ATOMIC BONDING IN SOLIDS / SECONDARY BONDING

Subject: Material Science - Lecture #4

مدرسة المادة : الدكتورة روژه برهان الدين عبدالرحمن

Kirkuk University - College of Science

Physics Department – 3rd grade

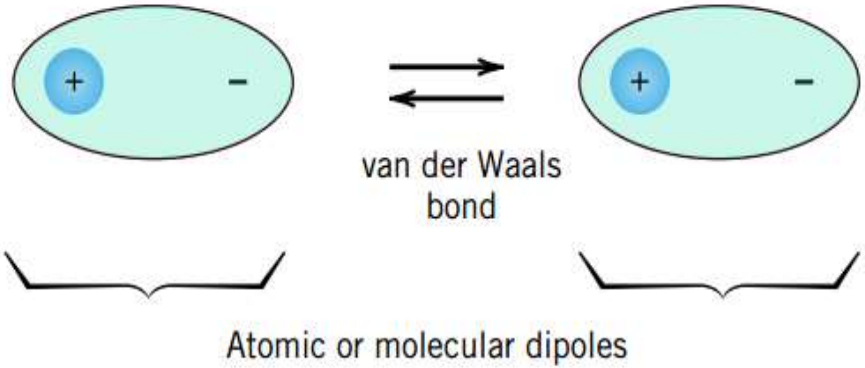
SECONDARY BONDING OR VAN DER WAALS BONDING

Secondary bonds, or **van der Waals (physical) bonds**, are weak in comparison to the primary or chemical bonds; bonding energies range between about 4 and 30 kJ/mol.

Substance	*Bonding Energy (kJ/mol)*	*Melting Temperature (°C)*
	van der Waals[a]	
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH_4	18	−182
Cl_2	31	−101

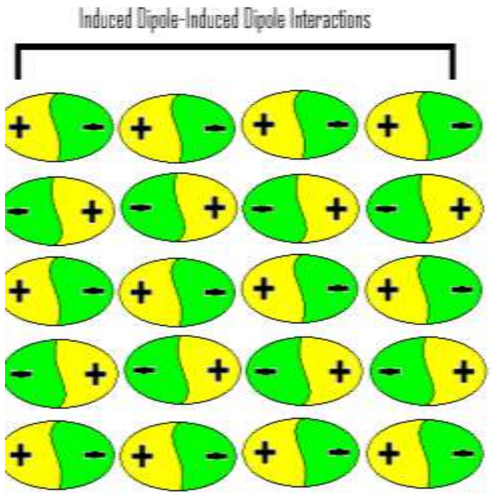
- Secondary bonding exists between virtually all atoms or molecules, but its presence may be shielded if any of the three primary bonding types is present.
- Secondary bonding is evidenced for the inert gases, which have stable electron structures.
- secondary (or **inter**molecular) bonds are possible between atoms or groups of atoms, which themselves are joined together by primary (or **intra**molecular) ionic or covalent bonds.

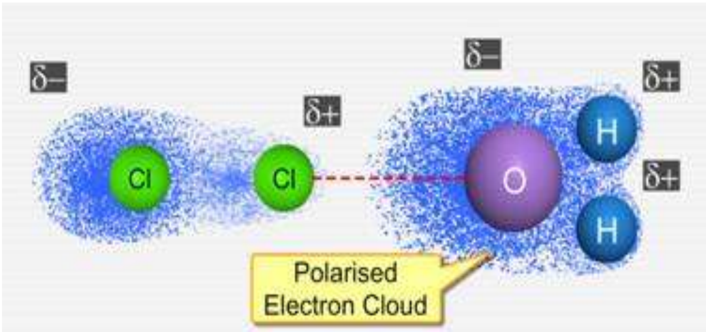
- Secondary bonding forces arise from atomic or molecular **dipoles**.
- An electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule.
- The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one, as indicated in Figure

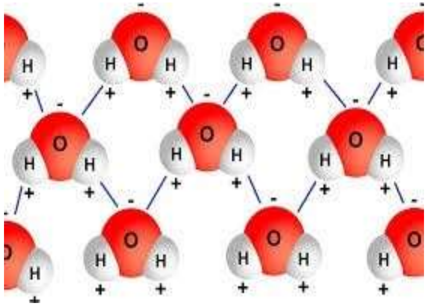


Dipole interactions occur :

- Between induced dipoles
- Between induced dipoles and polar molecules (which have permanent dipoles)
- Between polar molecules.



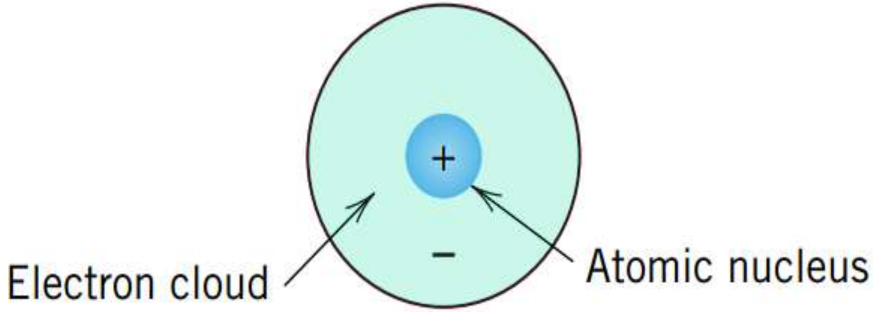




Hydrogen bonding, a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents.

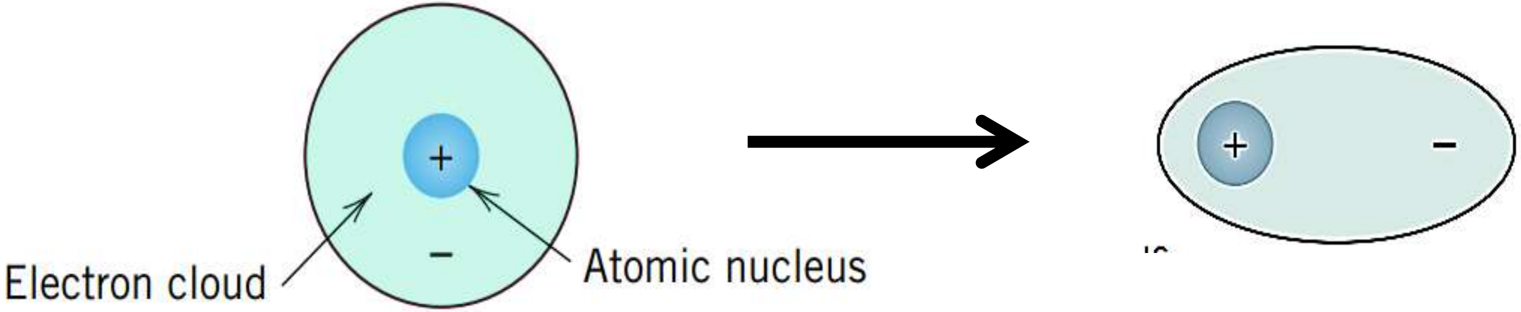
Fluctuating Induced Dipole Bonds

A dipole may be created or induced in an atom or molecule that is normally electrically <u>symmetric</u> (the spatial distribution of the electrons is symmetric with respect to the positively charged nucleus) ,

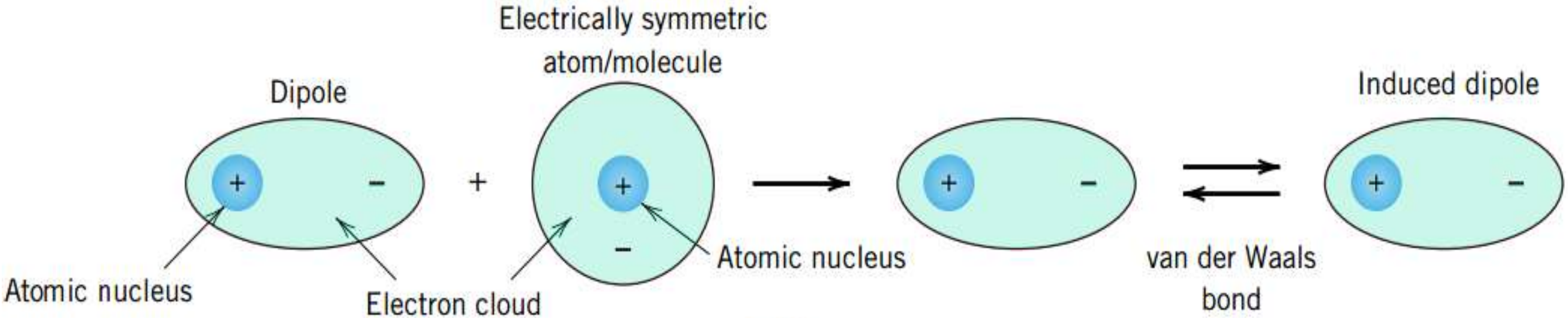


How an electric dipole induces an electrically symmetric atom/molecule to become a dipole—also the van der Waals bond between the dipoles ?

All atoms experience constant vibrational motion that can cause instantaneous and short-lived distortions of this electrical symmetry for some of the atoms or molecules and the creation of small electric dipoles.



One of these dipoles can in turn produce a displacement of the electron distribution of an adjacent molecule or atom, which induces the second one also to become a dipole that is then weakly attracted or bonded to the first; this is one type of van der Waals bonding.



(b)

- These attractive forces, which forces are temporary and fluctuate with time, may exist between large numbers of atoms or molecules.
- The liquefaction and, in some cases, the solidification of the inert gases and other electrically neutral and symmetric molecules such as H_2 and Cl_2 are realized because of this type of bonding.

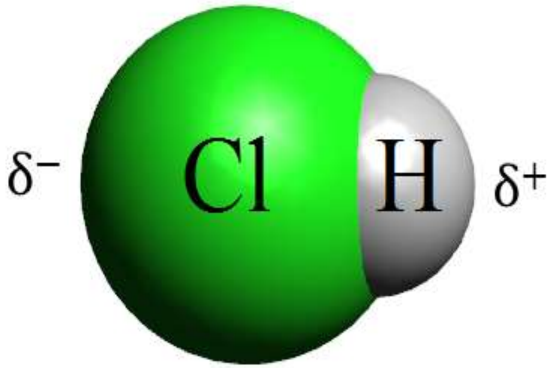
Melting and boiling temperatures are extremely low in materials for which induced dipole bonding predominates; of all possible intermolecular bonds, these are the weakest.

Substance	*Bonding Energy (kJ/mol)*	*Melting Temperature (°C)*
	van der Waals[a]	
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH_4	18	−182
Cl_2	31	−101

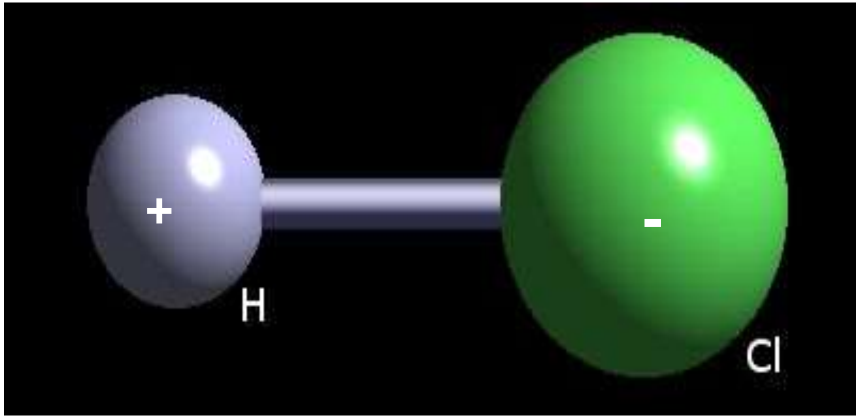
Polar Molecule–Induced Dipole Bonds

Permanent dipole moments exist in some molecules by virtue of an asymmetrical arrangement of positively and negatively charged regions; such molecules are termed **polar molecules**.

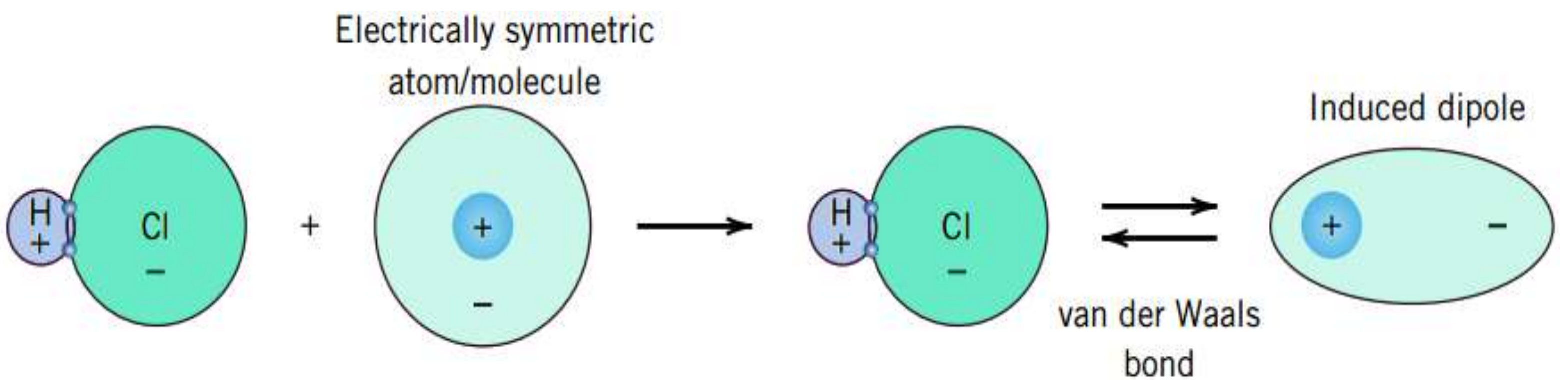
Schematic representations of a hydrogen chloride (HCl) molecule (dipole)



a permanent dipole moment arises from net positive and negative charges that are respectively associated with the hydrogen and chlorine ends of the HCl molecule.

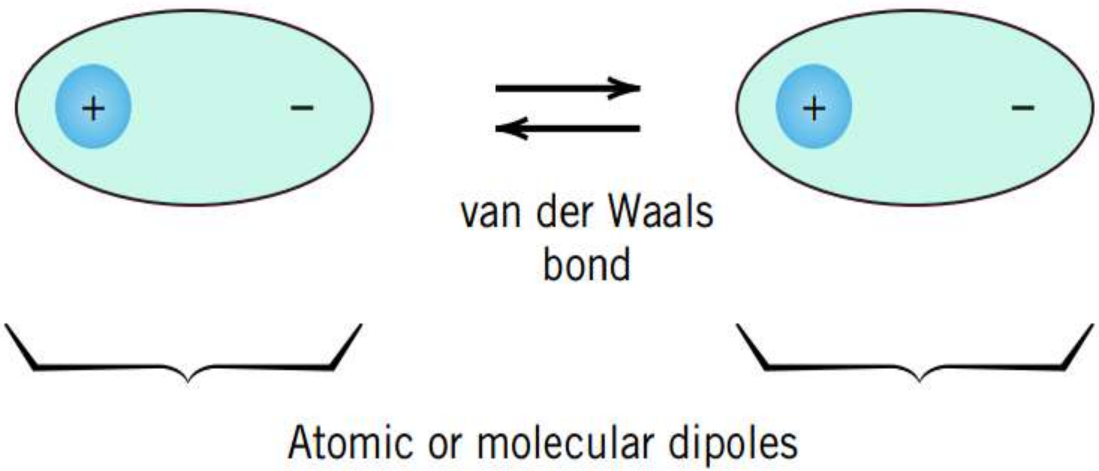


- Polar molecules can also induce dipoles in adjacent nonpolar molecules, and a bond forms as a result of attractive forces between the two molecules.
- the magnitude of this bond is greater than for fluctuating induced dipoles.

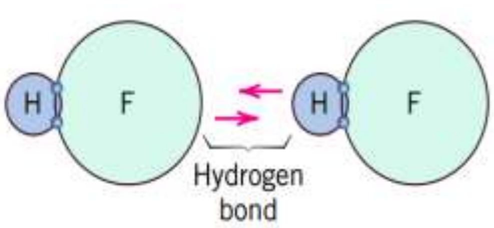


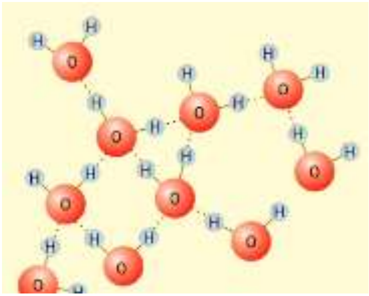
Permanent Dipole Bonds

Coulombic forces also exist between adjacent polar molecules as in Figure 2.20. The associated bonding energies are significantly greater than for bonds involving induced dipoles.

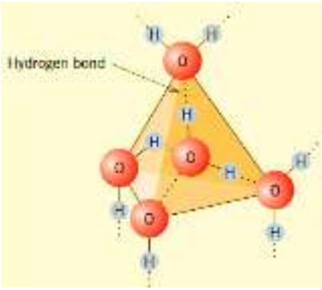


- The strongest secondary bonding type, the hydrogen bond, is a special case of polar molecule bonding.
- It occurs between molecules in which hydrogen is covalently bonded to fluorine (as in HF), oxygen (as in $\mathrm{H_2O}$), or nitrogen (as in $\mathrm{NH_3}$).
- For each $\mathrm{H-F}$, $\mathrm{H-O}$, or $\mathrm{H-N}$ bond, the single hydrogen electron is shared with the other atom.





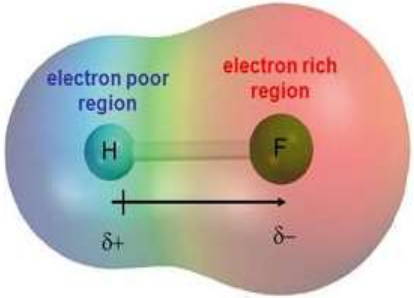
liquid water



solid ice

The single hydrogen electron is shared with the other atom.

Thus, the hydrogen end of the bond is essentially a positively charged bare proton unscreened by any electrons.



This highly positively charged end of the molecule is capable of a strong attractive force with the negative end of an adjacent molecule, as demonstrated in Figure for HF.

The magnitude of the hydrogen bond is generally greater than that of the other types of secondary bonds and may be as high as 51 kJ/mol, as shown in Table below.
Melting and boiling temperatures for hydrogen fluoride, ammonia, and water are abnormally high in light of their low molecular weights, as a consequence of hydrogen bonding.

Substance	*Bonding Energy (kJ/mol)*	*Melting Temperature (°C)*
	Hydrogen[a]	
HF	29	−83
NH_3	35	−78
H_2O	51	0

- In spite of the small energies associated with secondary bonds, they nevertheless are involved in a number of natural phenomena and many products that we use on a daily basis.
- Examples of physical phenomena include the solubility of one substance in another, surface tension and capillary action, vapor pressure, volatility, and viscosity.

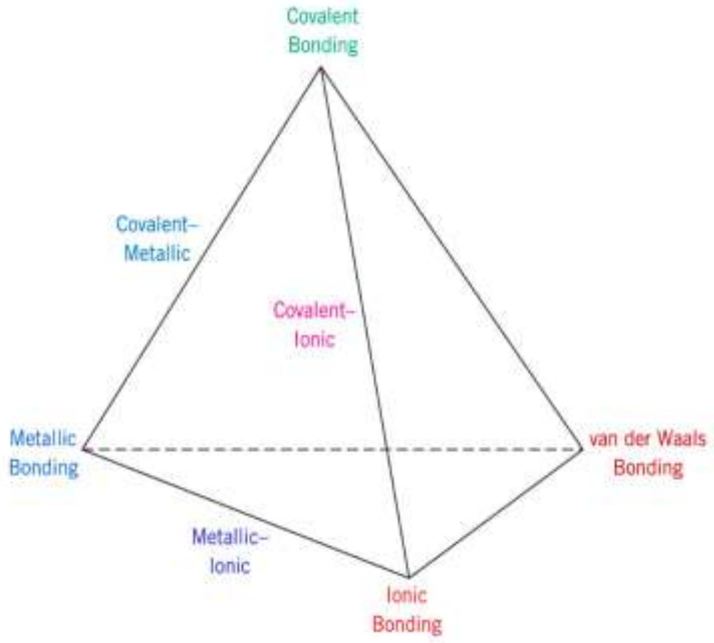
Common applications that make use of these phenomena include:

- adhesives—van der Waals bonds form between two surfaces so that they adhere to one another.
- surfactants—compounds that lower the surface tension of a liquid, and are found in soaps, detergents, and foaming agents;
- emulsifiers—substances that, when added to two immiscible materials (usually liquids), allow particles of one material to be suspended in another (common emulsions include sunscreens, salad dressings, milk, and mayonnaise)

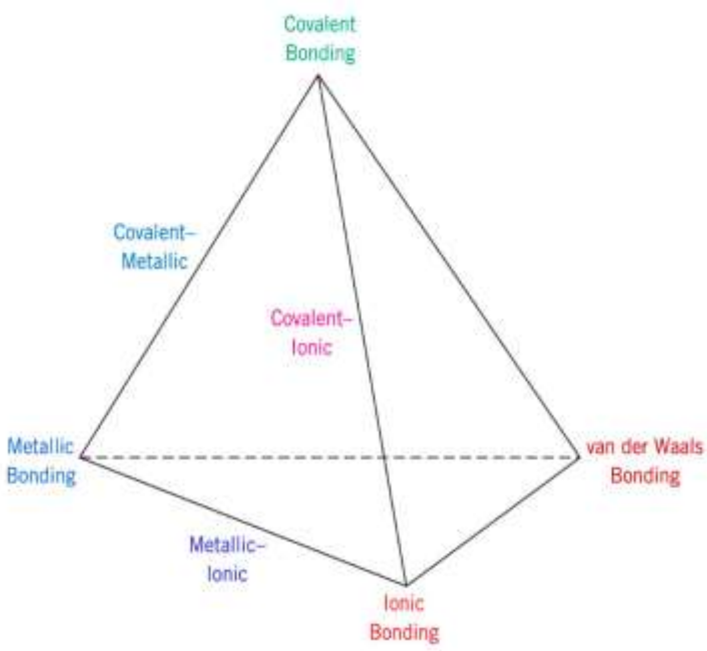
- desiccants—materials that form hydrogen bonds with water molecules (and remove moisture from closed containers—e.g., small packets that are often found in cartons of packaged goods)
- the strengths, stiffnesses, and softening temperatures of polymers, to some degree, depend on secondary bonds that form between chain molecules.

MIXED BONDING

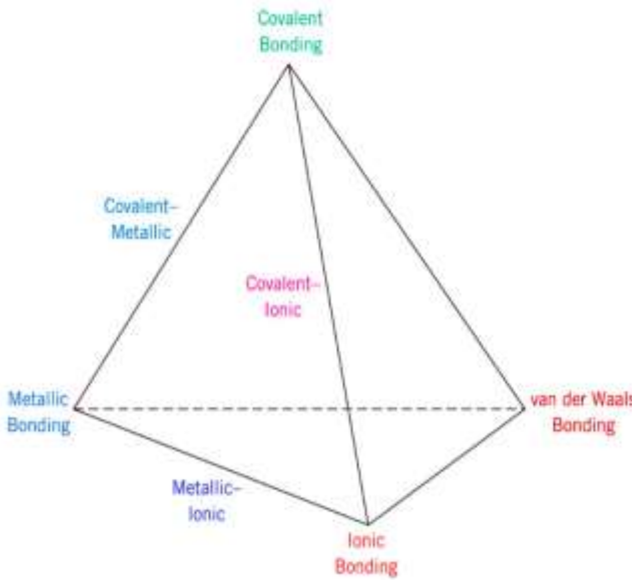
Sometimes it is illustrative to represent the four bonding types—ionic, covalent, metallic, and van der Waals—on what is called a bonding tetrahedron—a three-dimensional tetrahedron with one of these “extreme” types located at each vertex, as shown in Figure



- For many real materials, the atomic bonds are mixtures of two or more of these extremes (i.e., mixed bonds).
- Three mixed-bond types: covalent–ionic, covalent–metallic, and metallic–ionic are also included on edges of this tetrahedron;

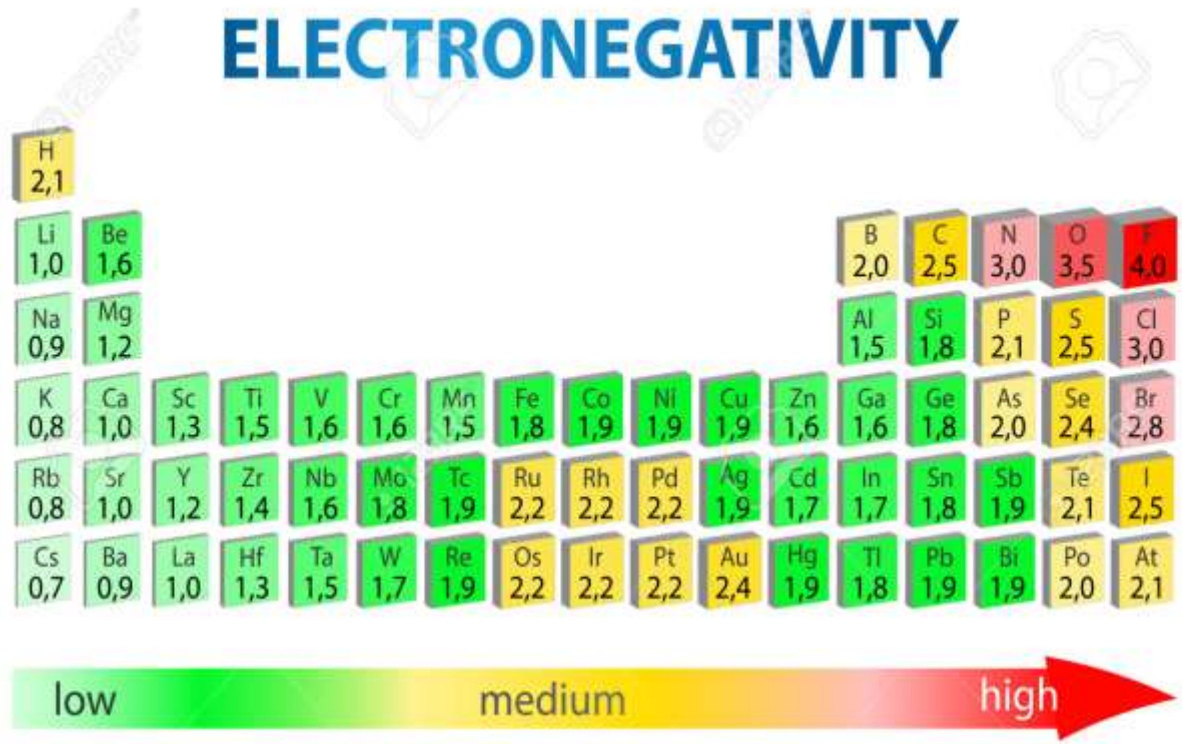


- For mixed covalent–ionic bonds, there is some ionic character to most covalent bonds and some covalent character to ionic ones. As such, there is a continuum between these two extreme bond types.
- This type of bond is represented between the ionic and covalent bonding vertices.

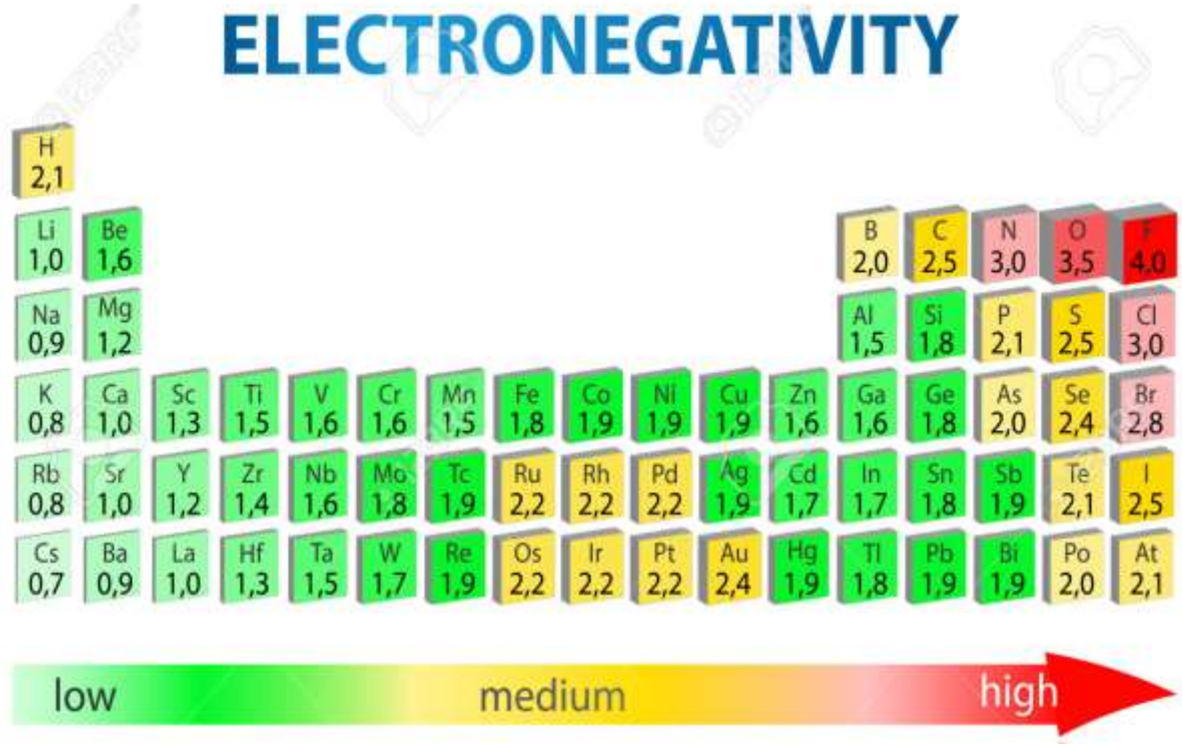


- The degree of either bond type depends on the relative positions of the constituent atoms in the periodic table or the difference in their electronegativities.

The wider the separation from the lower left to the upper right corner (i.e., the <u>greater the difference</u> in electronegativity), the more <u>ionic</u> is the bond.



Conversely, the closer the atoms are together (i.e., the smaller the difference in electronegativity), the greater is the degree of covalency.

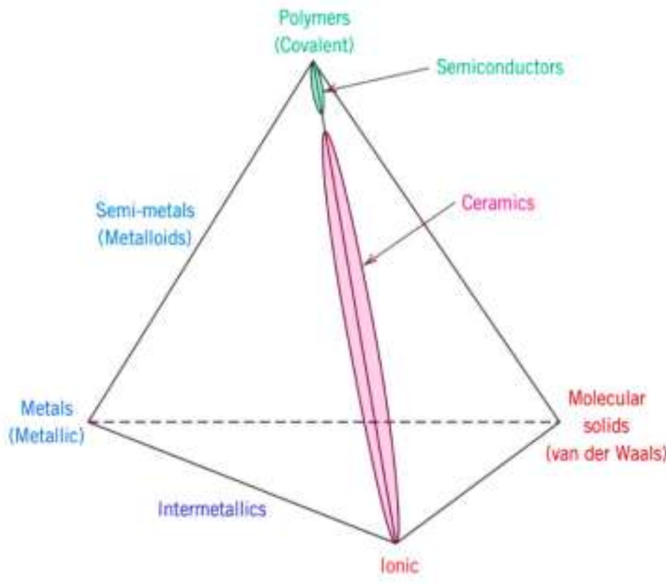


Percent ionic character (%IC) of a bond between elements A and B (A being the most electronegative) may be approximated by the expression

$$\%\mathrm{IC} = \left\{1 - e^{\left[-(0.25)(X_A - X_B)^2\right]}\right\} \times 100 \qquad \ldots\ldots\ldots (2.16)$$

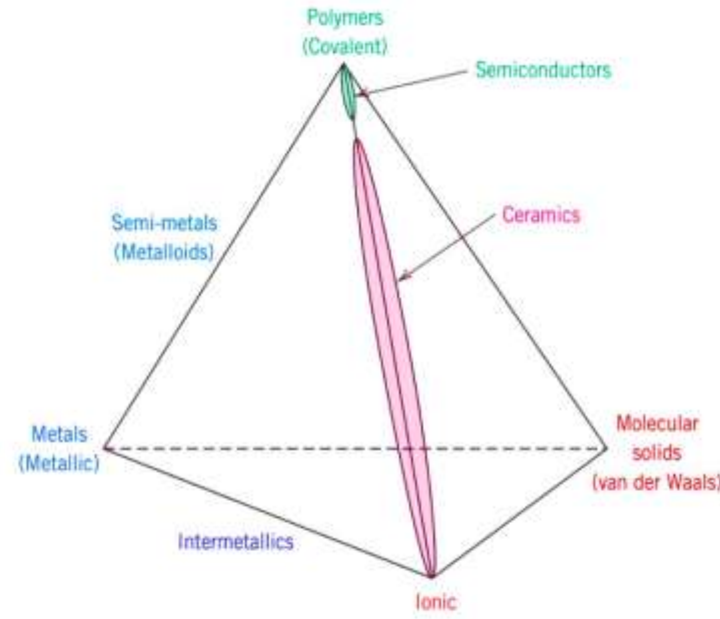
where X_A and X_B are the electronegativities for the respective elements.

- Another type of mixed bond is found for some elements in Groups IIIA, IVA, and VA of the periodic table (viz., B, Si, Ge, As, Sb, Te, Po, and At).
- Interatomic bonds for these elements are mixtures of metallic and covalent.
- These materials are called the metalloids or semi-metals, and their properties are intermediate between the metals and nonmetals.



- For Group IV elements, there is a gradual transition from covalent to metallic bonding as one moves vertically down this column
- For example, bonding in carbon (diamond) is purely covalent, whereas for tin and lead, bonding is predominantly metallic.

- Mixed metallic–ionic bonds are observed for compounds composed of two metals when there is a significant difference between their electronegativities.
- This means that some electron transfer is associated with the bond inasmuch as it has an ionic component.
- The larger this electronegativity difference, the greater the degree of ionicity.



For example, there is little ionic character to the titanium–aluminum bond for the intermetallic compound $\mathrm{TiAl_3}$ because electronegativities of both Al and Ti are the same 1.5.
However, a much greater degree of ionic character is present for $\mathrm{AuCu_3}$; the electronegativity difference for copper and gold is 0.5.

MOLECULES

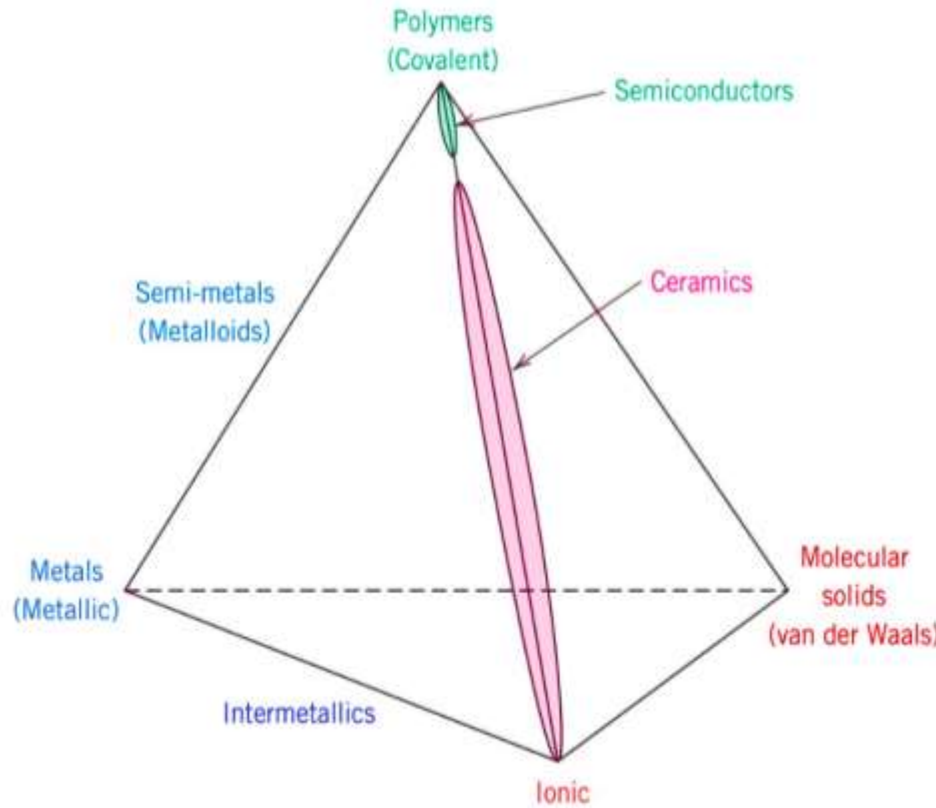
- Many common molecules are composed of groups of atoms bound together by strong covalent bonds, including
  - diatomic molecules (F_2, O_2, H_2, etc.)
  - compounds (H_2O, CO_2, HNO_3, C_6H_6, CH_4, etc.).
- In the condensed liquid and solid states, bonds between molecules are weak secondary ones. Consequently, molecular materials have relatively low melting and boiling temperatures.

- Most materials that have small molecules composed of a few atoms are gases at ordinary, or ambient, temperatures and pressures.
- However, many modern polymers, being molecular materials composed of extremely large molecules, exist as solids; some of their properties are strongly dependent on the presence of van der Waals and hydrogen secondary bonds.

BONDING TYPE-MATERIAL CLASSIFICATION CORRELATIONS

Some correlations have been drawn between bonding type and material classification—namely, ionic bonding (ceramics), covalent bonding (polymers), metallic bonding (metals), and van der Waals bonding (molecular solids).

- these correlations in the material type tetrahedron are summarized as shown in Figure
- the predominant bonding type for semiconducting materials is covalent, with the possibility of an ionic contribution.



Thank you for your attention

?