

ATOMIC BONDING IN SOLIDS / PRIMARY INTERATOMIC BONDS

Subject: Material Science - Lecture #3

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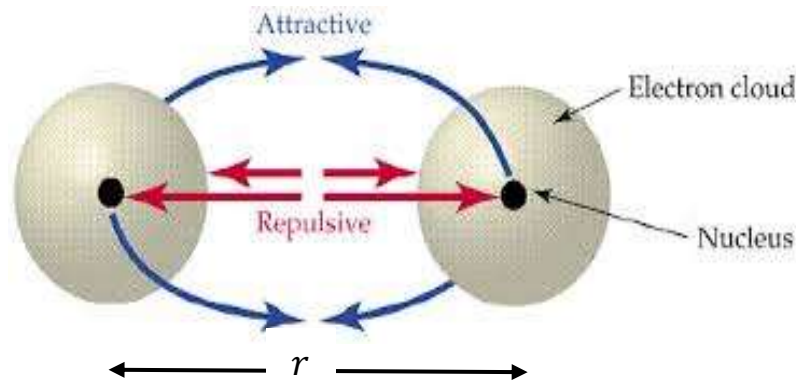
Physics Department – 3rd grade

Atomic Bonding in Solids

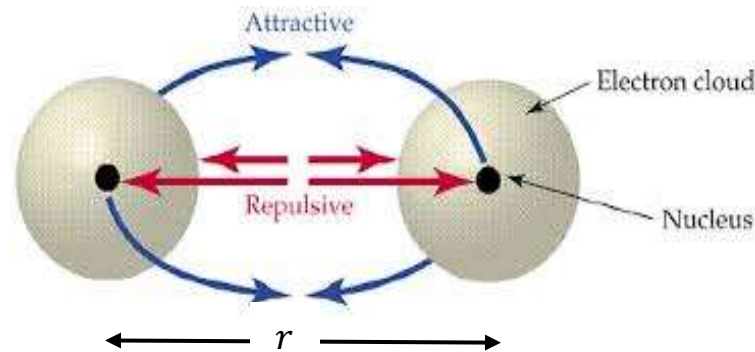
BONDING FORCES AND ENERGIES

- An understanding of many of the physical properties of materials is enhanced by a knowledge of the interatomic forces that bind the atoms together.
- the principles of atomic bonding are best illustrated by considering how two isolated atoms interact as they are brought close together from an infinite separation.

- At small separation distances, each atom exerts forces on the others. These forces are of two types, attractive (F_A) and repulsive (F_R).
- The magnitude of each depends on the separation or interatomic distance (r);



- The attractive force F_A depends on the type of bonding between the two atoms.
- Repulsive forces F_R arise from interactions between the negatively charged electron clouds for the two atoms and are important only at small values of r as the outer electron shells of the two atoms begin to overlap



- The net force F_N between the two atoms is just the sum of both attractive and repulsive components;

$$F_N = F_A + F_R \quad \dots \dots \dots (1)$$

- When F_A and F_R are equal in magnitude but opposite in sign, there is no net force and a state of equilibrium exists

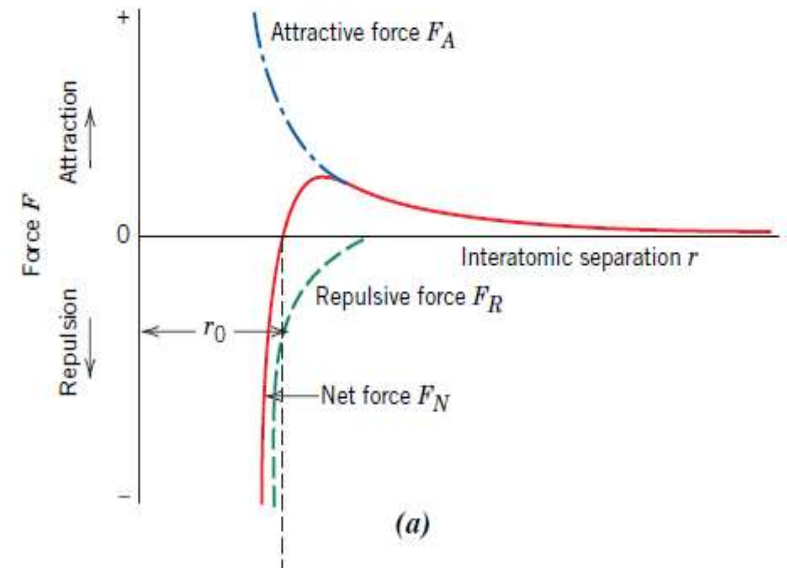
$$F_A + F_R = 0 \quad \dots \dots \dots (2)$$

- At state of equilibrium

$$F_A + F_R = 0 \quad \dots \dots \dots (3)$$

The centers of the two atoms remain separated by the equilibrium spacing r_0 .

- For many atoms, r_0 is approximately 0.3nm.
- Any attempt to move the two atoms farther apart is counteracted by the attractive force, while pushing them closer together is resisted by the increasing repulsive force.



Schematic plot of F_A and F_R versus r .

Sometimes it is more convenient to work with the potential energies between two atoms instead of forces.

Mathematically, energy (E) and force (F) are related as

$$E = \int F dr \quad \dots \dots \dots (4a)$$

or

$$F = \frac{dE}{dr} \quad \dots \dots \dots (4b)$$

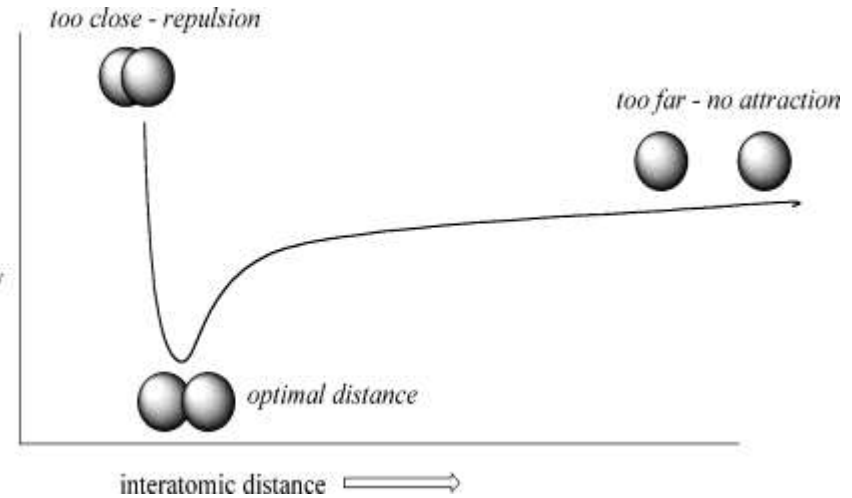
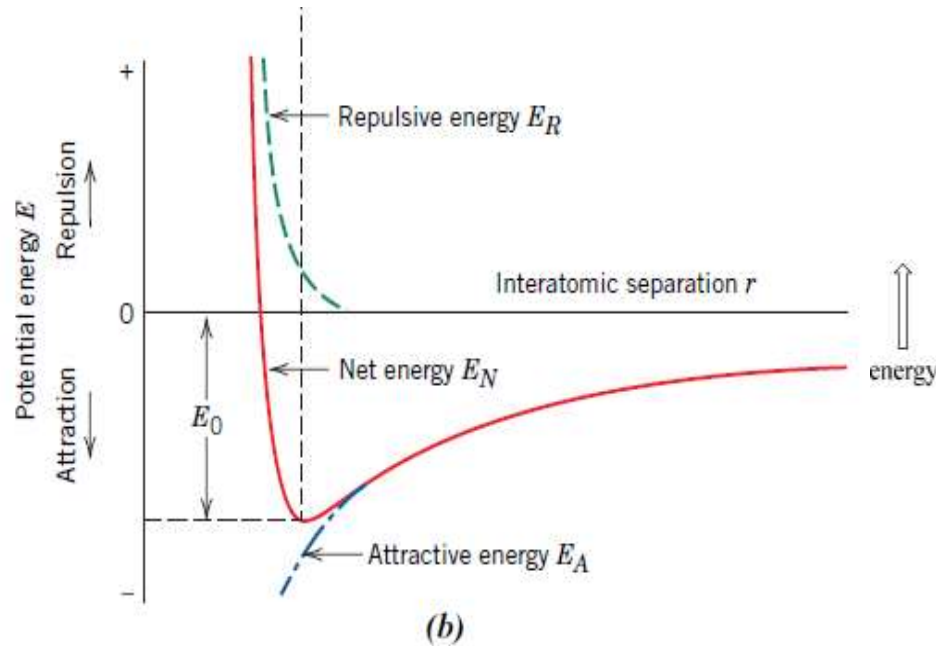
And, for atomic systems

$$E_N = \int_r^{\infty} F_N dr \quad \dots \dots \dots (5)$$

$$E_N = \int_r^{\infty} F_A dr + \int_r^{\infty} F_R dr \quad \dots \dots \dots (6)$$

$$E_N = E_A + E_R \quad \dots \dots \dots (7a)$$

in which E_N , E_A and E_R are, respectively, the net, attractive, and repulsive energies for two isolated and adjacent atoms



- attractive, repulsive, and net potential energies as a function of interatomic separation for two atoms.
- the net curve is the sum of the attractive and repulsive curves.
- The minimum in the net energy curve corresponds to the equilibrium spacing, r_0 .

- the **bonding energy** (E_0) for these two atoms, corresponds to the energy at this minimum point it represents the energy required to separate these two atoms to an infinite separation.
- The magnitude of this bonding energy and the shape of the energy–versus–interatomic separation curve vary from material to material, and they both depend on the type of atomic bonding.

Material properties depend on E_0 , the curve shape, and bonding type.

- For example, materials having large bonding energies typically also have high melting temperatures; at room temperature, solid substances are formed for large bonding energies, whereas for small energies, the gaseous state is favored; liquids prevail when the energies are of intermediate magnitude.

- Three different types of **primary bond** (chemical bond) are found in solids ionic, covalent, and metallic.
- For each type, the bonding necessarily involves the valence electrons
- the nature of the bond depends on the electron structures of the constituent atoms.

In general, each of these three types of bonding arises from the tendency of the atoms to assume stable electron structures, like those of the inert gases , by completely filling the outermost electron shell, argon (Ar, $1s^2 2s^2 2p^6 3s^2 3p^6$),

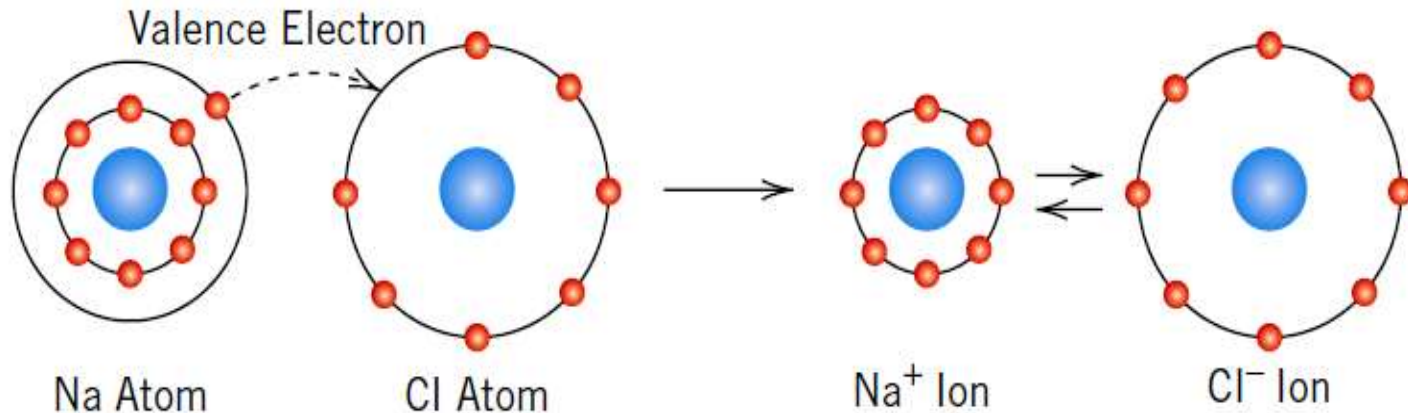
- Secondary bond or physical forces and energies are also found in many solid materials
- they are weaker than the primary ones but it is influence the physical properties of some materials.

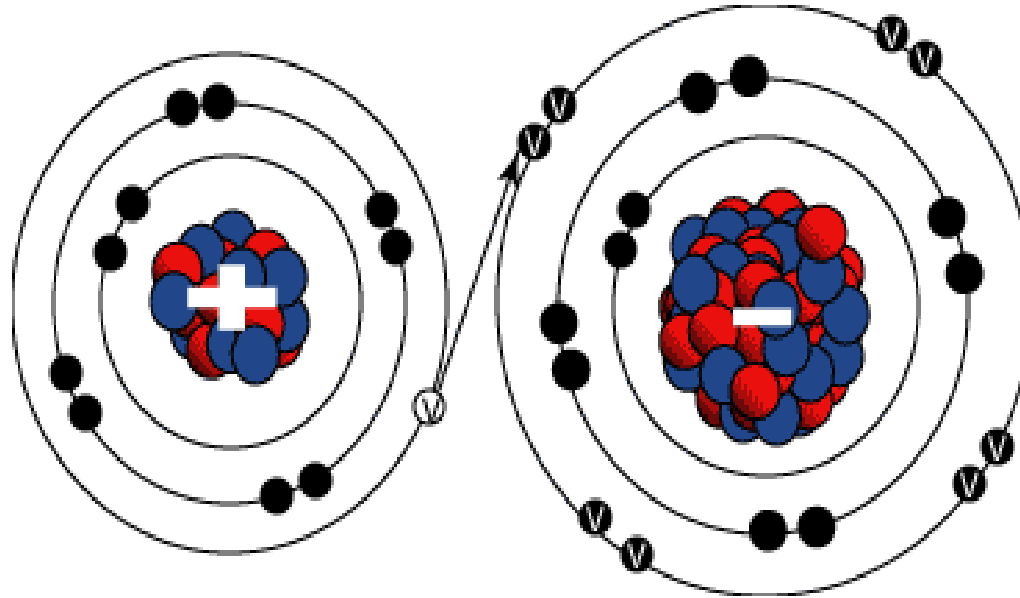
PRIMARY INTERATOMIC BONDS

Ionic Bonding

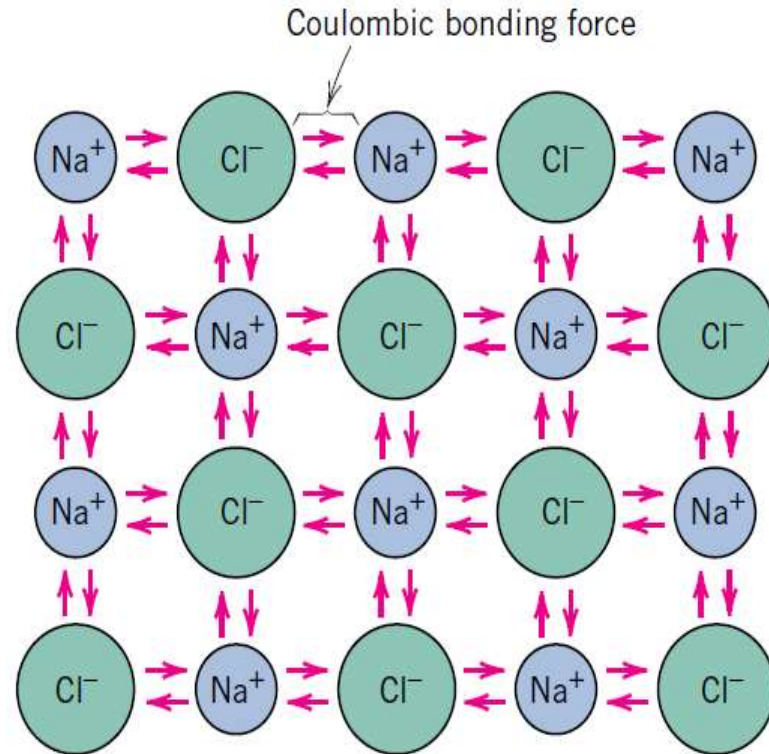
- **Ionic bonding** It is always found in compounds composed of both metallic and nonmetallic elements.
- Atoms of a metallic element easily give up their valence electrons to the nonmetallic atoms to have stable or completely filled orbital shells (like inert gas configurations).
- Sodium chloride (NaCl) is the classic ionic material.

- A sodium atom can assume the electron structure of neon (and a net single positive charge with a reduction in size) by a transfer of its one valence $3s$ electron to a chlorine atom. After such a transfer, the chlorine ion acquires a net negative charge, an electron configuration identical to that of argon; it is also larger than the chlorine atom.





The attractive bonding forces are **coulombic** that is, positive and negative ions, by virtue of their net electrical charge, attract one another.

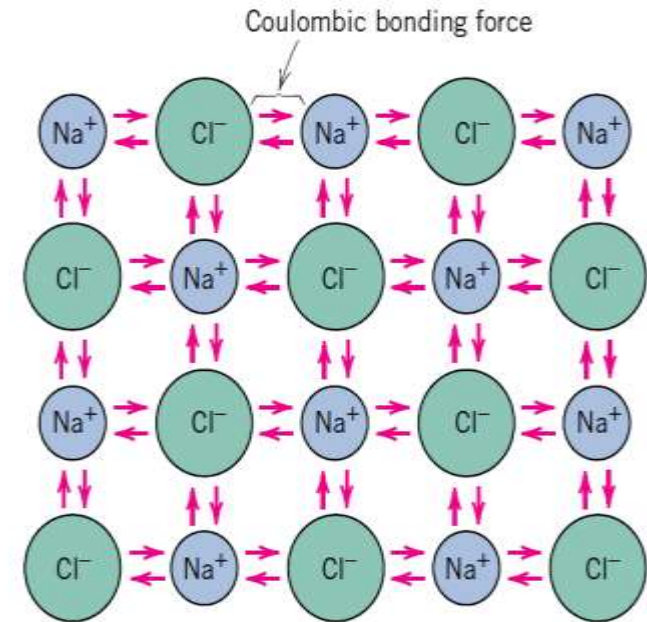


An analogous equation for the repulsive energy is

$$E_R = \frac{B}{r^n} \quad \dots \dots \dots (8)$$

In this expression, B and n are constants whose values depend on the particular ionic system. The value of n is approximately 8.

- Ionic bonding is termed nondirectional that is, the magnitude of the bond is equal in all directions around an ion.
- For ionic materials to be stable, all positive ions must have as nearest neighbors negatively charged ions in a three-dimensional scheme, and vice versa.



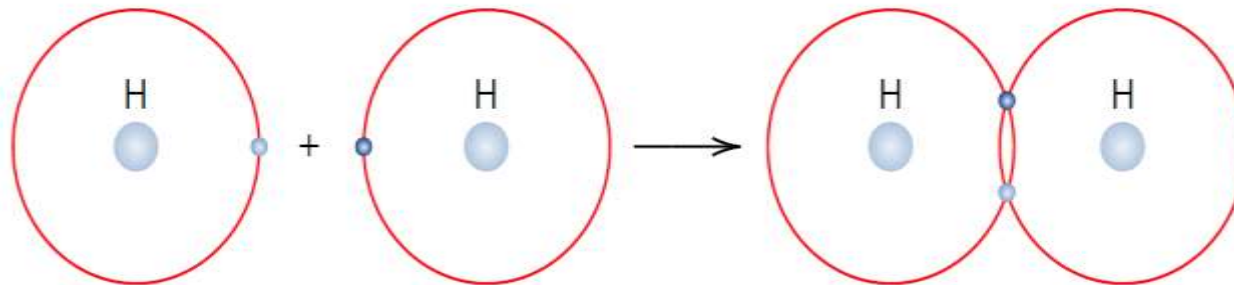
Bonding energies, which generally range between 600 and 1500 kJ/mol, are relatively large, as reflected in high melting temperatures, Table below

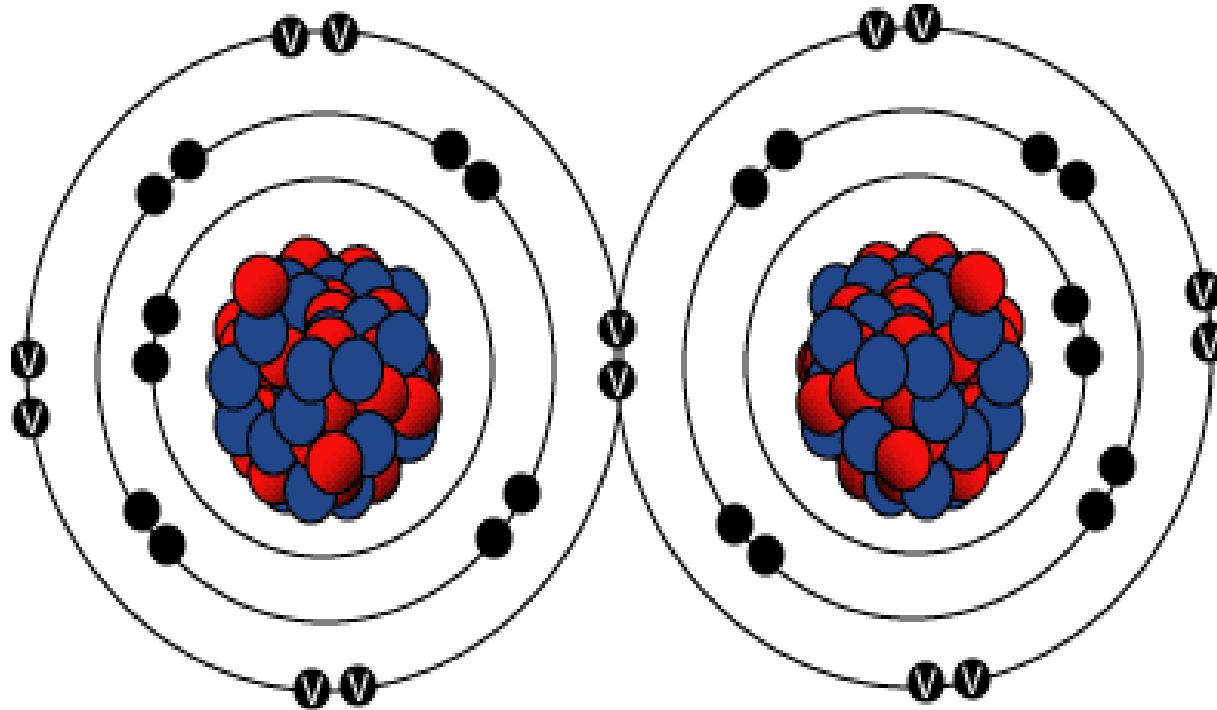
<i>Substance</i>	<i>Bonding Energy (kJ/mol)</i>	<i>Melting Temperature (°C)</i>
	Ionic	
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF ₂	1548	1418

Covalent Bonding

- A second bonding type, **covalent bonding**, is found in materials whose atoms have small differences in electronegativity (capable of giving up their few valence electrons to become positively charged ions) , that lie near one another in the periodic table.
- For these materials, stable electron configurations are assumed by the sharing of electrons between adjacent atoms.

- The hydrogen atom has a single $1s$ electron.
- Each of the atoms can acquire a helium electron configuration (two $1s$ valence electrons) when they share their single electron
- There is an overlapping of electron orbitals in the region between the two bonding atoms.
- The covalent bond is directional that is, it is between specific atoms and may exist only in the direction between one atom and another that participates in the electron sharing.





- Many nonmetallic elemental molecules (e.g., Cl_2 , F_2), as well as molecules containing dissimilar atoms, such as CH_4 , H_2O , HNO_3 , and HF , are covalently bonded.
- covalent bond is found in elemental solids such as diamond (carbon), silicon, and germanium and other
- covalent bond is found in solid compounds composed of elements that are located on the right side of the periodic table, such as gallium arsenide (GaAs), indium antimonide (InSb), and silicon carbide (SiC).

Covalent bonds may be very strong, as in diamond, which is very hard and has a very high melting temperature, $> 3550^{\circ}\text{C}$ (6400°F), or they may be very weak, as with bismuth, which melts at about 270°C (518°F) Table below.

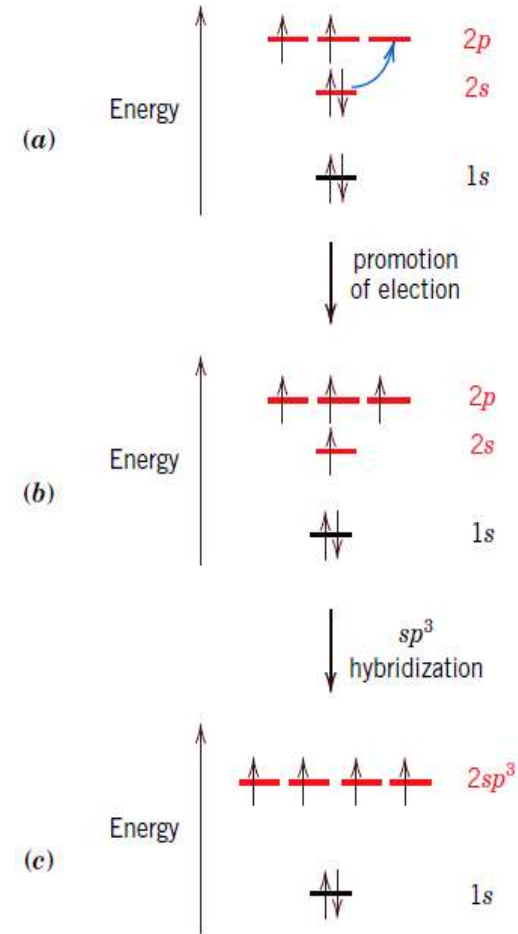
<i>Substance</i>	<i>Bonding Energy (kJ/mol)</i>	<i>Melting Temperature ($^{\circ}\text{C}$)</i>
Covalent		
Cl_2	121	-102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830

- Inasmuch as electrons participating in covalent bonds are tightly bound to the bonding atoms
- most covalently bonded materials are electrical insulators, or, in some cases, semiconductors.
- Mechanical behaviors of these materials vary widely: some are relatively strong, others are weak; some fail in a brittle manner, whereas others experience significant amounts of deformation before failure. It is difficult to predict the mechanical properties of covalently bonded materials on the basis of their bonding characteristics.

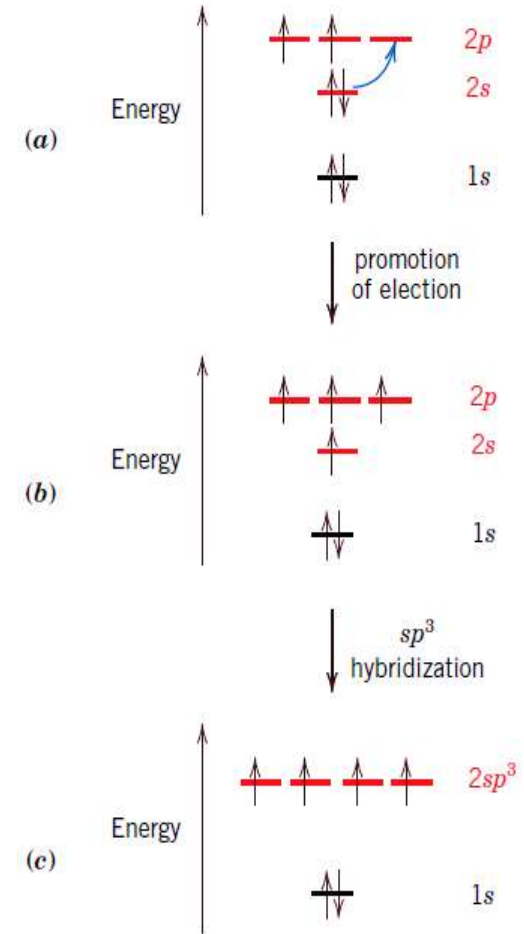
Bond Hybridization in Carbon

- Often associated with the covalent bonding of carbon (as well other nonmetallic substances)
- is the phenomenon of hybridization the mixing (or combining) of two or more atomic orbitals with the result that more orbital overlap during bonding results.

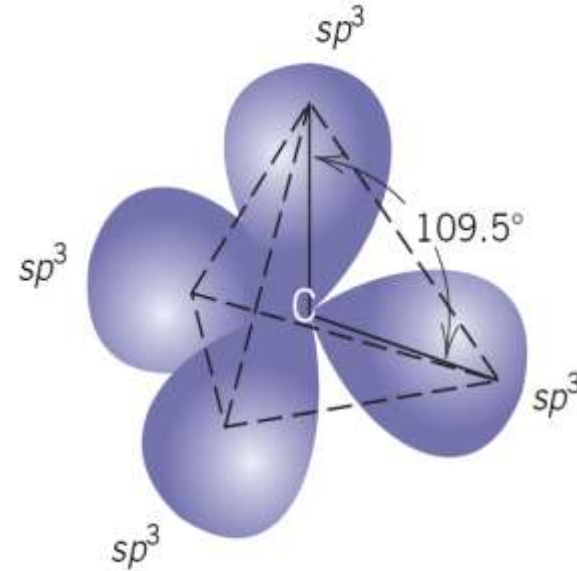
- For example, consider the electron configuration of carbon: $1s^2 2s^2 2p^2$.
- Under some circumstances, one of the 2s orbitals is promoted to the empty 2p orbital (Figure a), which gives rise to a $1s^2 2s^1 2p^3$ configuration (Figure b).

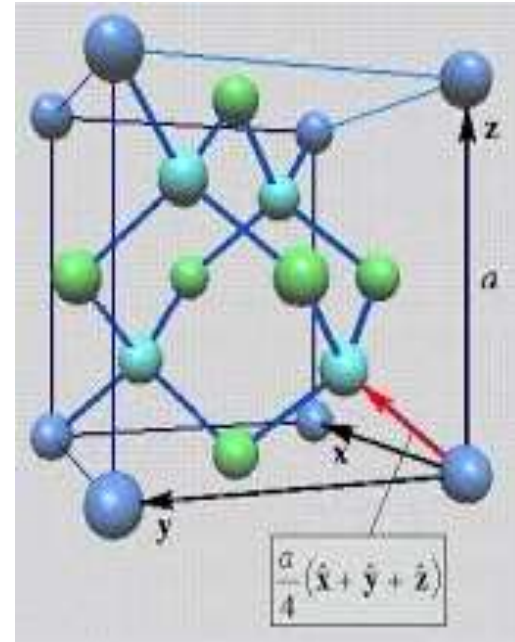
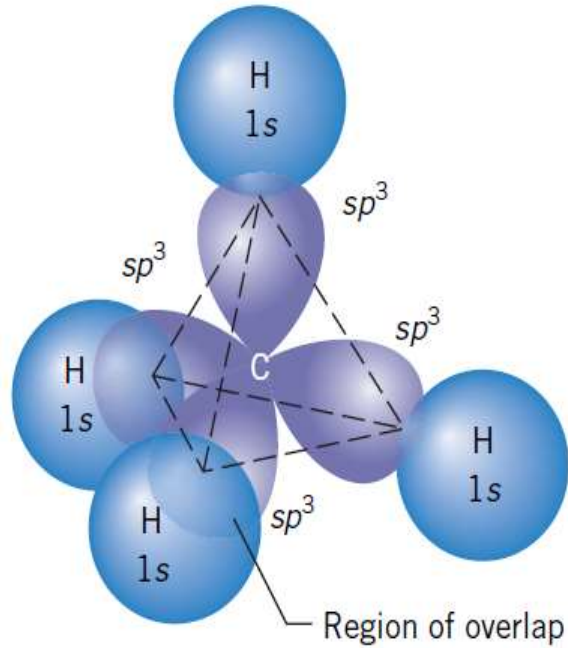


- Furthermore, the $2s$ and $2p$ orbitals can mix to produce four sp^3 orbitals that are equivalent to one another, have parallel spins, and are capable of covalently bonding with other atoms.
- This orbital mixing is termed **hybridization**
- each sp^3 orbital contains one electron, and, therefore, is half-filled.
- Bonding hybrid orbitals are directional in nature that is, each extends to and overlaps the orbital of an adjacent bonding atom.



- for carbon, each of its four sp^3 hybrid orbitals is directed symmetrically from a carbon atom to the vertex of a tetrahedron
- the angle between each set of adjacent bonds is 109.5° .

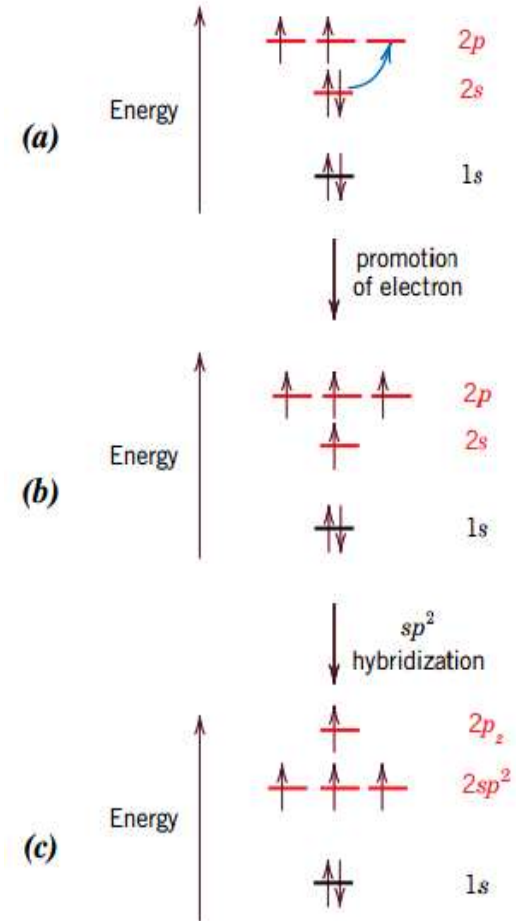




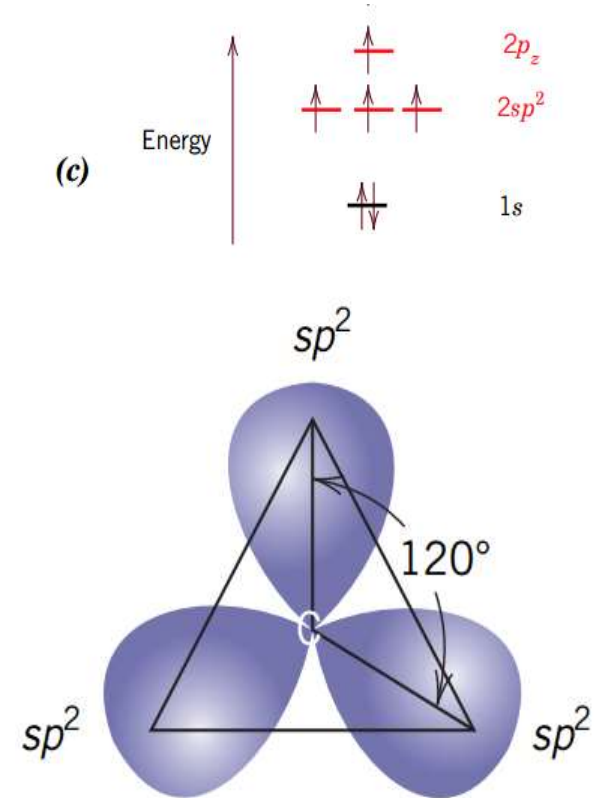
diamond structure

Other types of hybrid bonds are possible for carbon, as well as other substances.

- One of these is sp^2 , in which an s orbital and two p orbitals are hybridized.
- To achieve this configuration, one $2s$ orbital mixes with two of the three $2p$ orbitals, the third p orbital remains unhybridized. Here, $2p_z$ denotes the unhybridized p orbital.



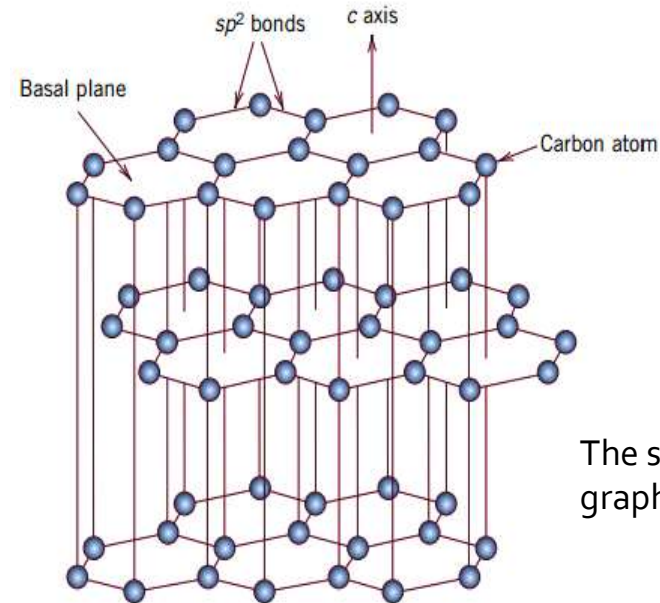
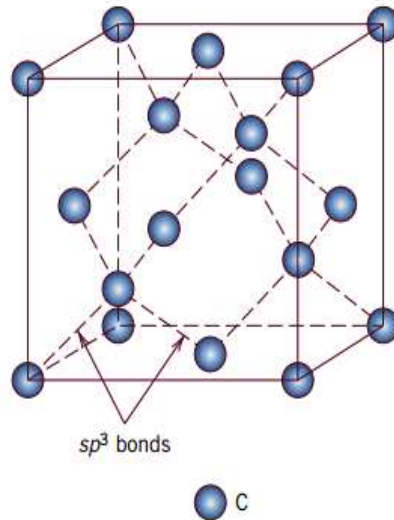
- Three sp^2 hybrids belong to each carbon atom, which lie in the same plane such that the angle between adjacent orbitals is 120°
- lines drawn from one orbital to another form a triangle.
- Furthermore, the unhybridized $2p_z$ orbital is oriented perpendicular to the plane containing the sp^2 hybrids.



These sp^2 bonds are found in graphite, another form of carbon, which has a structure and properties distinctly different from those of diamond.

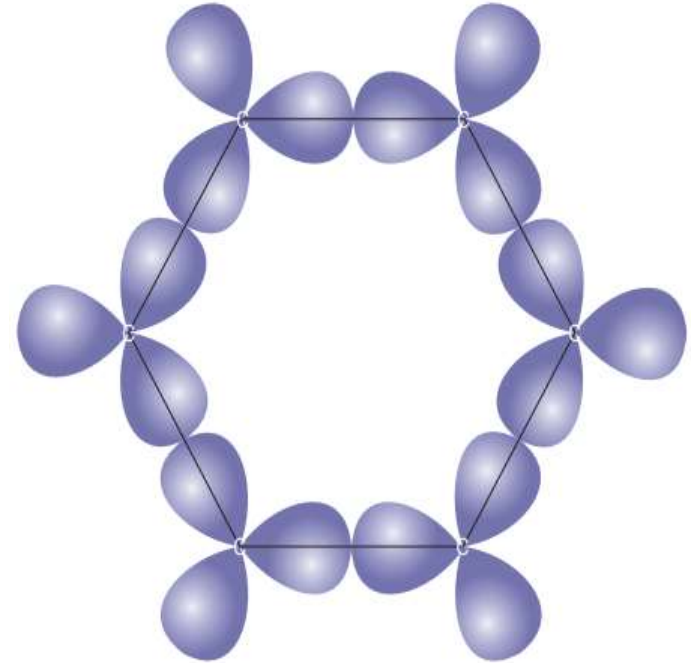
Graphite is composed of parallel layers of interconnecting hexagons.

A unit cell for the diamond cubic crystal structure.



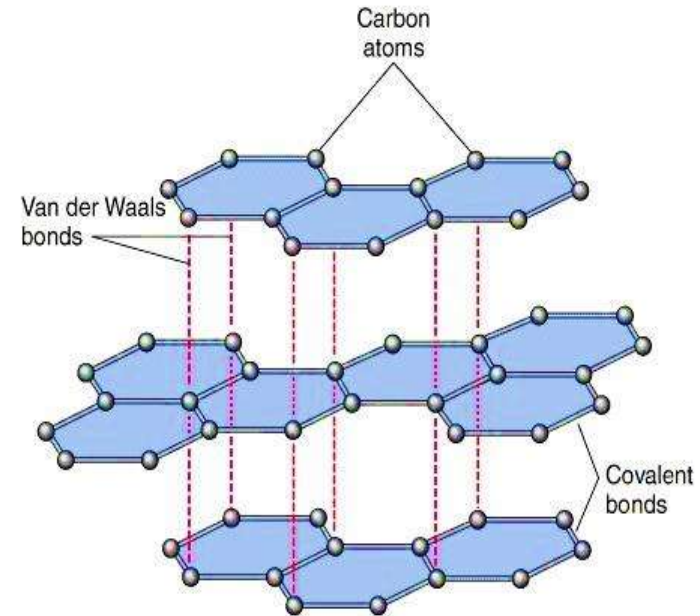
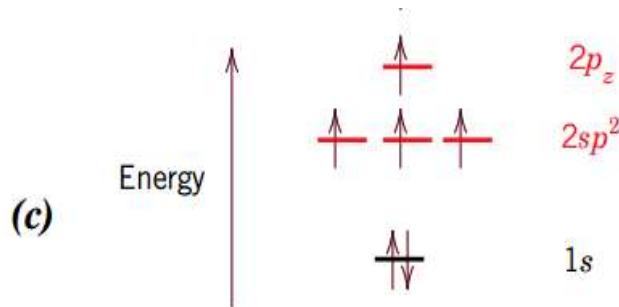
The structure of graphite.

- Hexagons form from planar sp^2 triangles that bond to one another in the manner presented in Figure
- a carbon atom is located at each vertex.
- In-plane sp^2 bonds are strong



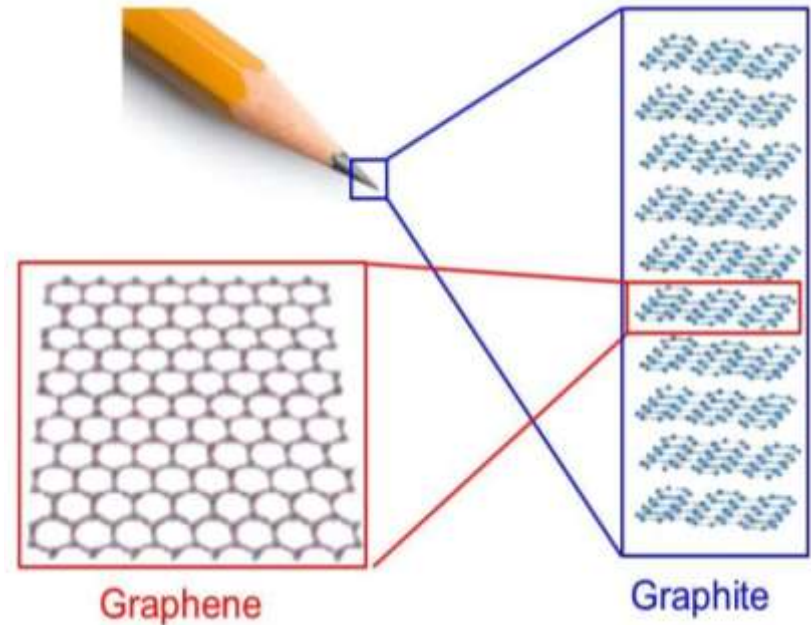
The formation of a hexagon by the bonding of six sp^2 triangles to one another.

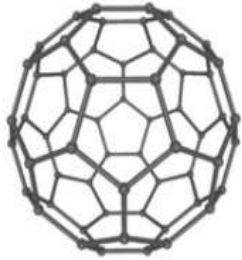
weak interplanar bonding results from van der Waals forces that involve electrons originating from the unhybridized $2p_z$ orbitals.



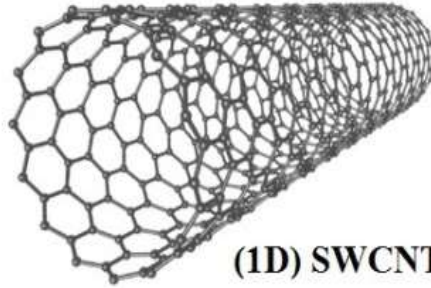
Graphene is simply one atomic layer of graphite - a layer of sp^2 bonded carbon atoms arranged in a hexagonal or honeycomb lattice.

Graphite is composed of many layers of graphene.

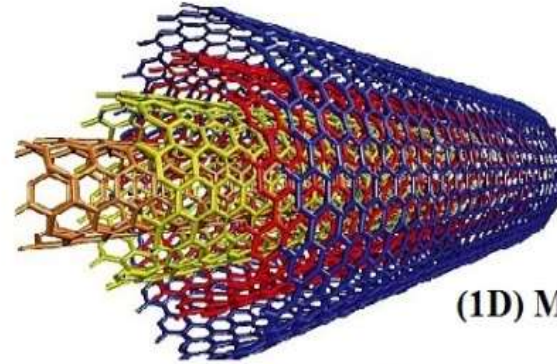




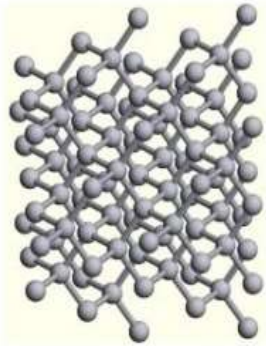
(0D) Fullerene



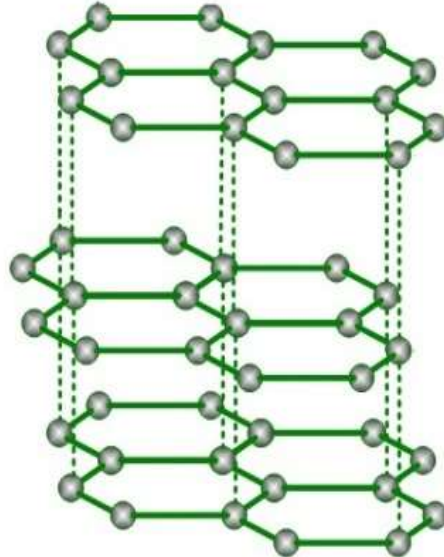
(1D) SWCNT



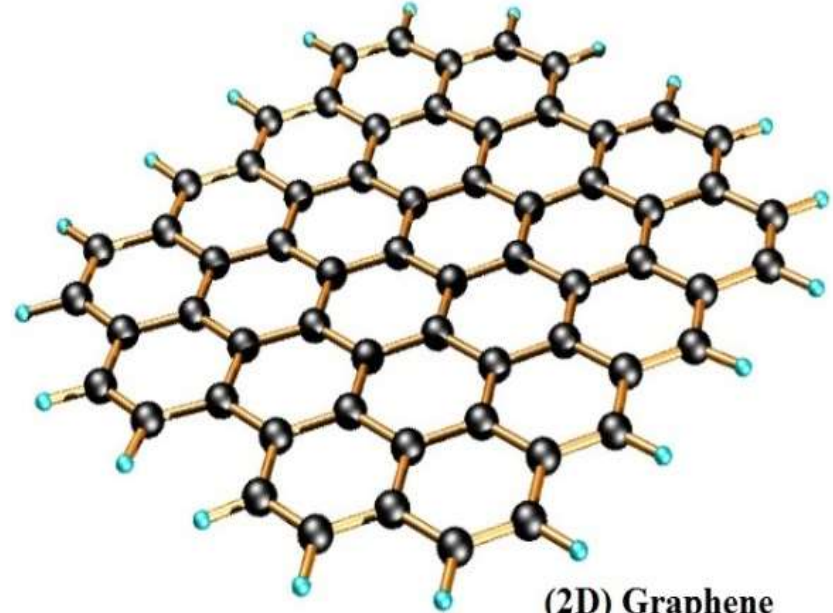
(1D) MWCNT



(3D) Diamond



(3D) Graphite

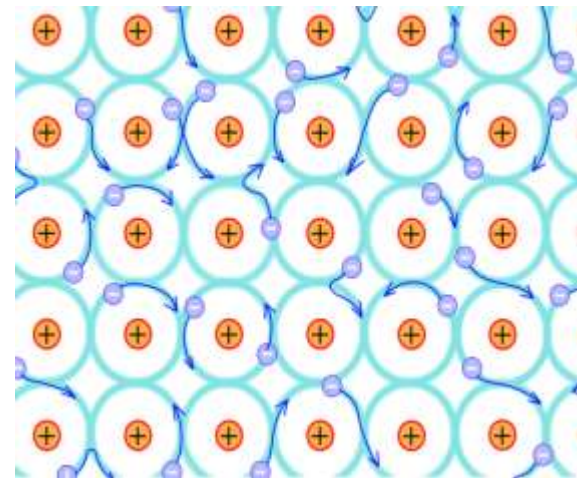
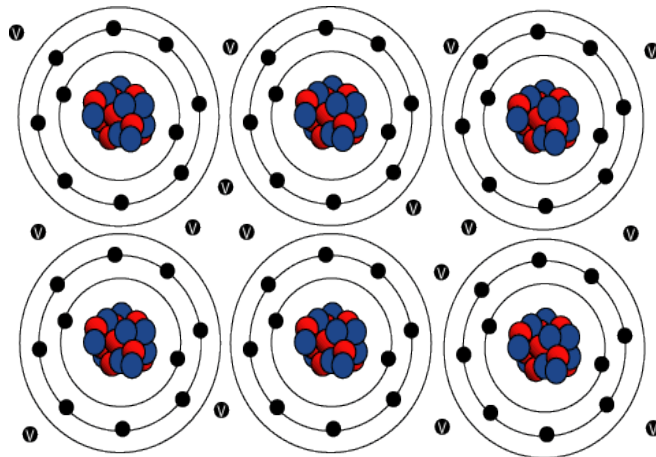


(2D) Graphene

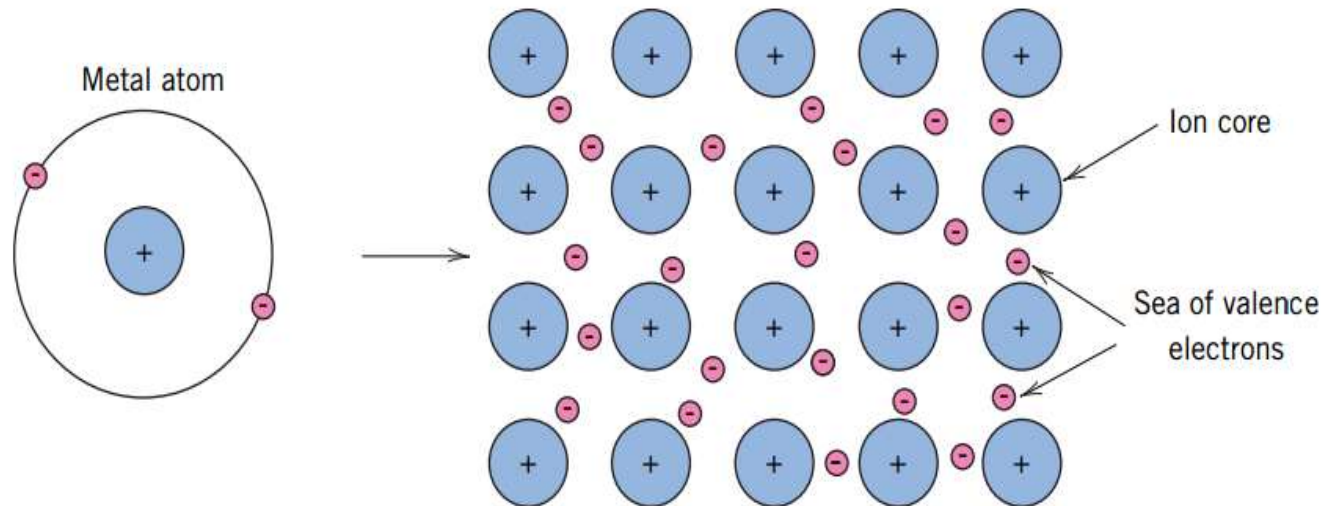
Metallic Bonding

Metallic bonding, is found in metals and their alloys.

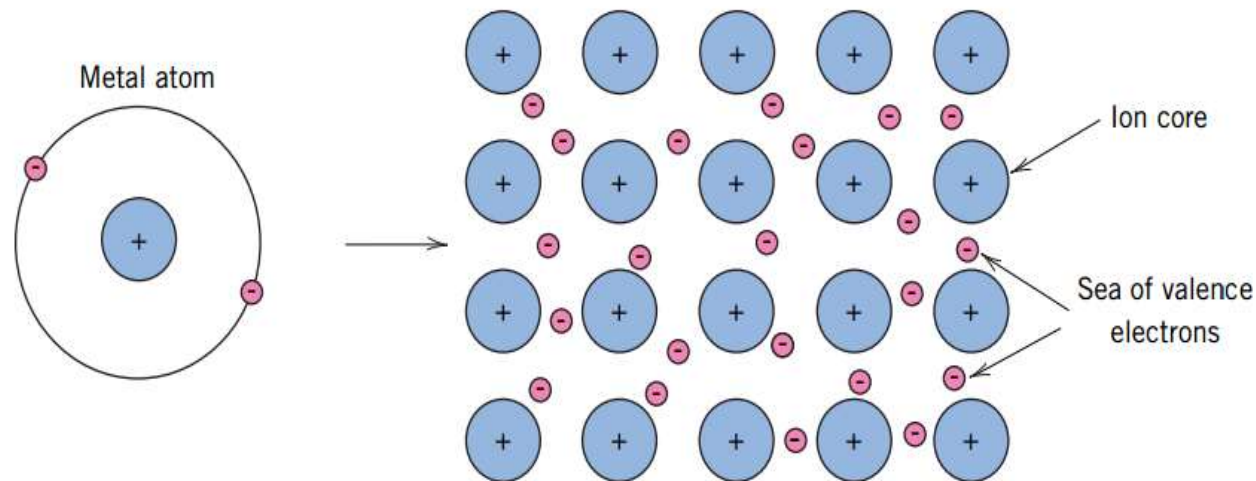
- The valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal.



- The valence electrons may be thought of as belonging to the metal as a whole, or forming a “sea of electrons” or an “electron cloud.”



- The remaining nonvalence electrons and atomic nuclei form what are called ion cores, which possess a net positive charge equal in magnitude to the total valence electron charge per atom.



The free electrons shield the positively charged ion cores from the mutually repulsive electrostatic forces that they would otherwise exert upon one another; consequently, the metallic bond is nondirectional in character.



Bonding energies and melting temperatures for several metals are listed in Table below.

<i>Substance</i>	<i>Bonding Energy (kJ/mol)</i>	<i>Melting Temperature (°C)</i>
Metallic		
Hg	62	−39
Al	330	660
Ag	285	962
W	850	3414

- Metals are good conductors of both electricity and heat as a consequence of their free electrons.
- At room temperature, most metals and their alloys fail in a ductile manner that is, fracture occurs after the materials have experienced significant degrees of permanent deformation, which is related to the characteristics of the metallic bond.

Thank you for your attention

