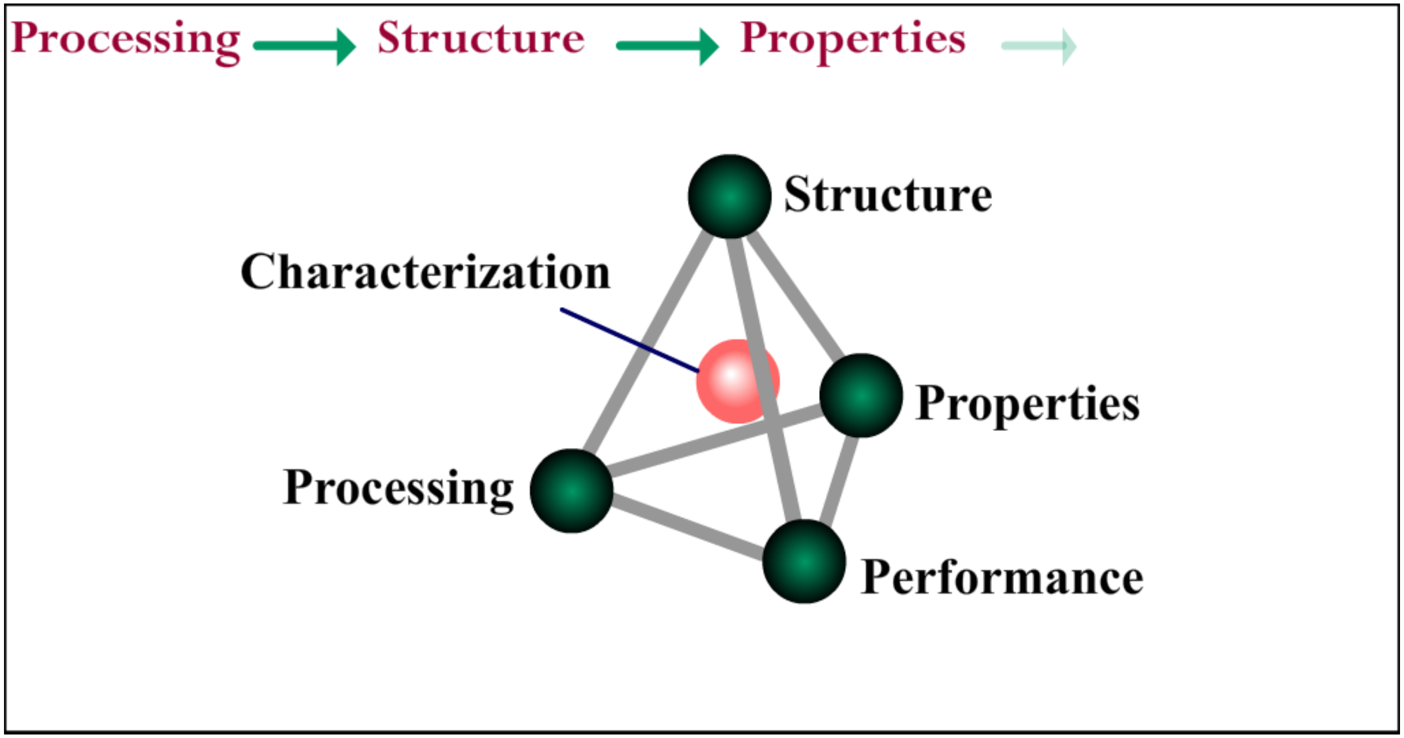
Materials Science

What is Materials Science??

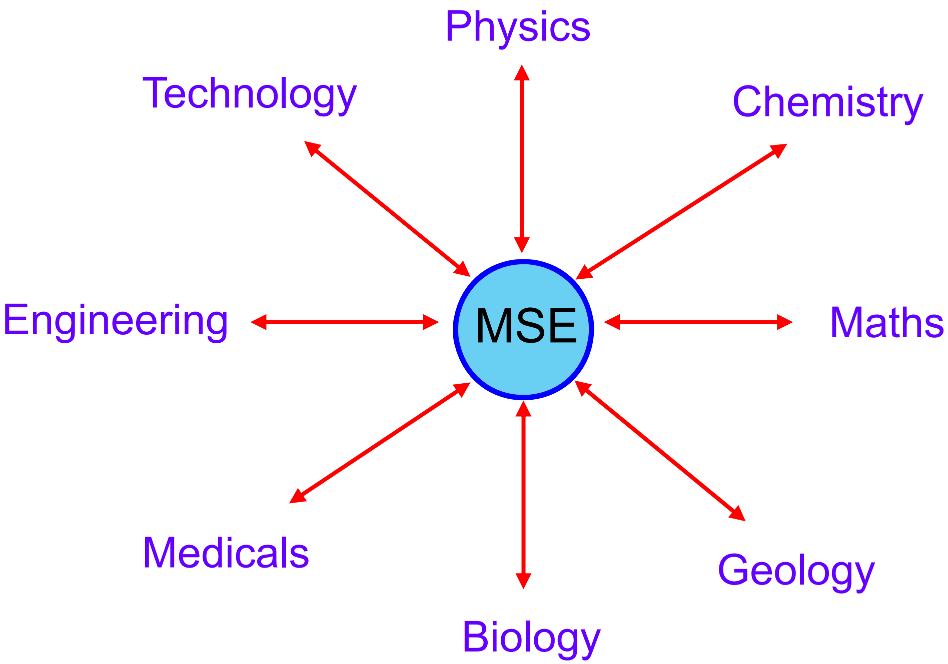


Material Science Tetrahedron

Material Science can be broadly defined as correlation between microstructure and properties.

The Materials Science Tetrahedron :-
Microstructure depends on the processing route while performance is dictated by properties.

Materials Science and Engineering (MSE)



Physics

Technology

Chemistry

Engineering

MSE

Maths

Medicals

Geology

Biology

Materials Science is an interdisciplinary area where many science and engineering streams merge together

Atomic structure

In order to understand the structure of materials and its correlation to property, we have to start form the basic element of matter – The Atom

- An atom consists of a nucleus composed of protons and neutrons and electrons which encircle the nucleus.
- Protons and electrons have same and opposite charge of 1.6 x 10^{-19} C.
- Atomic number (Z) = Number protons = number of electrons.
- Atomic mass (A) = proton mass + neutron mass.
- Isotopes are the same element having different atomic masses. Number of protons in isotopes remains same while number of neutrons varies.

Atomic structure

- Atomic mass unit (amu) = 1/12 mass of Carbon 12 (^{12}C)

- 1 mol of substance contains 6.023×10^{23} (Avogadro’s number) atoms or molecules.

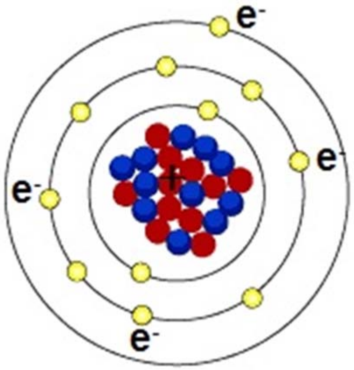
- Atomic weight = 1 amu/atom (or molecule) = 1 g/mol = Wt. of 6.023×10^{23} atoms or molecules.

- For example, atomic weight of copper is 63.54 amu/atom or 63.54 g/mole

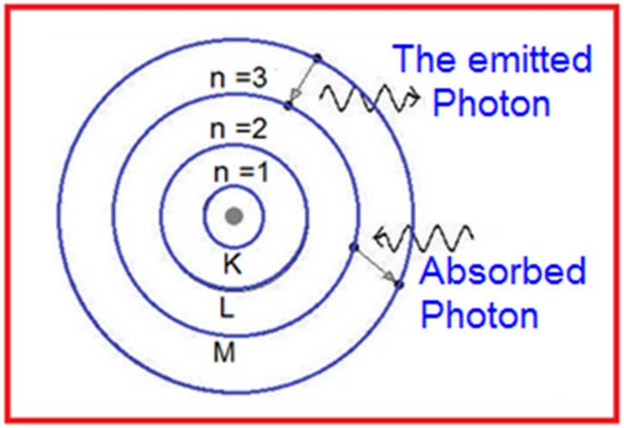
Atomic structure

The Bohr Model

(a)



(b)



- Electrons revolve around a positively charged nucleus in discrete orbits (K, L, M or n=1, 2, 3 respectively) with specific levels of energy.
- Electrons positions are fixed as such, however, an electron can jump to higher or lower energy level by absorption or emission of energy respectively as shown in Fig. (b)

Atomic structure

Limitations of the Bohr Model

Although the Bohr's model was the first and best model available at the time of its discovery, it had certain limitations and could not explain many phenomena involving electrons.

Heisenberg's uncertainty principle:
The position and momentum of an electron can not be determined simultaneously.

This also disapproves the hypothesis in the Bohr model that electrons revolve around certain circular orbits.

Wave-Mechanical Model

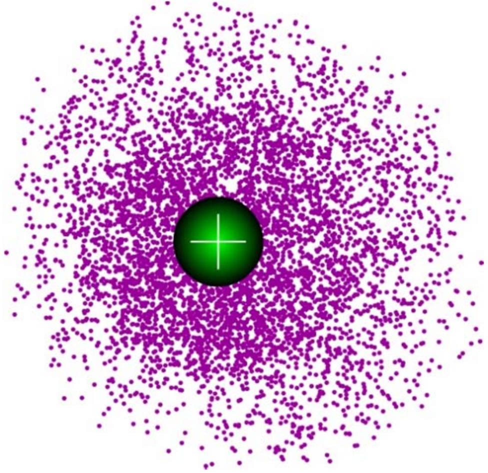
- The wave-mechanical or wave-particle model was proposed to address the limitations in the Bohr model.

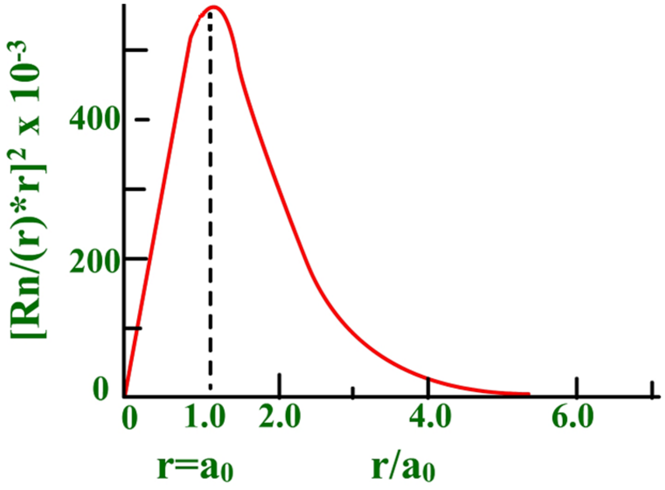
- The basic premise of this model is the wave-particle duality of electrons i.e. electrons are considered to have both wave-like and particle-like characteristics.

- The position of an electron is defined as the probability of finding it at different locations in an electron cloud around the nucleus i.e. position of an electron is described by a probability distribution instead of discrete orbits.

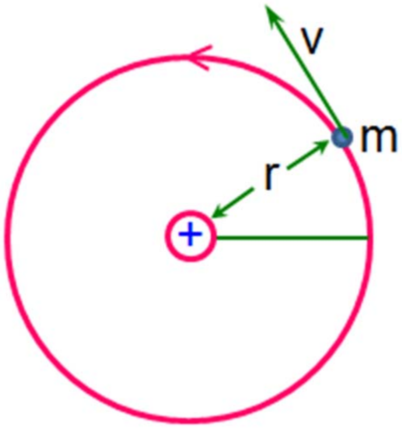
Wave-Mechanics Model

Probability distribution of electrons





Probability distribution vs. distance from nucleus



The Bohr radius, $r = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$

Probability of finding an electron is maximum at the Bohr radius

Quantum numbers

Four parameters or numbers called Quantum numbers are needed to describe the distribution and position of electrons in an atom.

The first three of them (n, ℓ, m_ℓ) describe the size, shape, and spatial orientation of the probability density distribution of electrons .

Principal quantum number, ***n***

It describes electron shells as shown in the Bohr model.

Values of n can be 1, 2, 3, 4 … corresponding to electron shells K, L, M, N …..

The value of ***n*** also determines the size or distance of the shells from the nucleus.

Number of electrons in a shell = $2n^2$.e.g. number of electrons in K shell (n =1)= 2. 1^2 = 2, L shell (n =2) 8 (2. 2^2) and so on

Quantum numbers

Azimuthal or Angular quantum number, ℓ

It signifies subshell or electron orbital – s, p, d, f and so on. ℓ can take values of from 0 to n-1. K shell, n = 1, one s orbital. L , n =2, two orbitals, s, p. M, n =3, three orbitals s, p, d. N, n =4, four orbitals s, p, d, f and so on.

The value of ℓ decides the shape of the orbital as shown in the figure below. s orbital ($\ell = 0$) – spherical, p ($\ell = 1$) – polar or dumbbell shaped, d ($\ell = 2$) – double-dumbbell shaped

$\ell = 0$ s $\ell = 1$ p $\ell = 2$ d

Quantum numbers

Magnetic quantum number, m_ℓ

Orbitals are associated with energy states. Magnetic quantum number determines the number of energy states in each orbital.

This number depends on the value of ℓ. m_ℓ Can take values from $-\ell$ to $+\ell$ e.g. $\ell = 1$ (p orbital) $m_\ell = -1, 0, +1$ (three states). Only one state for the s orbital ($\ell = 0$), as m_ℓ can take only one value (0). In general no. of states = $2\ell+1$

Orbital	s	p	d	f
No. of states	1	3	5	7

Quantum numbers

Spin quantum number, m_s

Each electron is associated with a spin moment. The fourth quantum number, m_s is related to this spin moment of electrons. It can have only two values, + ½ and – ½

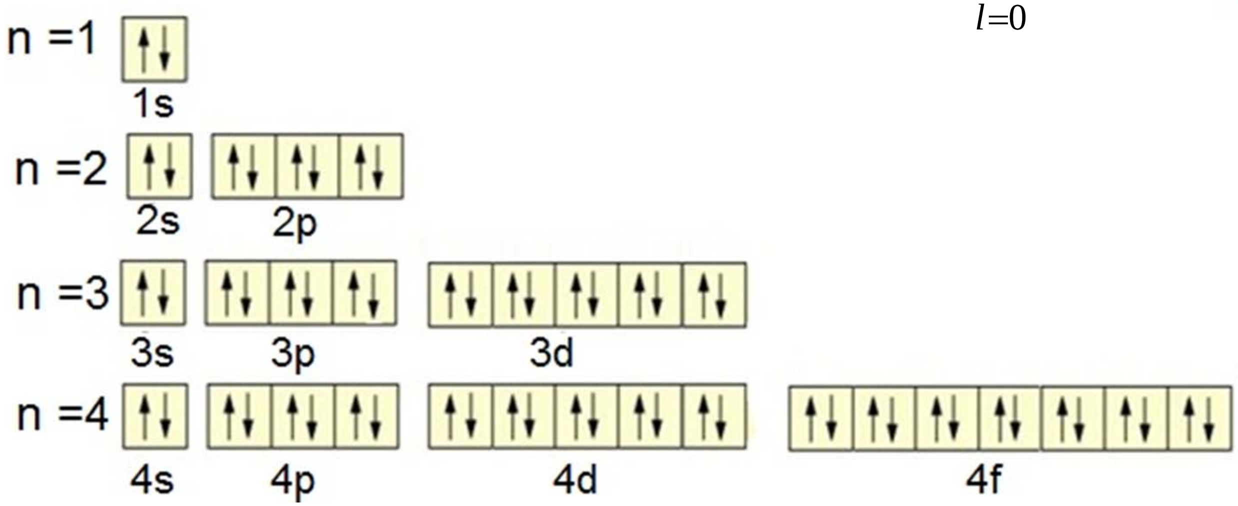
Pauli's exclusion principle:

It states that not more than two electrons having opposite spin can occupy the same energy state.

Based on this principle, number of electrons in different orbitals (s, p, d ….) can be obtained. For example, s orbital has only one energy state, so it can accommodate only two electrons having opposite spins.

Electron Configuration

The quantum mechanic principles as discussed before allow determination of electron configuration i.e. the manner in which electron states are occupied in a given atom.



$\sum_{l=0}^{n-1} 2(2l+1)$	Max no. of Electrons
n =1	2
n =2	8
n =3	18
n =4	32

Electron configuration based on quantum numbers. Total number of electrons in a shell is $2n^2$ or $\sum_{l=0}^{n-1} 2(2l+1)$

Electron Configuration

The manner or sequence of filling of electron orbitals is decided a by a set of two principles/rules:

1. Aufbau (German – meaning building up) principle

   It states that lower energy states will be filled up first.

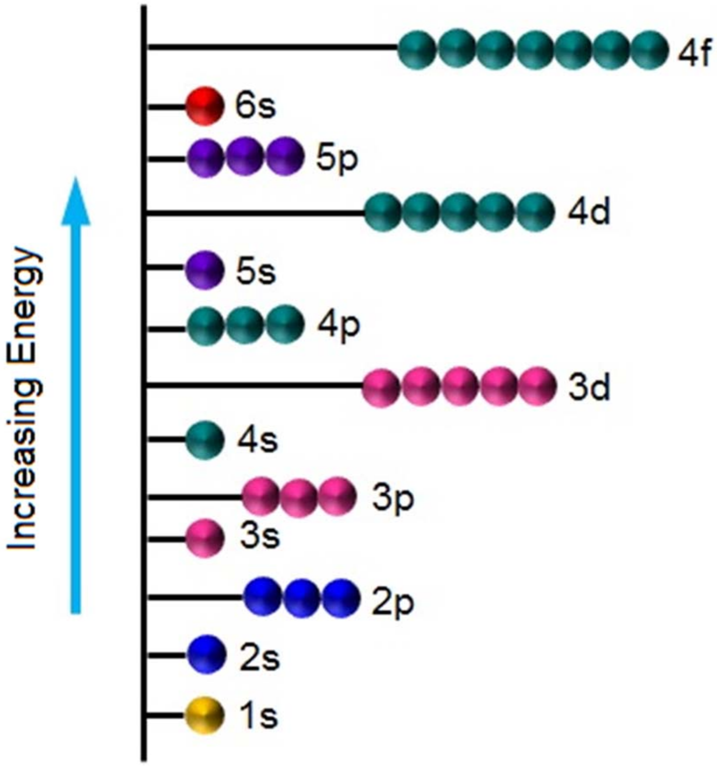
2. Madelung's rule:

➢Orbitals fill in the order of increasing $(n+\ell)$. 4s $(n+\ell = 4+0 = 4)$ will be filled before 3d $(n+\ell = 3+2 = 5)$ and 5s $(n+\ell = 5+0 = 5)$

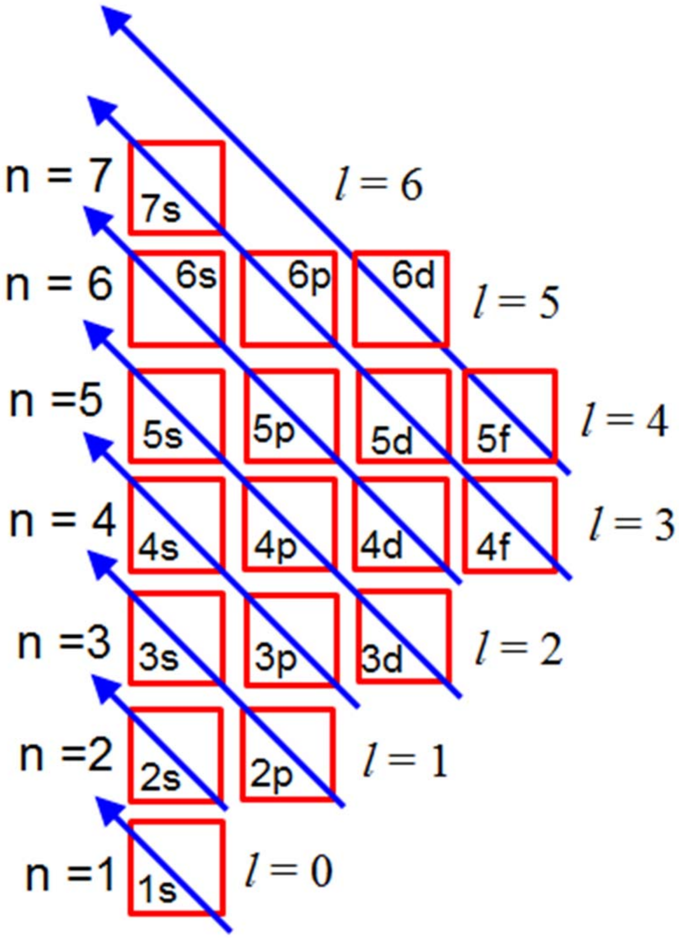
➢For orbital with same values of $(n+\ell)$, the one with lower n will be filled first. 3d will be filled before 4p

Electron Configuration

The Aufbau principle and Madelung rule



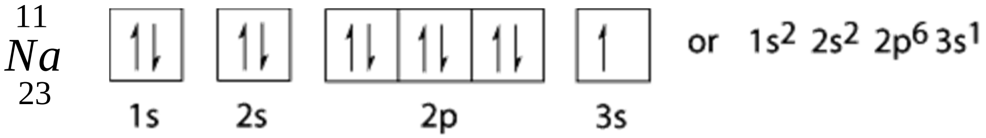
Aufbau principle

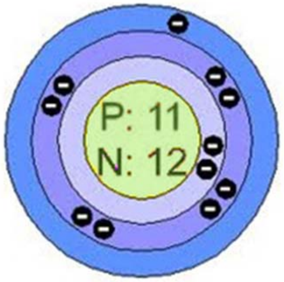


Madelung rule

Electron Configuration

Based on the foregoing discussion, it is now possible to find the electron configuration for a given atom. For example, Sodium, (Na_{23}^{11}) has 11 electrons – the configuration is shown in the first figure. The second picture shows the Bohr configuration.





Valence electrons

The electrons in the outer most shell are known as valence electrons. Na has one valence electron (the 3s electron).

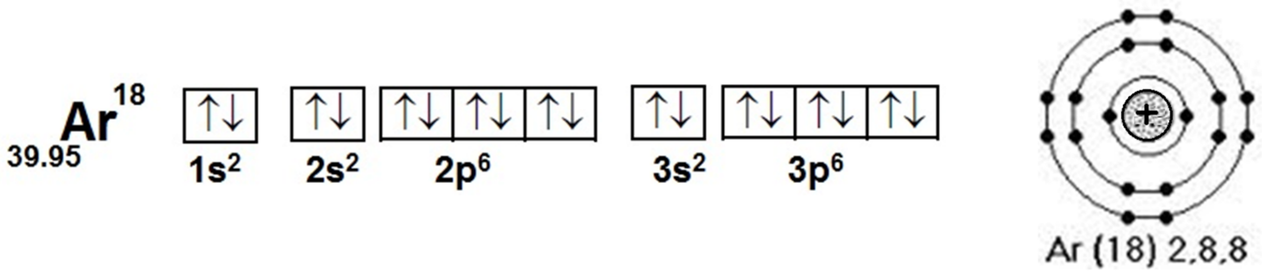
These electrons are responsible for chemical reaction and atomic bonding

Electron configuration of elements

Atomic No.	Symbol	Electron configuration	Atomic No.	Symbol	Electron configuration	Atomic No.	Symbol	Electron configuration
1	H	$1s^1$	21	Sc	[Ar] $4s^2 3d^1$	41	Nb	[Kr] $5s^1 4d^4$
2	He	$1s^2$	22	Ti	[Ar] $4s^2 3d^2$	42	Mo	[Kr] $5s^1 4d^5$
3	Li	[He] $2s^1$	23	V	[Ar] $4s^2 3d^3$	43	Tc	[Kr] $5s^2 4d^5$
4	Be	[He] $2s^2$	24	Cr	[Ar] $4s^1 3d^5$	44	Ru	[Kr] $5s^1 4d^7$
5	B	[He] $2s^2 2p^1$	25	Mn	[Ar] $4s^2 3d^5$	45	Rh	[Kr] $5s^1 4d^8$
6	C	[He] $2s^2 2p^2$	26	Fe	[Ar] $4s^2 3d^6$	46	Pd	[Kr] $4d^{10}$
7	N	[He] $2s^2 2p^3$	27	Co	[Ar] $4s^2 3d^7$	47	Ag	[Kr] $5s^1 4d^{10}$
8	O	[He] $2s^2 2p^4$	28	Ni	[Ar] $4s^2 3d^8$	48	Cd	[Kr] $5s^2 4d^{10}$
9	F	[He] $2s^2 2p^5$	29	Cu	[Ar] $4s^1 3d^{10}$	49	In	[Kr] $5s^2 4d^{10} 5p^1$
10	Ne	[He] $2s^2 2p^6$	30	Zn	[Ar] $4s^2 3d^{10}$	50	Sn	[Kr] $5s^2 4d^{10} 5p^2$
11	Na	[Ne] $3s^1$	31	Ga	[Ar] $4s^2 3d^{10} 4p^1$	51	Sb	[Kr] $5s^2 4d^{10} 5p^3$
12	Mg	[Ne] $3s^2$	32	Ge	[Ar] $4s^2 3d^{10} 4p^2$	52	Te	[Kr] $5s^2 4d^{10} 5p^4$
13	Al	[Ne] $3s^2 3p^1$	33	As	[Ar] $4s^2 3d^{10} 4p^3$	53	I	[Kr] $5s^2 4d^{10} 5p^5$
14	Si	[Ne] $3s^2 3p^2$	34	Se	[Ar] $4s^2 3d^{10} 4p^4$	54	Xe	[Kr] $5s^2 4d^{10} 5p^6$
15	P	[Ne] $3s^2 3p^3$	35	Br	[Ar] $4s^2 3d^{10} 4p^5$	55	Cs	[Xe] $6s^1$
16	S	[Ne] $3s^2 3p^4$	36	Kr	[Ar] $4s^2 3d^{10} 4p^6$	56	Ba	[Xe] $6s^2$
17	Cl	[Ne] $3s^2 3p^5$	37	Rb	[Kr] $5s^1$	57	La	[Xe] $6s^2 5d^1$
18	Ar	[Ne] $3s^2 3p^6$	38	Sr	[Kr] $5s^2$	58	Ce	[Xe] $6s^2 4f^1 5d^1$
19	K	[Ar] $4s^1$	39	Y	[Kr] $5s^2 4d^1$	59	Pr	[Xe] $6s^2 4f^3$
20	Ca	[Ar] $4s^2$	40	Zr	[Kr] $5s^2 4d^2$	60	Nd	[Xe] $6s^2 4f^4$

Stable Configuration

Look at the electron configuration of inert gases (He, Ne, Ar, Kr, Xe) in the previous table. Their valence electron cell is completely filled unlike any other element.



Argon (Ar) for example has 18 electrons and 3s and 3p orbitals of its valence shell are completely filled.

This is known as stable configuration. Since it is the lowest energy configuration, the valence electrons do not take part in any chemical reaction and hence, the inertness.

See the structure-property correlation here

Electron Configuration

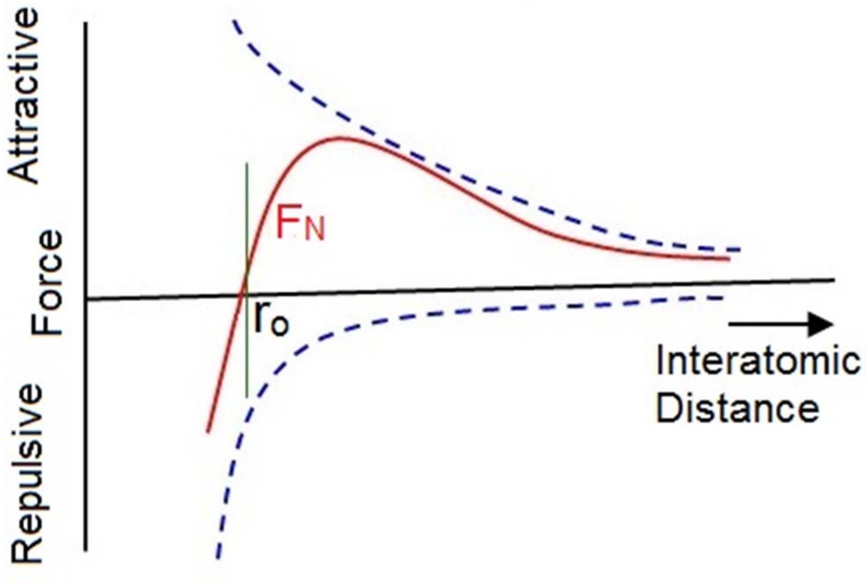
- Note that the configuration of higher atomic number elements can be expressed by the previous inert element configuration (see the previous table)

- It is the tendency of every element to attain the lowest energy stable configuration that forms the basis of chemical reactions and atomic bonding

Atomic Bonding

Atomic interaction

(a)



- When two neutral atoms are brought close to each other, they experience attractive and or repulsive force
- Attractive force is due to electrostatic attraction between electrons of one atom and the nucleus of the other.

Atomic interaction

- Repulsive force arises due to repulsion between electrons and nuclei of the atoms.

- The net force, F_N (Fig. a), acting on the atoms is the summation of attractive and repulsive forces.

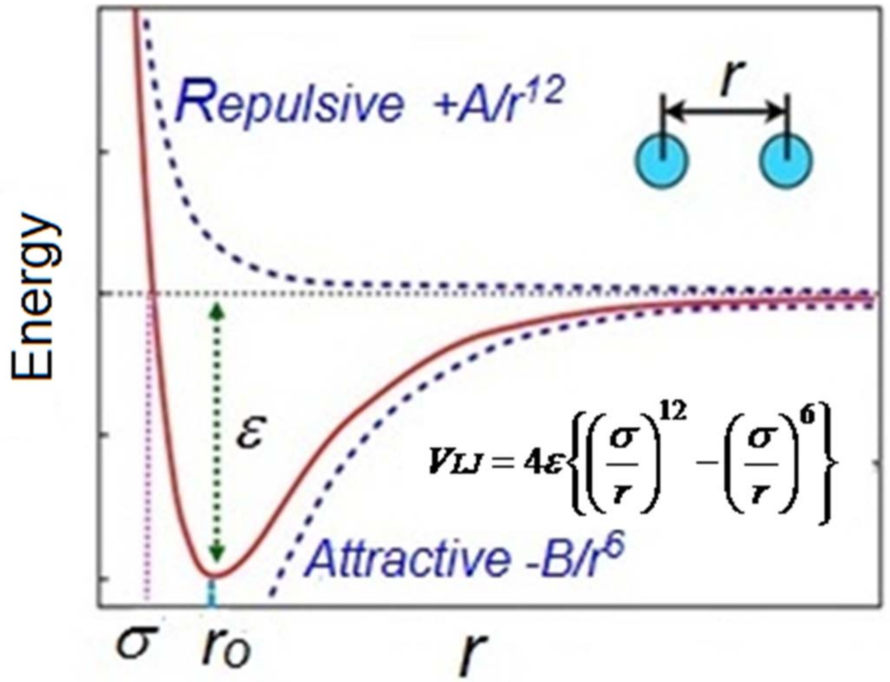
- The distance, at which the attraction and repulsion forces are equal and the net force is zero, is the equilibrium interatomic distance, r_o. The atoms have lowest energy at this position.

- Attraction is predominant above r_o and repulsion is dominant below r_o (see Fig. a).

Atomic interaction

Lennard-Jones potential

(b)



The interaction energy between the pair of atoms is given by the Lennard-Jones potential, V_r or V_{LJ}

$$V_{LJ} = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

Atomic interaction

- σ is the distance at which the interaction energy is zero. ε is the depth of the potential well (see Fig. b) and is a measure of the bonding energy between two atoms.

- *L-J* potential can be also expressed in the simplified form as $V_{LJ} = A/r^{12} - B/r^{6}$ and hence, is also known as 6-12 potential.

- A/r^{12} is predominant at short distances and hence, represents the short-range repulsive potential due to overlap of electron orbitals and $-B/r^{6}$ is dominant at longer distance and hence, is the long range attractive potential.

Atomic Bonding

- The mechanisms of bonding between the atoms are based on the foregoing discussion on electrostatic inter-atomic interaction.

- The types of bond and bond strength are determined by the electronic structures of the atoms involved.

- The valence electrons take part in bonding. The atoms involved acquire, loose or share valence electrons to achieve the lowest energy or stable configuration of noble gases.

- Atomic bonding can be broadly classified as i) primary bonding ii) secondary bonding

Atomic Bonding

Primary Bonds

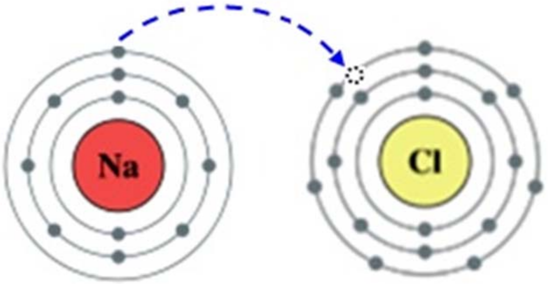
Three types primary bonds are found in solids

- Ionic
- Covalent
- Metallic

Majority of the engineering materials consist of one of these bonds. Many properties of the materials depend on the specific kind of bond and the bond energy.

Ionic Bond

Ionic bonds are generally found in compounds composed of metal and non-metal and arise out of electrostatic attraction between oppositely charged atoms (ions).

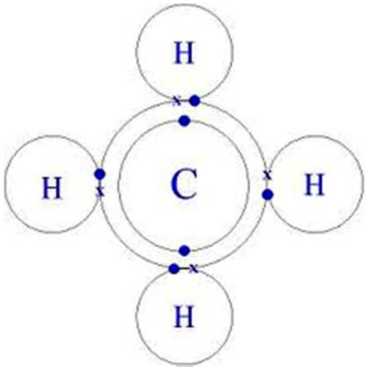


Number of electron in outer shell is 1 in Na and 7 in Cl . Therefore, Na will tend to reject one electron to get stable configuration of Ne and Cl will accept one electron to obtain Ar configuration. The columbic attraction between Na^+ and Cl^- ions thus formed will make an ionic bond to produce NaCl. Some other examples are CaF_2, CsCl , MgO, Al_2O_3.

Covalent Bond

In this type of bonding, atoms share their valence electrons to get a stable configuration.

❖Methane (CH_4): Four hydrogen atoms share their valence electrons with one carbon atom and the carbon atom in turn shares one valence electron with each of the four hydrogen atoms. In the process both H and C atoms get stable configuration and form a covalent bond.

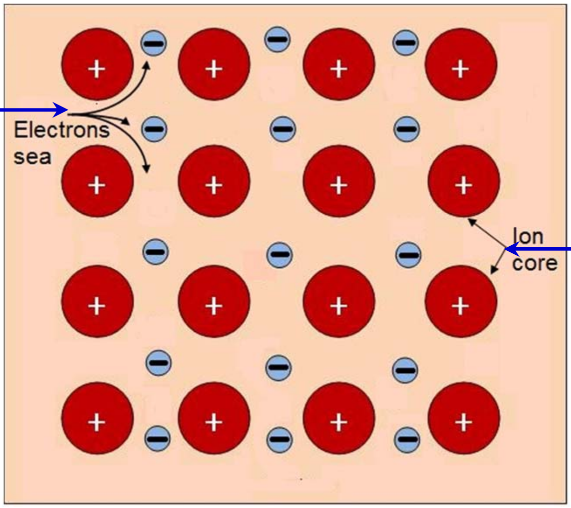


Covalent bond

- Covalent bonds are formed between atoms of similar electronegativity.
- C atoms in diamond are covalently bonded to each other.
- Si also has valency of four and forms SiC through covalent bonding with C atoms.

Metallic Bond

In metals the valence electrons are not really bound to one particular atom, instead they form a sea or cloud of valence electrons which are shared by all the atoms. The remaining electrons and the nuclei form what is called the ion core which is positively charged. The metallic bond arises out of the columbic attraction between these two oppositely charged species – the electron cloud and the ion cores.



Electrons sea

Ion core

Characteristics of primary bonds

Structure-property correlation

- Ionic and covalent bonds posses high bond energy –

450 – 1000 kJ/mole

- High bond strength in ionic and covalent solids results in

high melting point, high strength and hardness. e.g. diamond

- As the electrons are tightly bound to the atoms they are generally poor conductors of heat and electricity
- Are brittle in nature
- Most of the ceramics consist of covalent (SiC) or ionic bonds (Al_2O_3) or a mix of both and hence, exhibit all the properties described above.

Structure-property correlation

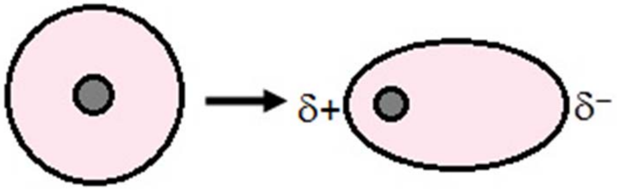
- Metallic bonds on the other hand provide good thermal and electrical conductivities as the valence electrons are free to move.
- The metallic bond energy is 68 kJ/mol (Hg) on the lower side and 850 kJ/mol (W, tungsten) on the higher side.
- Bond strength increases with atomic number as more electrons are available to form the bonds with the ion cores. As a result melting point, hardness and strength increases with atomic number.
- Metals are ductile as the free moving electrons provides agility to the bonds and allows plastic deformation.

Secondary Bonds

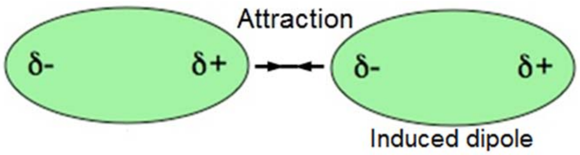
Van der Waals bonding

- Van der Waals bonding between molecules or atoms arise due to weak attraction forces between dipoles

- The natural oscillation of atoms leading to momentary break down of charge symmetry can generate temporary dipoles

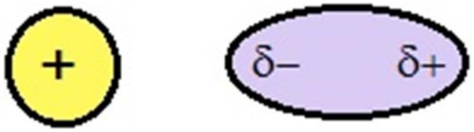


- Dipoles can induce dipoles and attraction between opposites ends of the dipoles leads to weak bonding

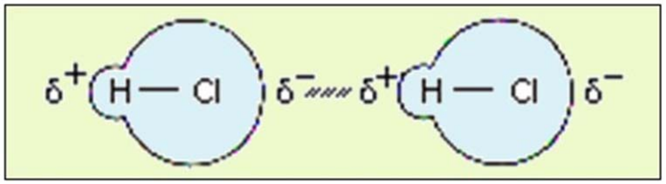


Van der Waals Bonding

- An ion can also induce a dipole



- Some molecules like HCl have permanent dipoles due to asymmetrical arrangement of +ve and –ve charges.

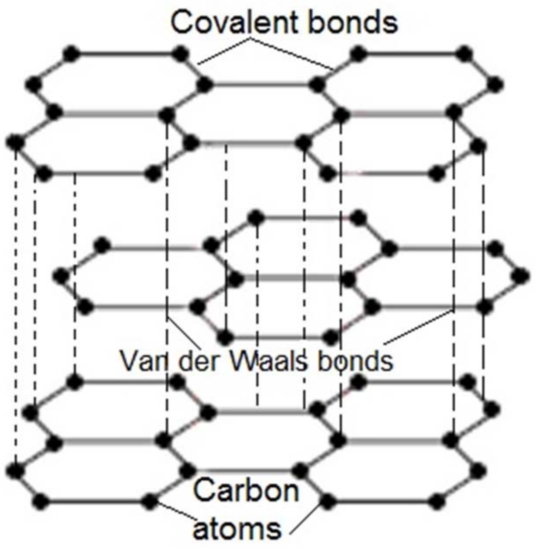


- Van der Waals bonding is much weaker compared to primary bonds. Bond energy lies in the range of 2 – 10 kJ/mol.

- Molecules in liquid and gas are held by weak Van der Waals forces

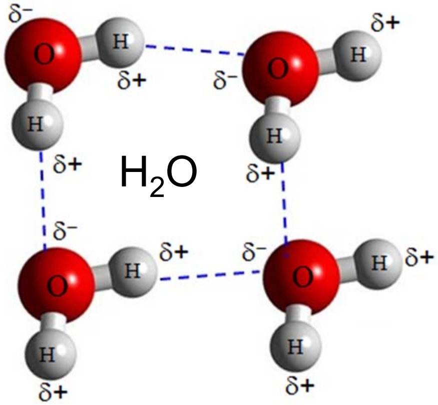
Van der Waals bonds

- The atomic layers in graphite are held together by weak van der Waals bonds. Therefore, the layers can move easily over each other and this imparts the lubricating property graphite is known for.



Hydrogen bonding

- ❖Hydrogen bond is a type of secondary bond found in molecules containing hydrogen as a constituent.
- ❖The bond originates from electrostatic interaction between hydrogen and another atom of high electronegativity such as fluorine or oxygen.
- ❖The strength of hydrogen bonds is in the range of 10 - 50 kJ/mol.
- ❖Water molecules, for example, are connected by hydrogen bonds (dashed lines in the picture).



Evaluation and Examples

At this point one should be able to

- Understand two quantum mechanics models of atomic structure and their fundamental differences.
- Understand quantum numbers and their significance.
- Find out electronic configuration of a given element.
- Understand atomic interactions and different types of atomic bonding.
- Explain some properties based on atomic bonding

Some examples are given next for further assistance

Examples

Example 1. How many Fe atoms are there in 1 g of Fe?

Solution: Atomic mass of Fe = 55.85 g/mol.
1 mol of substance has 6.023×10^{23} atoms (Avogadro's number).
Therefore, 1 mol or 55.85 g of Fe has 6.023×10^{23} atoms.
Hence, 1 g Fe has $(6.023 \times 10^{23}) \div 55.85 = 10.78 \times 10^{21}$ atoms

Example 2. Find the electronic configuration of Lead (Pb_{82})

Solution: Atomic number of Pb = 82. No. of electrons is 82.
The noble gas closest to Pb is Xe (54 – $[Kr]4d^{10}5s^{2}5p^{6}$).
Therefore electronic configuration of Pb can be expressed as
$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^{2}\ 6p^{2}$

Examples

Example 3: What is the attractive force between Na+ and Cl^- ions just touching each other?

Solution:

$F_{attractive} = -(Z_1Z_2e^2)/4\pi\varepsilon_o r_o$. Z_1 and Z_2 are valency of the ions (+1 for Na and -1 for Cl), r_o is the interatomic separation, e is the charge of an electron (1.60×10^{-19} C) and ε_o is the permittivity of vacuum (8.85×10^{-12} F/m)

As the ions just touch each other, r_o is the sum of the radii of the ions.

Ionic radius of Na and Cl are 0.095 nm and 0.181 nm respectively.

Substituting these values in the equation will yield

$F_{attractive} = 3.02 \times 10^{-9}$ N

Quiz

1. What is Materials science? What is material science tetrahedron?
2. What is atomic mass unit (amu)?
3. Briefly describe the Bohr atomic model.
4. Find out the Bohr radius for an hydrogen atom (see slide #8).
5. What is wave-particle duality? Briefly explain the wave mechanical model of atomic structure.
6. What is Heisenberg's uncertainty principle?
7. What is Paulis exclusion principle
8. What are Aufbau and Madelung rules?
9. Show that energy of an electron in hydrogen atom $E = 2\pi^2 me^4/n^2h^2 = -13.6/n^2$ eV

Clue: Refer to slide #8, equate centrifugal force of the electron, mv^2/r to Coulomb force k_eZe^2/r^2 ($k_e = 1/4\pi\varepsilon_o$), Energy is the sum of kinetic energy and the attractive energy.

Quiz

10. What is stable electron configuration?
11. Why are noble gases inert?
12. What is Lennard-Jones potential?
13. Briefly explain the primary bonds in solids.
14. How do secondary bonds form? What is hydrogen bond?
15. Why is graphite lubricating?
16. Why are ceramics hard and brittle? Why are they not conductive?
17. Why is boiling point of methane (CH_4) lower than water?
18. How many atoms are there in 1 g of copper?
19. Write the electron configuration of tungsten (74)
20. Why is Tungsten (74) much stronger than Aluminium (13) though both are metallic?
21. Calculate the attractive force between two K+ and Br- ions that just touch each other. Atomic radii of K+ and Br- are 0.133 and 0.196 nm respectively.

Quiz

22. If the attractive force between a pair of Cs+ and I^- ions is 2.83 x 10^{-9} N and the ionic radius of Cs+ is 0.165 nm, what is the ionic radius of I^- ion?

23. Calculate the attractive force between a pair of Ba^{2+} and S^{2-} ions which just touch each other. Ionic radius of Ba and S are 0.143 nm and 0.174 nm respectively. $\varepsilon_o = 8.85 \times 10^{-12}\ C^2/N.m^2$

24. Does the size of Na and Cl atoms remain same when they react to from NaCl? Give reasons for your answer.

25.If energy of an electron, $E = - 13.6/n^2$ eV, find out the energy, wavelength and frequency of the photon emitted for a jump from M to L shell. $h = 4.14 \times 10^{-15}$ eV.s

References

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Key words: Materials tetrahedron; Atomic structure; Bohr model; Quantum numbers; Atomic bonding; Ionic, Covalent, Metallic bonding; Van der Waals bonds