Department of Civil Engineering
IIT Madras

Review of Atomic Bonding

Modern Construction Materials – Lecture 2
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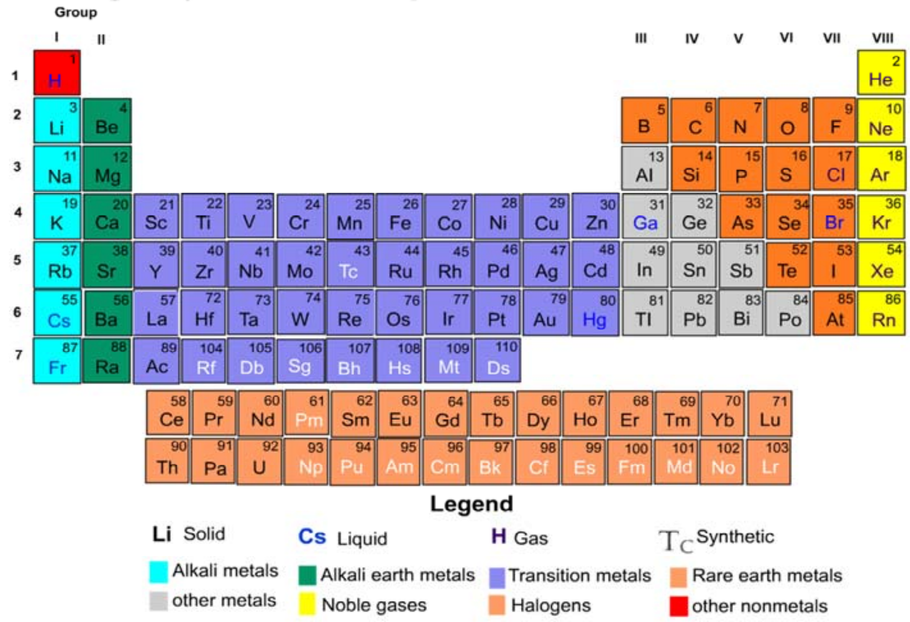
IIT Madras

Elements

Mendeleyev (or Mendeléef) Periodic Table

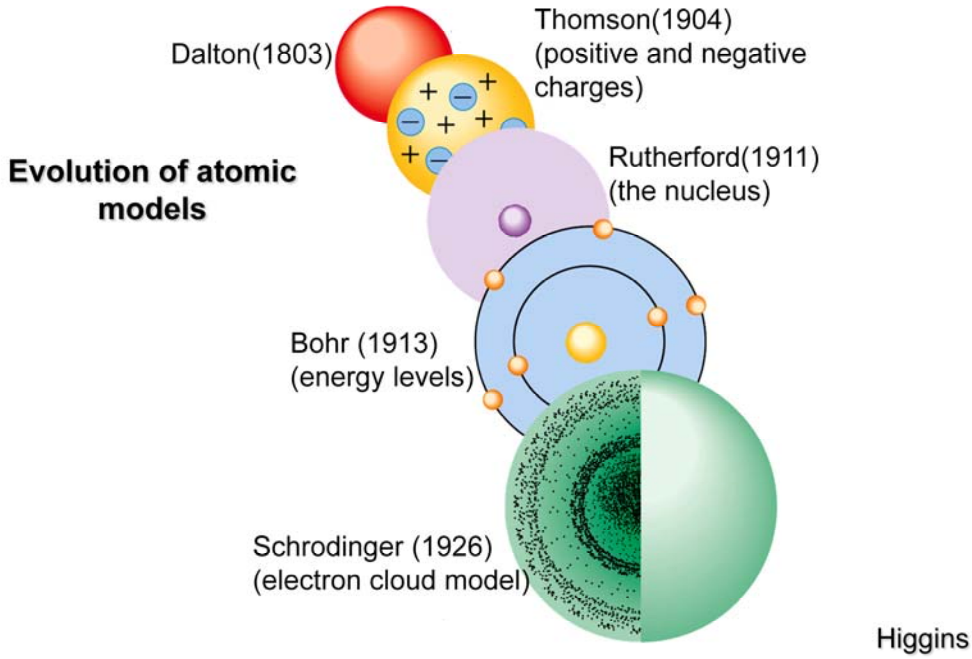


Elements

Mendeleyev Periodic Table

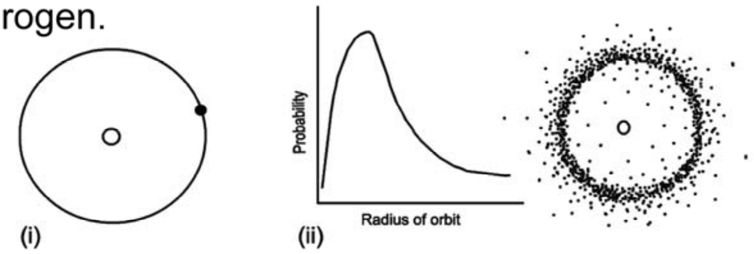
- A way of presenting all the elements so as to show their similarities and differences.
- The elements are arranged in increasing order of the atomic number (from left to right).
- The horizontal rows are called periods and the vertical columns are called groups.
- The elements of a group have a similar electronic configuration. The number of electrons in the outer shell is the same as the group number.

Elements


Evolution of atomic models
Dalton(1803)
Thomson(1904)
(positive and negative charges)
Rutherford(1911)
(the nucleus)
Bohr (1913)
(energy levels)
Schrodinger (1926)
(electron cloud model)
Higgins

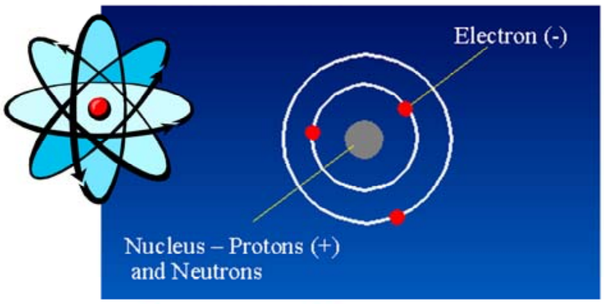
Elements

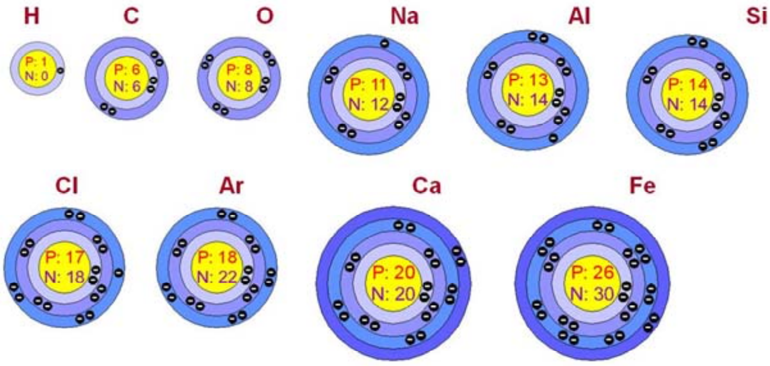
- The Bohr model, though still of considerable use, has been modified. Instead of definite *orbits*, the term *orbital* is used to represent the distribution of the electron with the space occupied by the atom.
- In the modern idea of the atom, the electron, instead of having a fixed orbit, is indicated by a probability of it occupying any location. This is illustrated below for hydrogen.



Elements

Electronic Configuration
(Simplified Bohr model)





Elements

Electronic Configuration

- The electrons in the outermost shell are responsible for bonding with other atoms, and are called *valence* electrons.
- The atomic structure is stable when the outermost shell contains eight electrons (*octet configuration*).
- The number of electrons in the outermost shell determines the *valency* (i.e., number of bonds which can be formed with other atoms). Valency is the number of valence electrons to be lost or gained to reach the octet configuration.

Illston & Domone

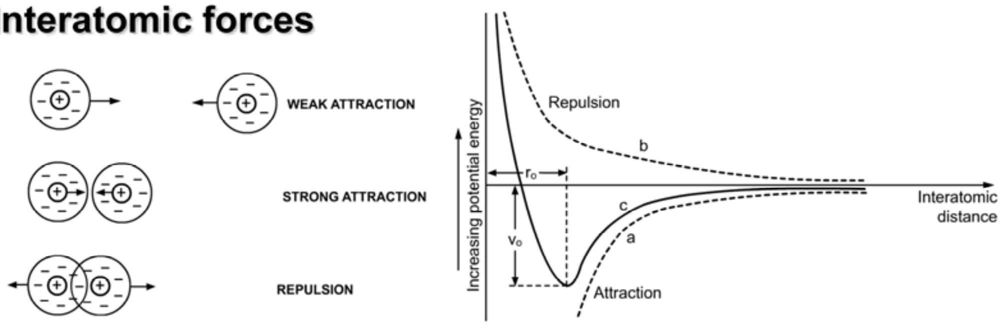
Elements

Electronic Configuration

H																	He
1																	2
Li	Be											B	C	N	O	F	Ne
2,1	2,2											2,3	2,4	2,5	2,6	2,7	2,8
Na	Mg											Al	Si	P	S	Cl	Ar
2,8,1	2,8,2											2,8,3	2,8,4	2,8,5	2,8,6	2,8,7	2,8,8
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
2,8,8,1	2,8,8,2	2,8,9,2	2,8,10,2	2,8,11,2	2,8,13,1	2,8,13,2	2,8,14,2	2,8,15,2	2,8,16,2	2,8,18,1	2,8,18,2	2,8,18,3	2,8,18,4	2,8,18,5	2,8,18,6	2,8,18,7	2,8,18,8
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
2,8,18, 8,1	2,8,18, 8,2	2,8,18, 9,2	2,8,18 10,2	2,8,18 12,1	2,8,18 13,1	2,8,18 14,1	2,8,18 15,1	2,8,18 16,1	2,8,18 18,0	2,8,18 18,1	2,8,18 18,2	2,8,18 18,3	2,8,18 18,4	2,8,18 18,5	2,8,18 18,6	2,8,18 18,7	2,8,18 18,8
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
2,8,18, 18,8,1	2,8,18 18,8,2		2,8,18 32,10,2	2,8,18 32,11,2	2,8,18 32,12,2	2,8,18 32,13,2	2,8,18 32,14,2	2,8,18 32,15,2	2,8,18 32,17,1	2,8,18 32,18,1	2,8,18 32,18,2	2,8,18 32,18,3	2,8,18 32,18,4	2,8,18 32,18,5	2,8,18 32,18,6	2,8,18 32,18,7	2,8,18 32,18,8

Interaction of Atoms

Interatomic forces



- When atoms are far from each other, there is a weak attraction between them. The attractive force (a) increases as the interatomic distance decreases.
- At close range, a repulsive force (b) builds up and ultimately balances the attractive force.

Higgins

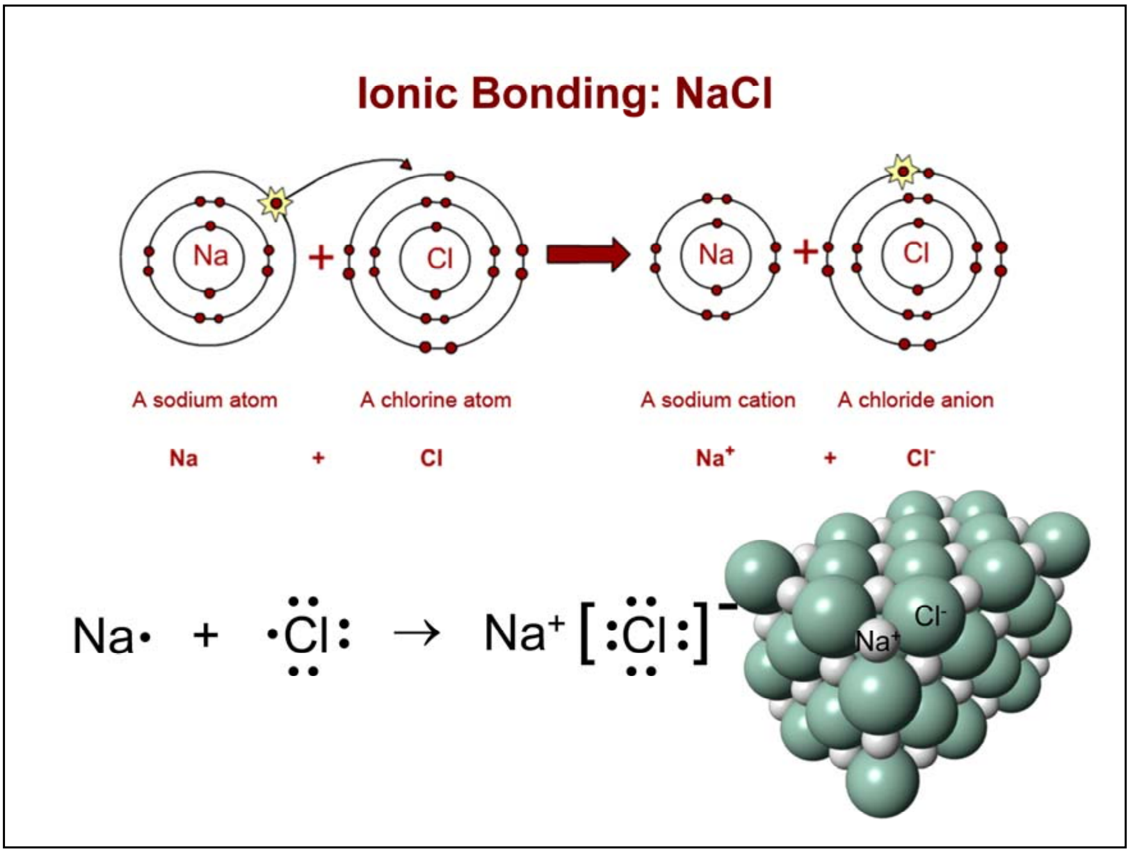
Interatomic Bonds

Primary Bonding Forces

- Ionic
- Covalent
- Metallic

Secondary Bonding Forces

- Van der Waals
- Hydrogen bonding


Ionic Bonding: NaCl
Na
Cl
Na
Cl
A sodium atom
A chlorine atom
A sodium cation
A chloride anion
Na + Cl
Na+ + Cl-
Na• + •Cl: → Na+ [:Cl:]-
Cl-
Na+

Ionic Bonding: NaCl

- Sodium has 1 valence electron (valency = +1) and chlorine has 7 valence electrons (valency = -1). By the transfer of 1 electron from Na to Cl, both attain the octet configuration.
- However, the electrical neutrality of the atoms is disturbed, and Na becomes positively charged and Cl becomes negatively charged *ions* (Na^+ & Cl^-).
- The overall neutrality of the material is maintained.

Ionic (or Electrovalent) Bonding

- The atom can attain the octet configuration by losing or gaining electrons. An ionic bond is formed when all the bonded atoms realise their octet configurations by donating/borrowing valence electrons. (Can only occur between atoms of different elements.)
- The atoms are attracted to each other by electrostatic forces.
- The strength of the bond between atoms A and B is proportional to $e_A e_B / r$, where e_A and e_B are the charges on the atoms, and r is the interatomic separation.

Illston & Domone

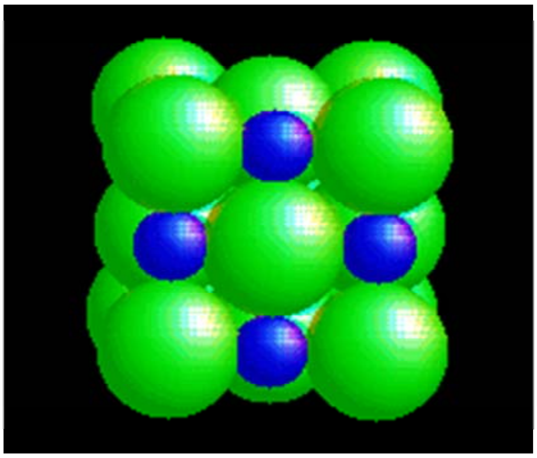
Ionic Bonding

- Ionic bonds are strong; the strength increases when two or more electrons are transferred.
- The strength of the ionic bond is reflected in properties such as the melting point.
- The melting point of NaCl is 801°C (1 electron transfer), that of MgO is 2640°C (2 electron transfer) and that of ZrC is 3500°C (4 electron transfer).

Ionic Bonding

The ionic bond is non-directional; i.e., the ions are arranged symmetrically.

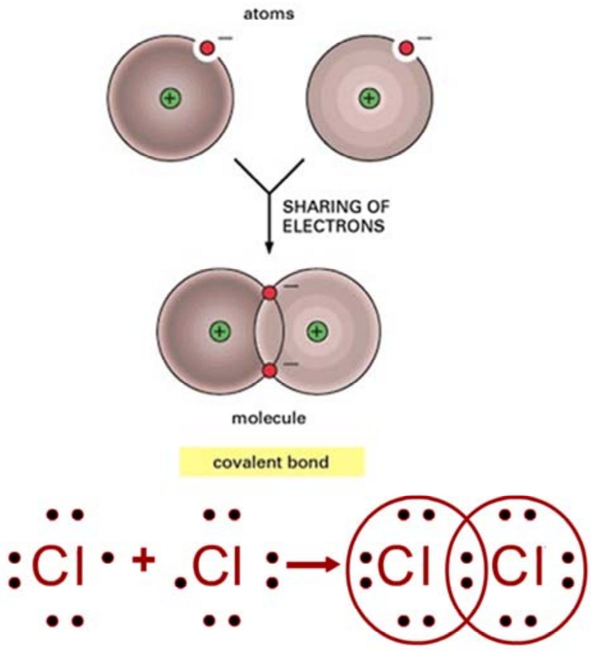
Face-centred-cubic structure

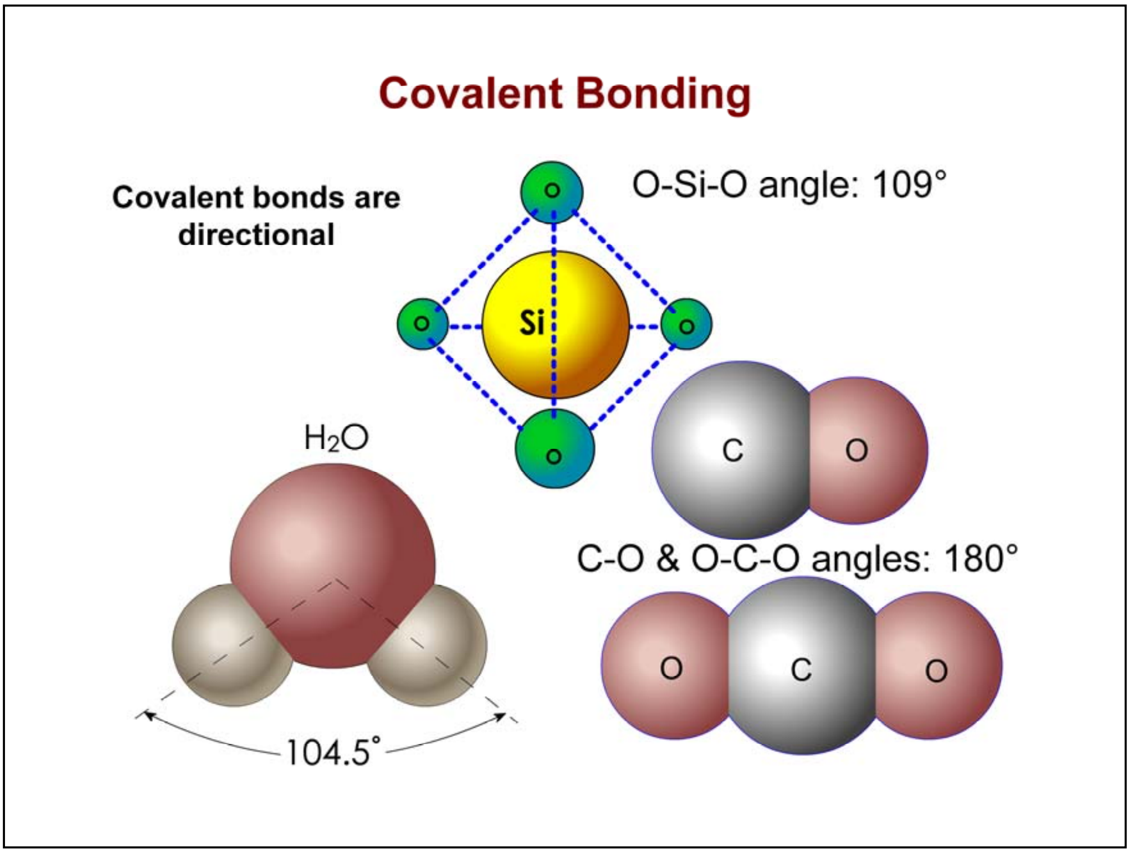


Covalent Bonding

- Where atoms are of the electron acceptor type (i.e., -ve valency or with close to 8 valence electrons), octet structures can be attained by the sharing of 2 or more valence electrons between the atoms.
- This the basic mechanism of aggregation among elements of Groups IV, V and VI.
- The covalent bonding obeys the (8-*N*) rule, where *N* is the number of valence electrons. The number of nearest neighbours to each atom is 8-*N*.

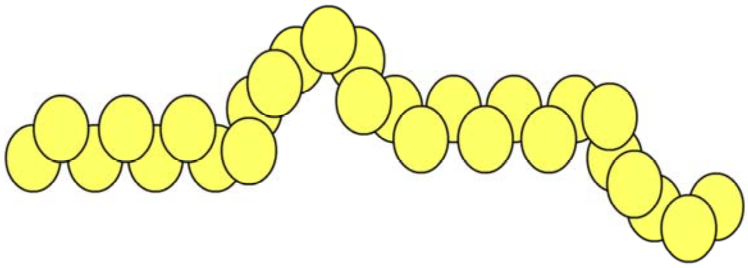
Covalent Bonding




Covalent Bonding
Covalent bonds are directional
O-Si-O angle: 109°
O
Si
O
O
O
H2O
C
O
C-O & O-C-O angles: 180°
O
C
O
104.5°

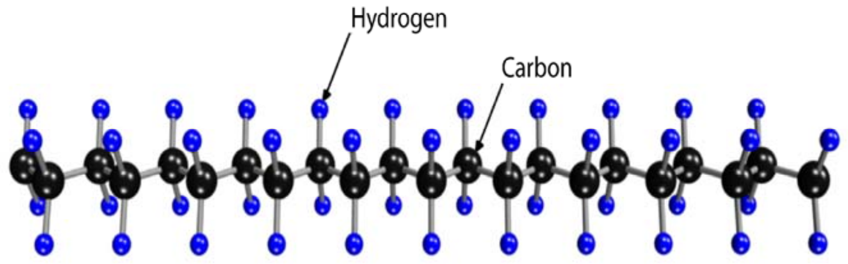
Covalent Bonding

Thus, chlorine (*N*=7) has only one neighbour; sulphur (*N*=6) occurs in long chains; bismuth (*N*=5) occurs in long sheets; and with carbon (*N*=4) a three-dimensional network can occur, as in diamond.

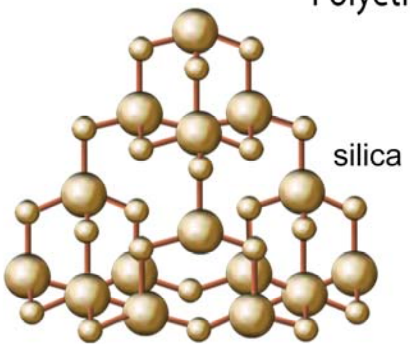


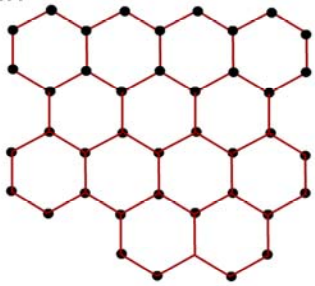
Part of a Molecule of Plastic Sulphur

Covalent Bonding



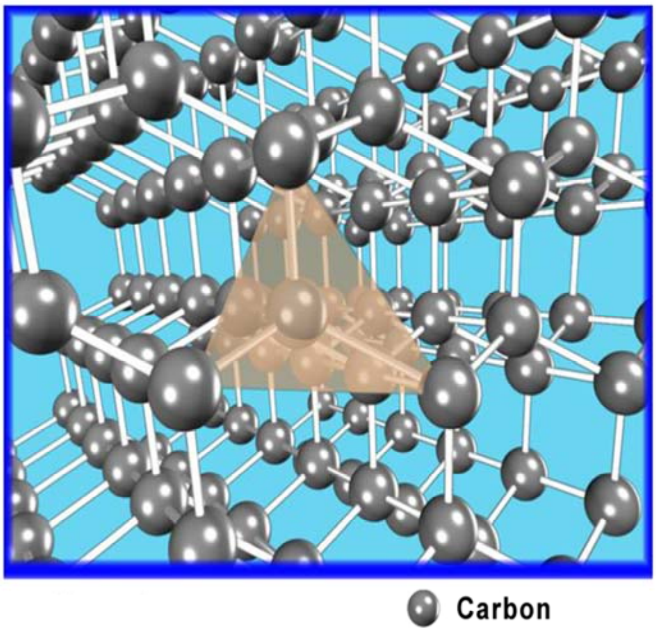
Polyethylene Chain





One layer of graphite

Covalent Bonding



Diamond

Covalent Bonding

- The covalent bond is saturated by the individual atoms participating in it.
- In chlorine, there is no extension of the covalent bonding beyond the molecule. Similarly, in the chains of sulphur and sheets of bismuth, there is no bond between chains and sheets.
- Materials with covalent bonds do not have a three-dimensional structure, with the exception of diamond & silica.
- Generally, covalent elements have poor strength, even though the covalent bond is strong (as seen in diamond). The chains coil in spirals leading to high elasticity in some cases (e.g., rubber).

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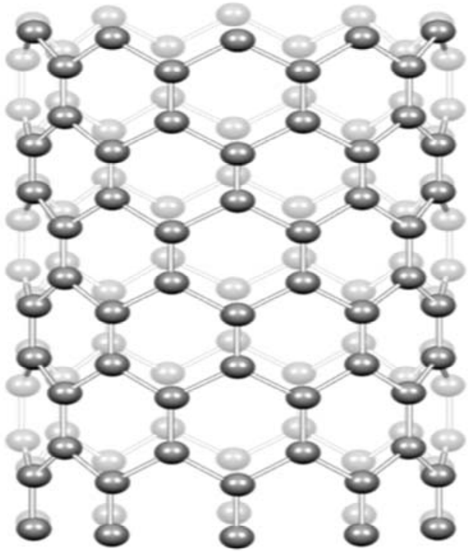
Covalent Bonding

Carbon nanotubes

Nanotubes have carbon atoms in continuous hexagon arrangements rolled into tube-like structures that form tiny fibers 10 to 12 times stronger than steel.

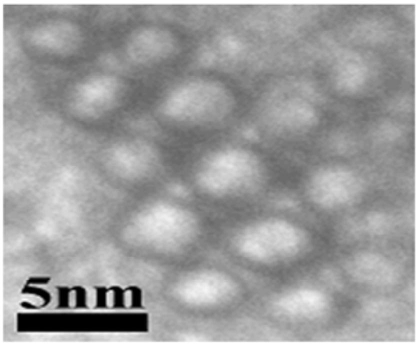


Covalent Bonding

Nanotubes having strands narrower than a human hair and 10 times stronger than steel were first prepared in 1997.

Uses may include cables, sports equipment, fabrics for bulletproof vests, and low-friction bearings for micromachines.

nanotube bundle



Metallic Bonding

- Metallic atoms have few valence electrons (i.e., elements of Groups I, II and III), and cannot bond with themselves covalently.
- In a metallic crystal, the valence electrons are detached or delocalised from their atoms and move freely between the positive ions.
- The positive ions are arranged regularly in a crystal lattice, and the electrostatic attraction between the positive ions and the free negative electrons provides the cohesive strength of the metal.

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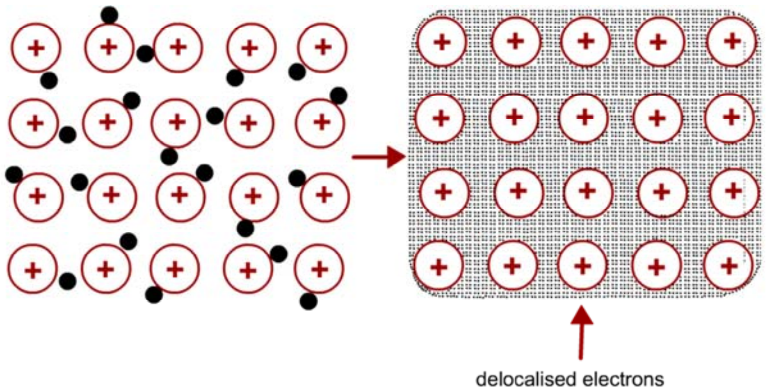
Metallic Bonding



The metallic bond can be considered as a special case of the covalent bond, in which the octet structure is attained by a generalised donation of the valence electrons, which form a cloud that permeates throughout the lattice.

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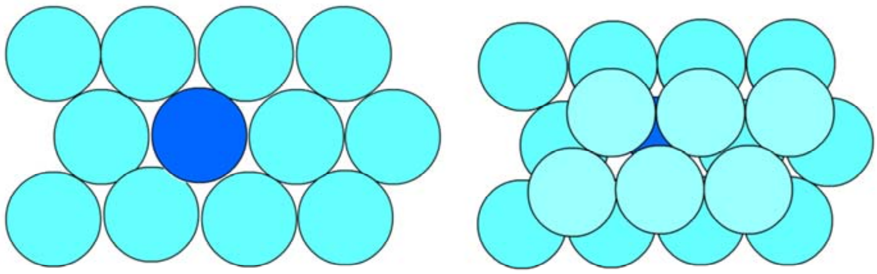
Metallic Bonding

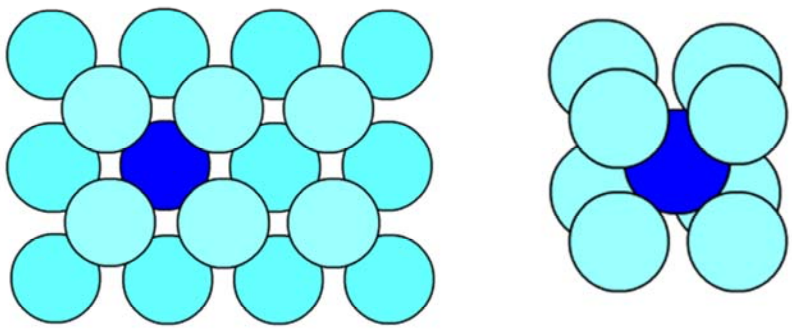
Metal structures are densely packed with atoms

12-coordination: Each atom in a structure has 12 touching neighbours. Each atom has 6 atoms touching it in a layer and touches 3 atoms each of the layer above and below.



Metallic Bonding

8-coordination: Each atom in a structure has 8 touching neighbours. The atoms do not touch each other within a layer but each atom touches 4 atoms each in the layer above and below.



Metallic Bonding

- Since the electrostatic attraction between ions and electrons is non-directional, metallic crystals can grow in three dimensions.
- Metallic bonding leads to high thermal and electrical conductivity, malleability and ductility in metals.
- High reflectivity and opacity of metals have also been attributed to the absorption of energy by the free electrons and subsequent emission of light when they fall back to their original energy levels.
- The ability of metals to form alloys is also explained by the free electron theory.

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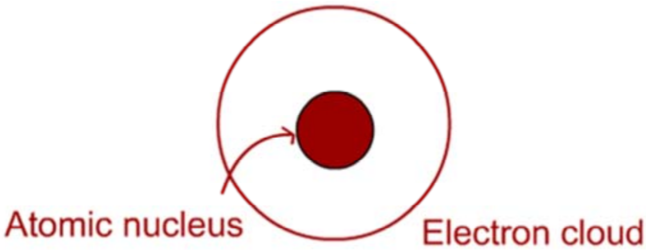
Van der Waals Bonding

Weak bonds exist between atoms and molecules that are called Van der Waals bonds.

Electrically symmetric atom

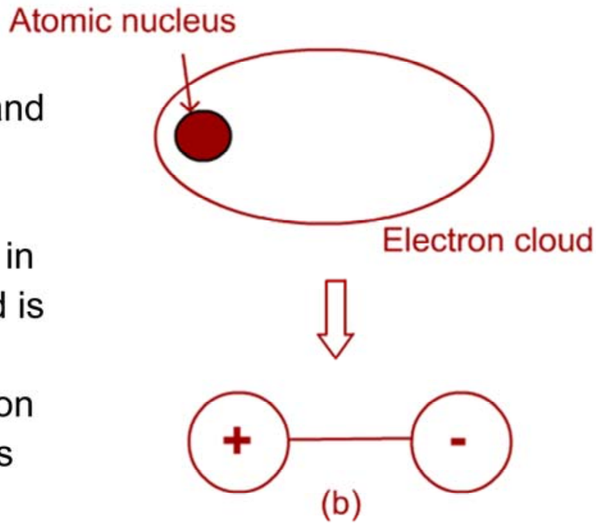


(a)

Van der Waals Bonding

The electron charge is spread around the atom and over a period of time it is symmetrically distributed. However, at any instance in time, the electrostatic field is continuously fluctuating. This results in the formation of dynamic electric dipoles (i.e., the centres of the positive and negative charges do not coincide).

Instantaneous distortion



Induced atomic dipole

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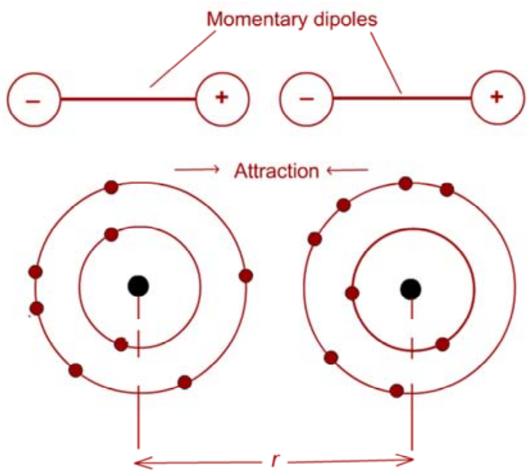
Van der Waals Bonding

When another atom is brought into proximity, the dipoles of the two atoms interact resulting in a weak non-directional electrostatic bond.



Van der Waals Bonding

The attractive force between two atoms is:

$$F = \alpha_1 \, \alpha_2 \, / \, r^6$$

where α_1 and α_2 are the polarisabilities of the two atoms (i.e., ease with which a dipole can be formed), and r is the distance between them.

Polarisability increases with atomic number, since the valence electrons are farther from the nucleus (can be more easily pulled towards neighbouring atoms).

Van der Waals Bonding

- Van der Waals bonding is responsible for the viscosity and surface tension of liquids.
- Heat can be used to break Van der Waals bonds; e.g., boiling of liquids, melting of thermoplastic materials.

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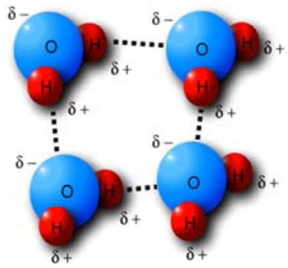
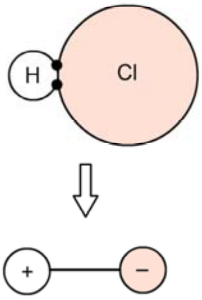
Hydrogen Bonding

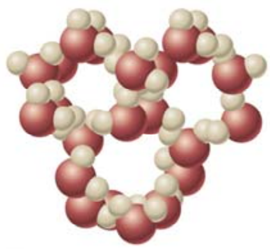
- The strongest of dipole interactions occurs when the hydrogen atom is involved. This is called the hydrogen bond.

Water bond

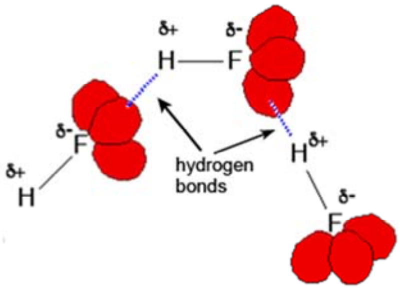


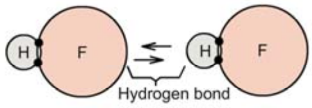


Ice bond – open crystal structure



Hydrogen Bonding





- This is responsible for the high melting point of ice and boiling point of water.

- Hydrogen bonding contributes to high mechanical performance and heat resistance of some modern polymers (e.g., nylon, Kevlar).

Illston & Domone

Atomic Bonding: Summary of bond types

Bond Type	Bond Energies (kJ . mol^{-1})	Typical Materials	Typical Elements	Remarks
Ionic	500-1200[a]	Ceramic Oxides Gypsum Rock salt Calcite	Compounds of Gp I, Gp II	All exist as crystalline solids.
Covalent	150-750[a,b]	Diamond Glasses Silicon carbide	Gp IV, Gp V, Gp VI	States of matter at room temperature depend on intermolecular attraction.
Metallic	50-850[a]	Metals	Elements of Gp I-III, Transition metals. Heavy elements of Gp IV and V.	May be liquid or solid depending on binding energies.

Atomic Bonding: Summary of bond types

Bond Type	Bond Energies (kJ . mol^{-1})	Typical Materials	Typical Elements	Remarks
Hydrogen	10-30[c]	Water	F, O, N	Can be considered weak ionic or strong van der Waals. Strongly influences material behaviour.
van der Waals	0.05-5	Thermoplastic polymers	Compounds of all elements	Primarily intermolecular bonds. Dominate the behavior and microstructure of construction materials, such as concrete and asphalt.

[a] Lattice energies of crystal.
[b] Isolated multiple covalent bonds (as formed in N_2, for example can be as strong as 950 kJ·mol^{-1}.
[c] Single hydrogen bond is about 2 kJ·mol^{-1}.

Young et al.

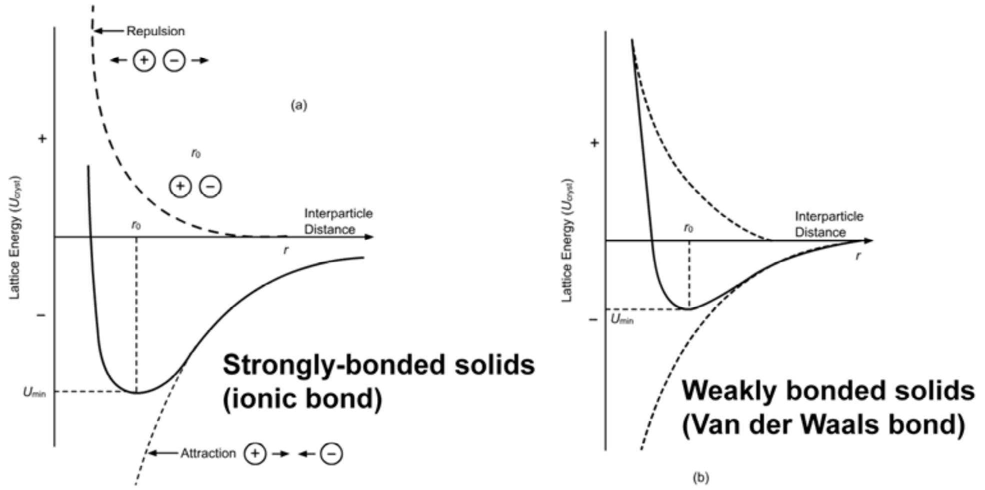
Mixed Bonding

In most materials, bonding is a mixture of two (or even three) types:

- Plastics: covalent and Van der Waals
- Metallic alloys: covalent and metallic, Van der Waals across grain boundaries
- Ceramics that may contain metallic and non-metallic elements: may be covalently and ionically bonded with Van der Waals bonds across grain boundaries

Bonding Energies

Net attractive energy (U_{cryst}) versus distance (r) between the bonded ions – *Condon-Morse diagram*



Young et al.

Bonding Energies

- Depth of the potential energy "well" (U_{min}) indicates the strength of the cohesive forces within the solid
- The value of r that corresponds to U_{min} is the interatomic distance r_0 (i.e., equilibrium distance between ions in the crystal)
- Primary bond lengths are in the range of 0.1-0.2 nm, secondary bond lengths are in the range of 0.2-0.5 nm
- The boiling point of a material is proportional to the value of U_{min}

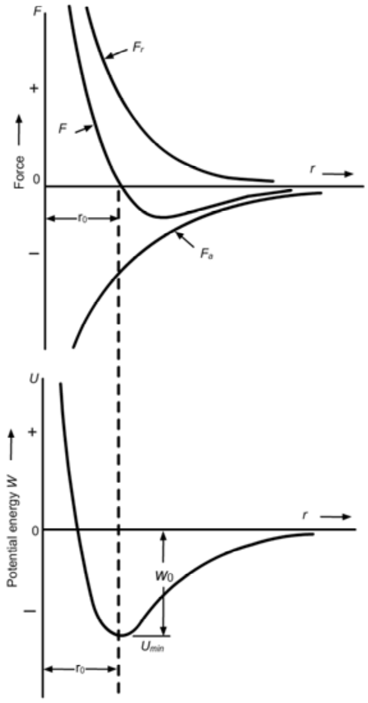
Young et al.

Bonding Energies

The bonding force (i.e., force of attraction) between adjacent atoms is

$$F = \frac{dU}{dr}$$

The slope of the resulting curve about r_0 is approximately linear and gives a measure of the restoring force that acts on the atoms for small displacements from the equilibrium position (Young's modulus of elasticity)



Bonding Energies

Other consequences:

- Since the $F(r)$ diagram is symmetrical at r_0, the elastic modulus is nearly the same in compression and tension
- At large strains, the $F(r)$ diagram is no longer straight; response becomes nonlinear
- At high tensile strains, the material ruptures since the attractive force reaches a maximum value (tensile strength).
- There is no possibility of failure under pure compression since the repulsive force always increases.

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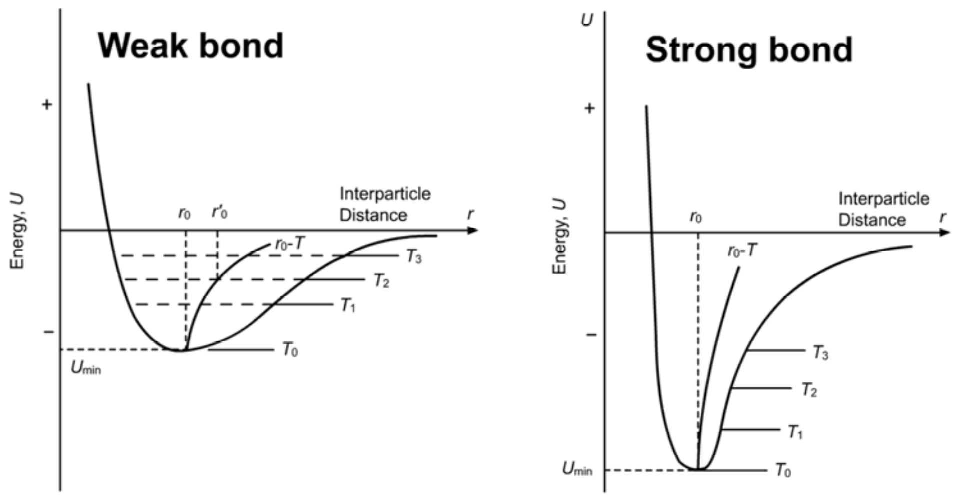
Bonding Energies

Effect of temperature on interatomic distances



Bonding Energies

- The mean interatomic distance increases with temperature; only at 0°K (-273°C), $U_{solid} = U_{min}$.
- For a deeper well, the change in interatomic distance from r_0 to r_0' is smaller, when temperature increases.
- Strongly bonded solids have lower thermal expansion.

Young et al.

Bonding Energies

Other consequences:

- Higher interatomic separation leads to more vibration of the atoms; as temperature increases, the material expands in all directions
- If the heating continues, the atomic bonds are eventually broken; liquids evaporate
- At higher temperatures, less extra energy is required to break the bond; the tensile strength decreases with an increase in temperature

Illston & Domone

References

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