

CH. 1: Structure of atoms:

Each atom consists of a very small nucleus composed of protons and neutrons, electrons moving around the nucleus.

Atoms = nucleus (protons and neutrons) + electrons

Charges:

- ✓ Electrons and protons have negative and positive charges of the same magnitude, 1.6×10^{-19} Coulombs.
- ✓ Neutrons are electrically neutral.

Masses:

- ❖ Protons and Neutrons have the same mass, 1.67×10^{-27} kg.
- ❖ Mass of an electron is much smaller, 9.11×10^{-31} kg and can be neglected in calculation of atomic mass.

- protons gives chemical identification of the element
- Each chemical element is characterized by the number of protons in the nucleus, or the **atomic number (Z)**.
- This atomic number ranges in integral units from 1 for hydrogen to 92 for uranium
- **protons = atomic number (Z)**

- The **atomic mass (A)** of a specific atom may be expressed as the sum of the masses of protons and neutrons within the nucleus.
- **The atomic mass (A)** = mass of protons + mass of neutrons
- Atoms of some elements have two or more different atomic masses, which are called **isotopes**
- neutrons defines isotope number

The bonding mechanisms between atoms are closely related to the structure of the atoms themselves.

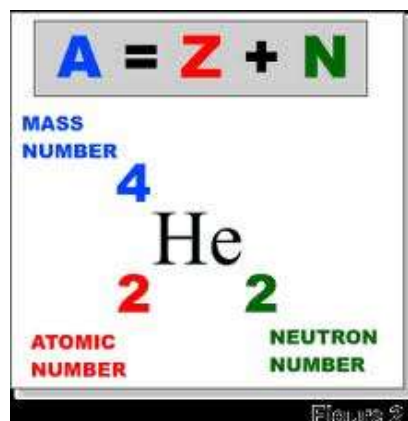


Figure 2

Atomic mass units. Atomic weight.

- **The atomic mass unit (amu)** is often used to express atomic weight.
- 1 amu is defined as 1/12 of the atomic mass of the most common isotope of carbon atom that has 6 protons ($Z=6$) and six neutrons ($N=6$).
- $M_{\text{proton}} \approx M_{\text{neutron}} = 1.66 \times 10^{-24} \text{ g} = 1 \text{ amu}$.
- The atomic mass of the ^{12}C atom is 12 amu.
- **The atomic weight of an element** = weighted average of the atomic masses of the atoms naturally occurring isotopes.
- Atomic weight of carbon is 12.011 amu.
- The atomic weight is often specified in mass per mole.
- **A mole** is the amount of matter that has a mass in grams equal to the atomic mass in amu of the atoms (A mole of carbon has a mass of 12 grams).
- A mole is the amount of matter that has 6.032×10^{23} (Avogadro's number) atoms or molecules,

1 amu/atom = 1 gram/mol

Example:

Atomic weight of iron = 55.85 amu/atom = 55.85 g/mol

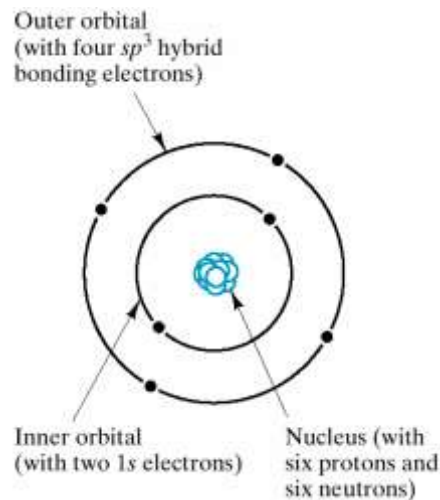
The number of atoms per cm^3 , n , for material of density d (g/cm^3) and atomic mass M (g/mol):

- $n = N_{\text{av}} \times d / M$
Graphite (carbon): $d = 2.3 \text{ g/cm}^3$, $M = 12 \text{ g/mol}$
 $n = 6 \times 10^{23} \text{ atoms/mol} \times 2.3 \text{ g/cm}^3 / 12 \text{ g/mol} = 11.5 \times 10^{22} \text{ atoms/cm}^3$
- Diamond (carbon): $d = 3.5 \text{ g/cm}^3$, $M = 12 \text{ g/mol}$
 $n = 6 \times 10^{23} \text{ atoms/mol} \times 3.5 \text{ g/cm}^3 / 12 \text{ g/mol} = 17.5 \times 10^{22} \text{ atoms/cm}^3$
- Water (H_2O) $d = 1 \text{ g/cm}^3$, $M = 18 \text{ g/mol}$
 $n = 6 \times 10^{23} \text{ molecules/mol} \times 1 \text{ g/cm}^3 / 18 \text{ g/mol} = 3.3 \times 10^{22} \text{ molecules/cm}^3$
- For material with $n = 6 \times 10^{22} \text{ atoms/cm}^3$ we can calculate mean distance between atoms $L = (1/n)^{1/3} = 0.25 \text{ nm}$.
- The scale of atomic structures in solids – a fraction of 1 nm or a few Å.

Electrons in Atoms (I)

The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.

This picture looks like a mini planetary system. But quantum mechanics tells us that this analogy is not correct:



Electrons move not in circular orbits, but in fuzzy orbits. Actually, we cannot tell how it moves, but only can say what is the probability of finding it at some distance from the nucleus.

Only certain “orbits” or shells of electron probability densities are allowed. The shells are identified by:

- Quantum Numbers - each electron characterised by four parameters; the size, shape and special orientation of an electron’s probability density are specified by three of these quantum numbers.
- A **principal quantum number n** , which can be related to the size of the shell, $n = 1$ is the smallest; $n = 2, 3, \dots$ are larger. ($n=1, 2, 3, 4, 5 \dots$ or $K, L, M, N, O \dots$)
- **The second quantum number l** , defines subshells within each shell. Which is denoted by a lowercase letter—an $s, p, d,$ or f
- The number of these subshells is restricted by the magnitude of n .
- The number of energy states for each subshell is determined by the third quantum number,
- For an s subshell, there is a single energy state,
- whereas for $p, d,$ and f subshells, three, five, and seven states exist, respectively
- In the absence of an external magnetic field, the states within each subshell are identical.
- However, when a magnetic field is applied these subshell states split, each state assuming a slightly different energy.
- Fourth quantum number define associated spin moment of electron $+1/2$ or $-1/2$ orientation (up or down)

Electrons in Atoms (II)

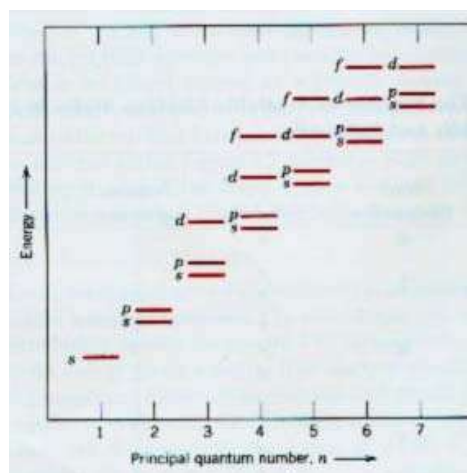
- The quantum numbers arise from solution of Schrodinger's equation
- Pauli Exclusion Principle: only one electron can have a given set of the four quantum numbers.

The number of available states in electron shells & subshells

Principal Q. N., n	Subshells	Number of States	Number of Electrons Per Subshell	Per Shell	
1 (l=0)	s	1	2	2	K-shell
2 (l=0)	s	1	2	8	L-shell
2 (l=1)	p	3	6		
3 (l=0)	s	1	2	18	M-shell
3 (l=1)	p	3	6		
3 (l=2)	d	5	10		
4 (l=0)	s	1	2	32	N-shell
4 (l=1)	p	3	6		
4 (l=2)	d	5	10		
4 (l=3)	f	7	14		

- Each "orbit" or shell can accommodate only a maximum number of electrons, which is determined by quantum mechanics.
- In brief, the most inner *K-shell* can accommodate only two electrons, called *s-electrons*;
- the next *L-shell* two *s-electrons* and six *p-electrons*;
- the *M-shell* can host two *s-electrons*, six *l electrons*,
- and ten *d-electrons*; and so on.

Electrons in Atoms (III)



- Electrons that occupy the outermost filled shell – **the valence electrons** – they are responsible for bonding.
- Electrons fill quantum levels in order of increasing energy (only n, l make a significant difference).

Examples: Argon, Z = 18: $1s^2 2s^2 2p^6 3s^2 3p^6$

Iron, Z = 26: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Subshells by energy: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4s, 4p, 5s, 4d, 5p, 6s, 4f, \dots$

Electrons in Atoms (IV)

- Electron configurations where all states within valence electron shell are filled are stable → unreactive inert or noble gas.

Periodic Table:

The first accepted periodic table of elements was published in 1869 by Mendeleev. In the same year, a German chemist Lothar Meyer independently published a very similar table, but his contribution is generally ignored. All elements in the periodic table have been classified **according to the electron configuration**.

Periodic Table

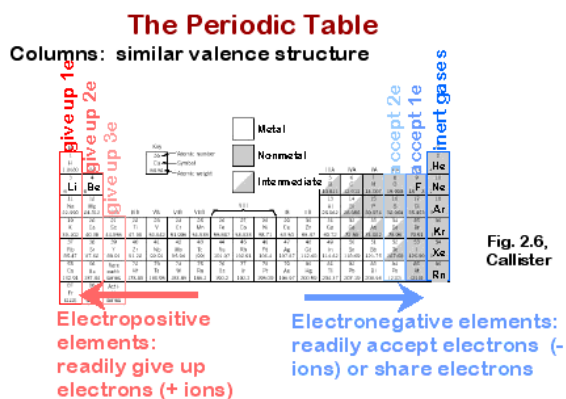


Fig. 2.6, Callister

- Group IA : Give up 1 electron,
- Group IIA: Give up 2 electrons,
- Group VIIA: Accept 1 electron,
- Group VIA : Accept 2 electrons.

Elements in the same column (Elemental Group) share similar properties.

Group number indicates the number of electrons available for bonding.

0: Inert gases (He, Ne, Ar...) have filled subshells: chemically inactive

IA: Alkali metals (Li, Na, K...) have one electron in outermost occupied s subshell - eager to give up electron – chemically active

VIIA: Halogens (F, Br, Cl...) missing one electron in outermost occupied p shell
- want to gain electron - chemically active

Electropositive elements: Readily give up electrons to become + ions.

Electronegative elements: Readily acquire electrons to become - ions.

Periodic Table – Electronegativity

Electronegativity - a measure of how willing atoms are to accept electrons

Subshells with one electron → low electronegativity
Subshells with one missing electron → high electronegativity.

Metals are electropositive – they can give up their few valence electrons to become positively charged ions.

The electron volt (eV) – energy unit convenient for description of atomic bonding

Electron volt - the energy lost / gained by an electron when it is taken through a potential difference of one volt.

$$E = q \times V$$

for $q = 1.6 \times 10^{-19}$ Coulombs and $V = 1$ volt

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

The electronic structure of atoms defines the character of their interaction among each other. Filled outer shells result in a stable configuration as in noble inert gases. Atoms with incomplete outer shells strive to reach this noble gas configuration by sharing or transferring electrons among each other for maximal stability. Strong “**primary**” bonding results from the electron sharing or transfer.

Types of Bonding:

Primary bonding: e- are transferred or shared

Strong (100-1000 KJ/mol or 1-10 eV/atom)

- Ionic: Strong Coulomb interaction among negative atoms (have an extra electron each) and positive atoms (lost an electron). Example - Na^+Cl^-
- Covalent: electrons are shared between the molecules, to saturate the valency. Example - H_2
- Metallic: the atoms are ionized, losing some electrons from the valence band. Those electrons form an electron sea, which binds the charged nuclei in place.

Secondary Bonding: no e- transferred or shared

Interaction of atomic/molecular dipoles

Weak (< 100 KJ/mol or < 1 eV/atom)

- Fluctuating Induced Dipole (inert gases, H₂, Cl₂...)
- Permanent dipole bonds (polar molecules - H₂O, HCl...)
- Polar molecule-induced dipole bonds (a polar molecule induces a dipole in a nearby nonpolar atom/molecule)

Ionic Bonding (I)

Ionic Bonding: is typical for elements that are situated at the horizontal extremities of the periodic table.

Atoms from the left (metals) are ready to give up their valence electrons to the (non-metallic) atoms from the right that are happy to get one or a few electrons to acquire stable or noble gas electron configuration.

As a result of this transfer mutual ionization occurs:

Atom that gives up electron(s) becomes positively charged ion (*cation*),

Atom that accepts electron(s) becomes negatively charged ion (*anion*).

Formation of ionic bond:

1. Mutual ionization occurs by electron transfer

- Ion = charged atom
- Anion = negatively charged atom
- Cation = positively charged atom

2. Ions are attracted by strong columbic interaction

- Oppositely charged atoms attract each other
- An ionic bond is non-directional (ions may be attracted to one another in any direction)

Ionic Bonding (II)

Example: (NaCl)

Na has 11 electrons, 1 more than needed for a full outer shell (Neon)

Cl has 17 electrons, 1 less than needed for a full outer shell (Argon)

11 Protons Na 1S₂ 2S₂ 2P₆ 3S₁ donates electron

11 Protons Na⁺ 1S₂ 2S₂ 2P₆ 10 electrons left

17 Protons Cl 1S₂ 2S₂ 2P₆ 3S₂ 3P₅ receives electrons

17 Protons Cl⁻ 1S₂ 2S₂ 2P₆ 3S₂ 3P₆ 18 electrons

- Electron transfer reduces the energy of the system of atoms
- Note relative sizes of ions: Na shrinks and Cl expands

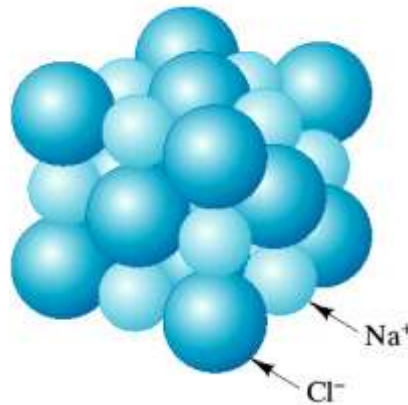
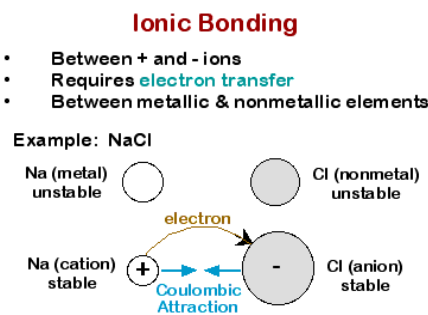
Ionic Bonding (III)

Ionic bonds: very strong, non directional bonds: that is, the magnitude of the bond is equal in all directions around an ion.

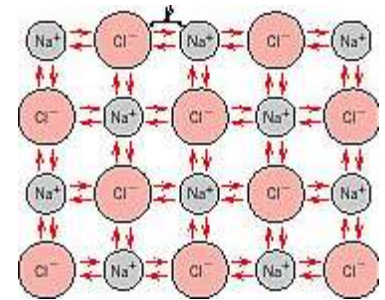
A strong electrostatic attraction between positively charged Na^+ ions and negatively charged Cl^- atoms along with $\text{Na}^+ - \text{Na}^+$ and $\text{Cl}^- - \text{Cl}^-$ repulsion result in the NaCl crystal structure which is arranged so that each sodium ion is surrounded by Cl^- ions .

Any mechanical force that tries to disturb the electrical balance in an ionic crystal meets strong resistance: **ionic materials are strong and brittle.**

In some special cases, however, significant plastic deformation can be observed, e.g. NaCl single crystals can be bent by hand in water.



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Examples: Ionic Bonding

- Predominant bonding in ceramics

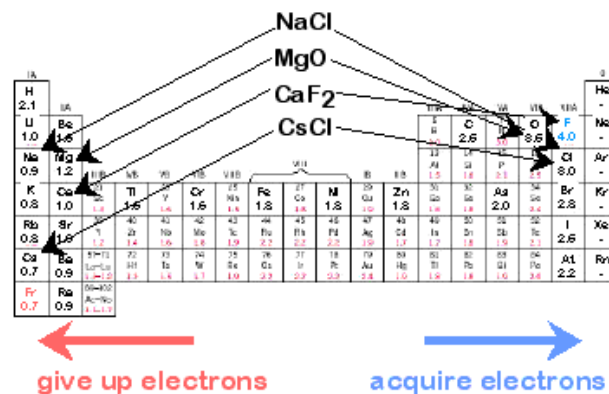


Fig. 2.7 Callister

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Covalent Bonding (I)

In covalent bonding, electrons are *shared* between the molecules, to saturate the valency. In this case the electrons are not transferred as in the ionic bonding, but they are localized between the neighboring ions and form *directional* bond between them. The ions repel each other, but are attracted to the electrons that spend most of the time in between the ions.

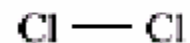
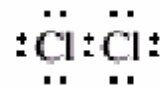
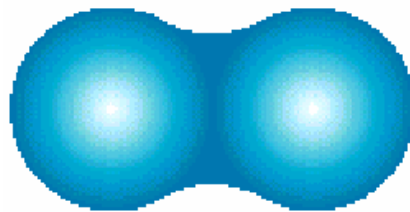
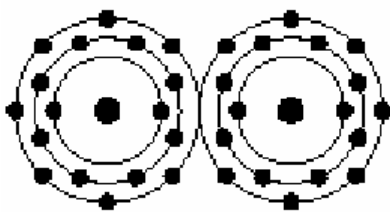
Many nonmetallic elemental molecules (H₂, Cl₂, F₂, etc.) as well as molecules containing dissimilar atoms, such as CH₄, H₂O, HNO₃, and HF, are covalently bonded.

Formation of covalent bonds:

- Cooperative sharing of valence electrons
- Can be described by orbital overlap
- Covalent bonds are *highly directional*
- Bonds - in the direction of the greatest orbital overlap
- Covalent bond model: an atom can covalently bond with at most $8 - N'$, $N' =$ number of valence electrons.

Example: Cl₂ molecule. $Z_{Cl} = 17$ ($1S^2 2S^2 2P^6 3S^2 3P^5$)

$N' = 7, 8 - N' = 1 \rightarrow$ can form only one covalent bond



Examples: Covalent Bonding

Covalent Bonding

- Requires shared electrons

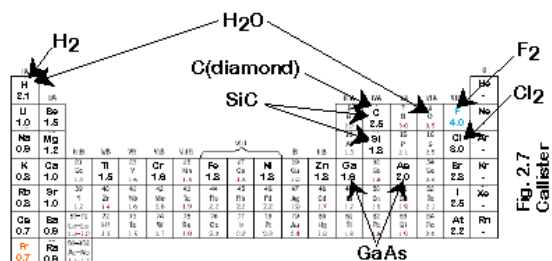
Example: CH₄

C: has 4 valence e⁻, needs 4 more

H: has 1 valence e⁻, needs 1 more

Electronegativities are comparable

Fig. 2.10 Callister



- Molecules w/nonmetals: H₂, Cl₂, F₂
- Molecules w/metals & nonmetals: H₂O, CH₄, HF
- Elemental solids (RHS of PT): C(diamond), Si, Ge
- Compound solids (about IVA): SiC, GaAs, BN, CdTe

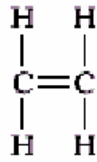
Anderson 2005- 2-10

Covalent Bonding (II)

Example: Carbon materials. $Z_c = 6$ ($1S^2 2S^2 2P^2$)

$N^v = 4, 8 - N^v = 4 \rightarrow$ can form up to four covalent bonds

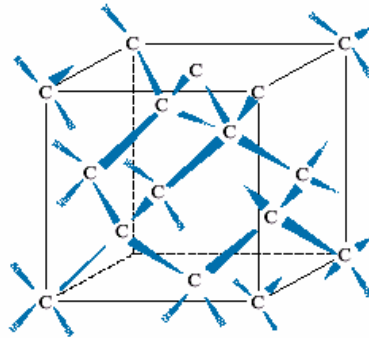
Ethylene molecule:



Diamond:

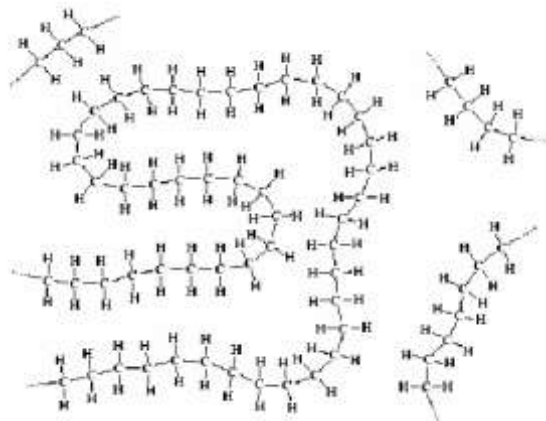
(Each C atom has four covalent bonds with four other carbon atoms)

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).

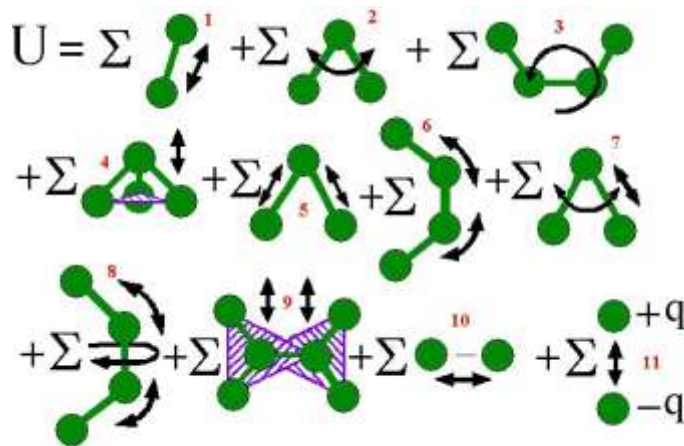


Covalent Bonding (III)

2-D schematic of the “spaghetti-like” structure of solid polyethylene



The potential energy of a system of covalently interacting atoms depends not only on the distances between atoms, but also on angles between bonds...



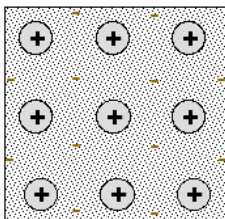
Metallic Bonding:

The final primary bonding type is found in metals and their alloys. Valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the positive ions together.

- A metallic bond is non-directional (bonds form in any direction) → atoms pack closely

Metallic Bonding

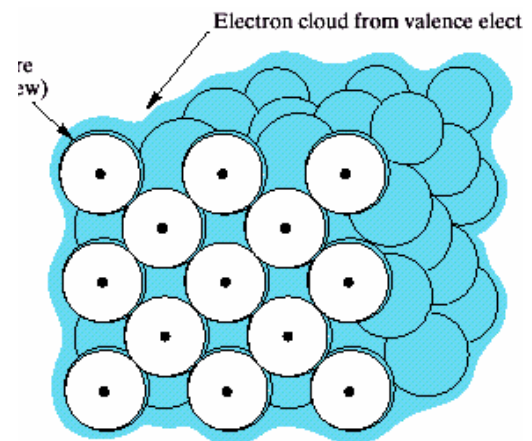
- Arises from sea of donated valence electrons (1, 2, or 3 from each atom)



- Primary bond for metals and their alloys

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Ion core



The "bonds" do not "break" when atoms are rearranged – metals can experience a significant degree of plastic deformation.

Metallic materials have one, two, or at most, three valence electrons.

Examples of typical metallic bonding: Cu, Al, Au, Ag, etc.

Transition metals (Fe, Ni, etc.) form mixed bonds that comprise of metallic bonds and covalent bonds involving their 3d-electrons. As a result the transition metals are more brittle (less ductile) than Au or Cu.

Bonding may be weak or strong; energies range from 68 kJ/mol (0.7 eV/atom) for mercury to 850 kJ/mol (8.8 eV/atom) for tungsten.

Secondary Bonding (I)

Secondary = van der Waals = physical (as opposite to chemical bonding that involves e- transfer) bonding results from interaction of atomic or molecular dipoles and is weak, ~ 0.1 eV/atom or ~ 10 kJ/mol.

Permanent dipole moments exist in some molecules (*called polar molecules*) due to the asymmetrical arrangement of positively and negatively regions (HCl, H₂O).

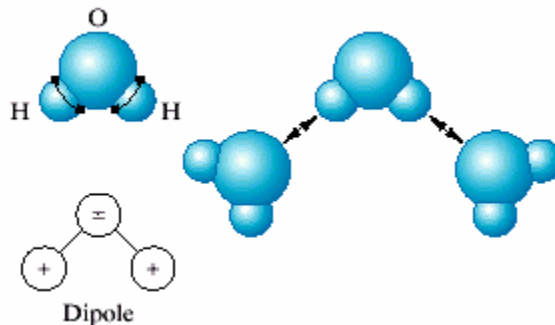
Bonds between adjacent polar molecules – *permanent dipole bonds* – are the strongest among secondary bonds.

Polar molecules can *induce* dipoles in adjacent non-polar molecules and bond is formed due to the *attraction between the permanent and induced dipoles*.

Even in electrically symmetric molecules/atoms an electric dipole can be created by fluctuations of electron density distribution. Fluctuating electric field in one atom A is felt by the electrons of an adjacent atom, and induces a dipole momentum in this atom. *This bond due to fluctuating induced dipoles is the weakest (inert gases, H₂, Cl₂).*

Secondary Bonding (II)

Example: hydrogen bond in water. The H end of the molecule is positively charged and can bond to the negative side of another H₂O molecule (the O side of the H₂O dipole)

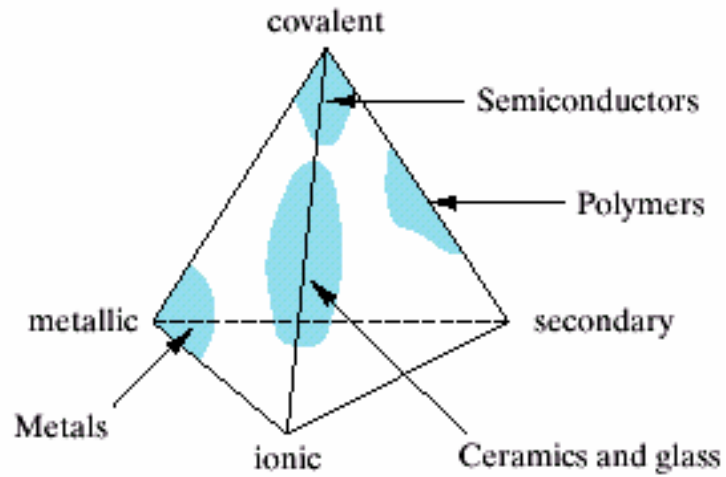


“Hydrogen bond”
formed between
dipoles in adjacent water molecules.

– secondary bond
two **permanent**

Bonding in real materials

In many materials more than one type of bonding is involved
Ionic and covalent in ceramics,
Covalent and secondary in polymers,
Covalent and ionic in semiconductors.



Examples of bonding in Materials:

Metals: Metallic

Ceramics: Ionic / Covalent

Polymers: Covalent and Secondary

Semiconductors: Covalent or Covalent / Ionic