Welcome to APS104S – Introduction to Materials & Chemistry

Lecture 3

January 8, 2016

Instructor: Gisele Azimi

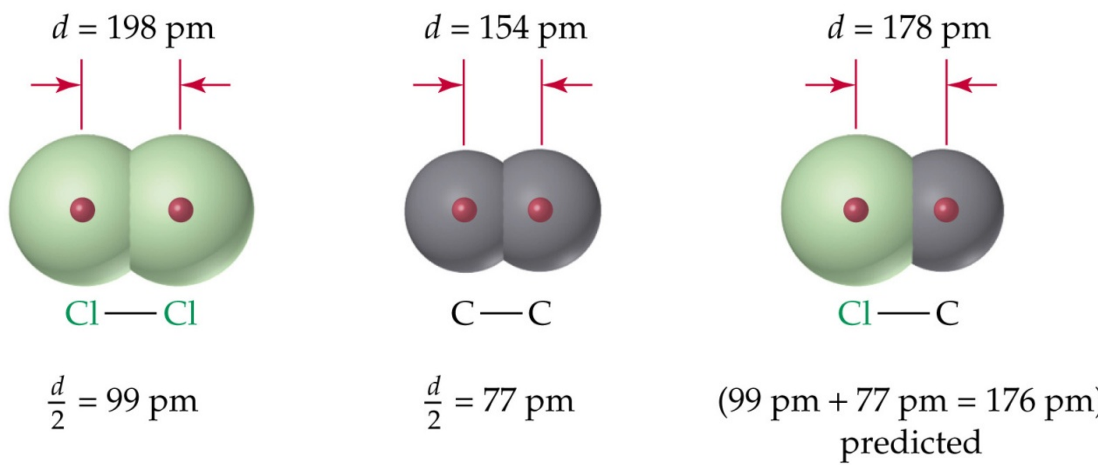
Subjects we will study today

- Atomic and ionic radii
- Bond formation
- Primary interatomic bonding
- Secondary bonding

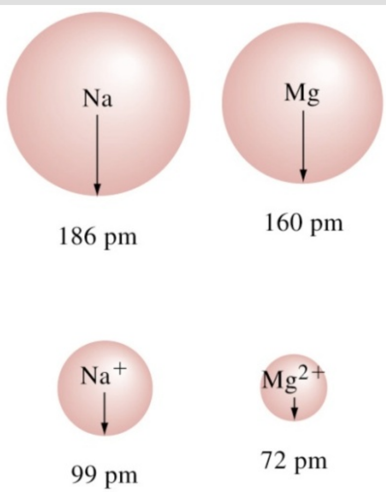
Atomic and ionic radii

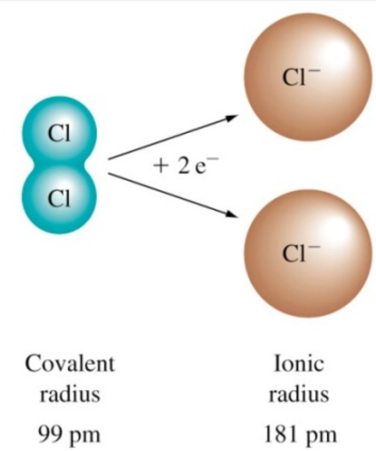
Atomic Radii

Atomic radius is half the distance between the nuclei of two identical atoms when they are bonded together.



A comparison of atomic and ionic sizes





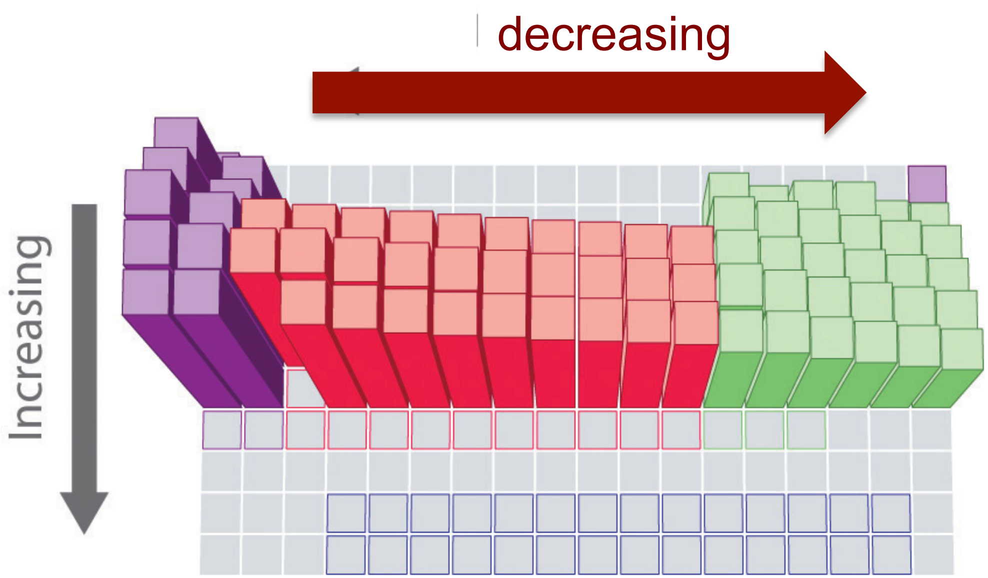
In general all **cations** are **smaller** than their **parent atoms**.

In general all **anions** are **larger** than their **parent atoms**.

Periodic trend in atomic radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, *chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions*. These values provide a way to compare the intrinsic sizes of all elements.

Because the number of shell are increasing



Calculated atomic radius (pm), *s*-, *p*-, and *d*-block elements

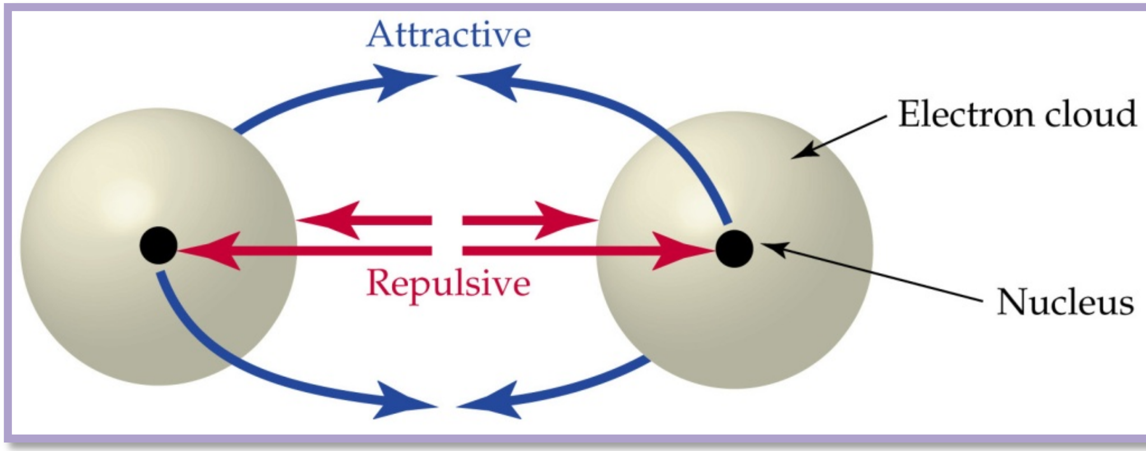
Because in a row, the number of shell is constant, but the numbers of protons is increasing from left to right → the effective nuclear charge (Z_{eff}) increases and the outer most electrons are more attracted to the nucleus → smaller atomic radii

Averill & Eldredge book

s block *p* block *d* block *f* block

Bond formation

Bond formation

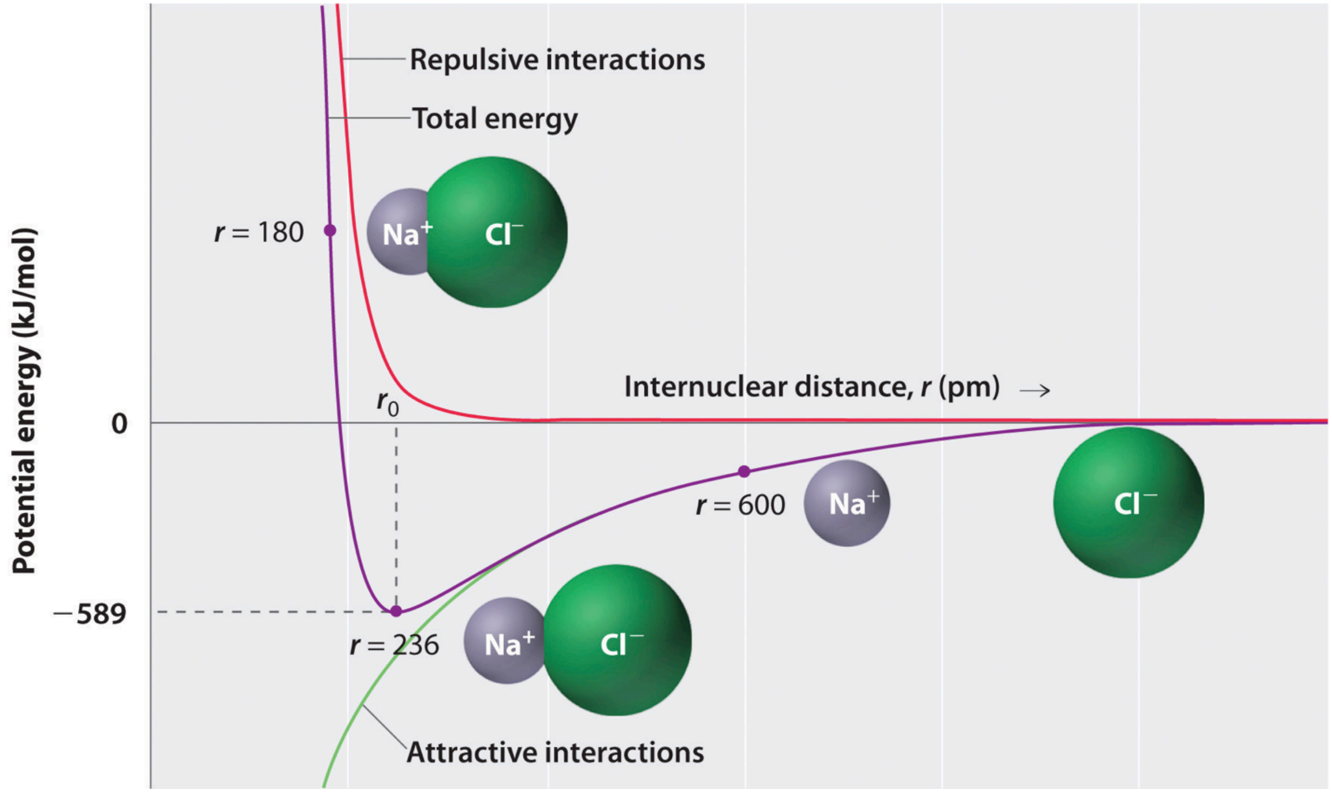


attractive forces = **repulsive forces**

bond formation

If the atoms are **too far apart**, attraction are weak and no bonding occurs.
If the atoms are **too close**, strong repulsions occur.
When atoms are **optimally separated**, net force is zero, and the energy is at a minimum → that's when bond forms.

Generic bonding curve



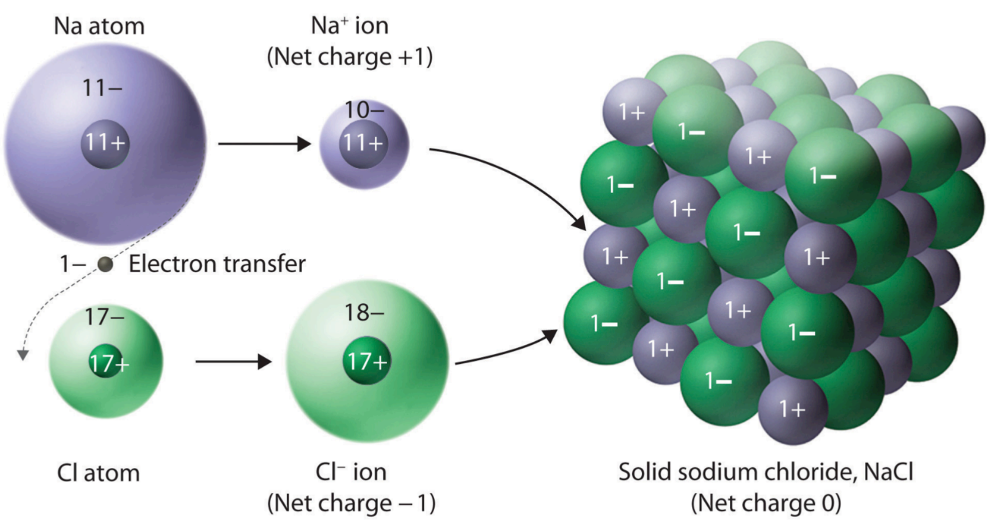
- At r_0, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).

Primary interatomic bonding (between atoms)

Primary interatomic bonds

1 - Ionic bonds – between metals and non-metals – the metal gives up its valence electron (cation) & the non-metal receives the electron (anion) – columbic interaction between positive and negative ions

Ionic bonds are **non-directional** – anions and cations pack closely together in mineral structures.



Ionic bonds

Properties (nature of ionic bonding in solids):

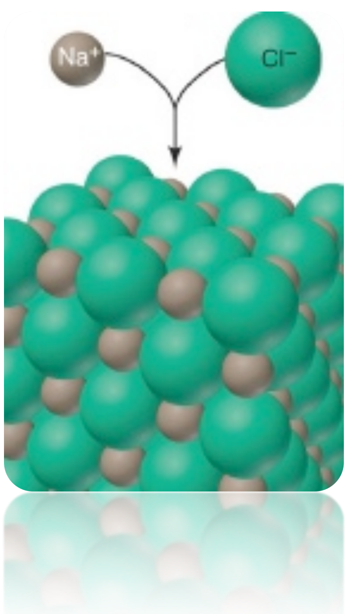
- Exchange of electron between the metal and non-metal
- Bonding energy high → high melting T
- Hard
- Brittle
- Electrically and thermally insulative (no free electrons)

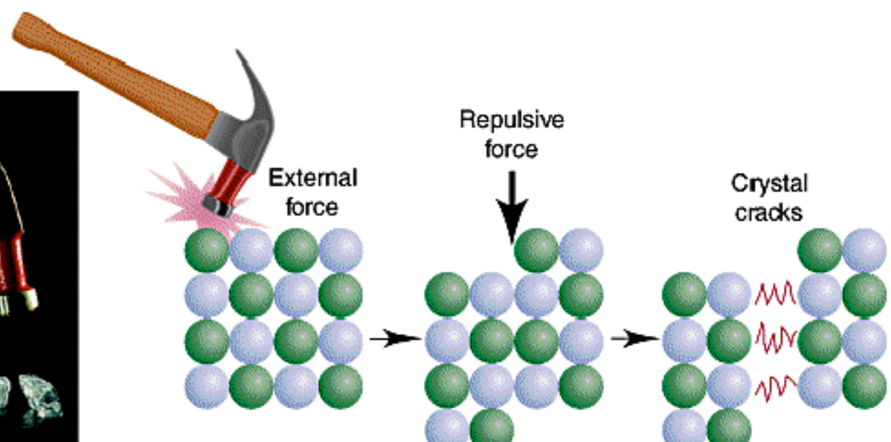
electrostatic attraction

high melting points

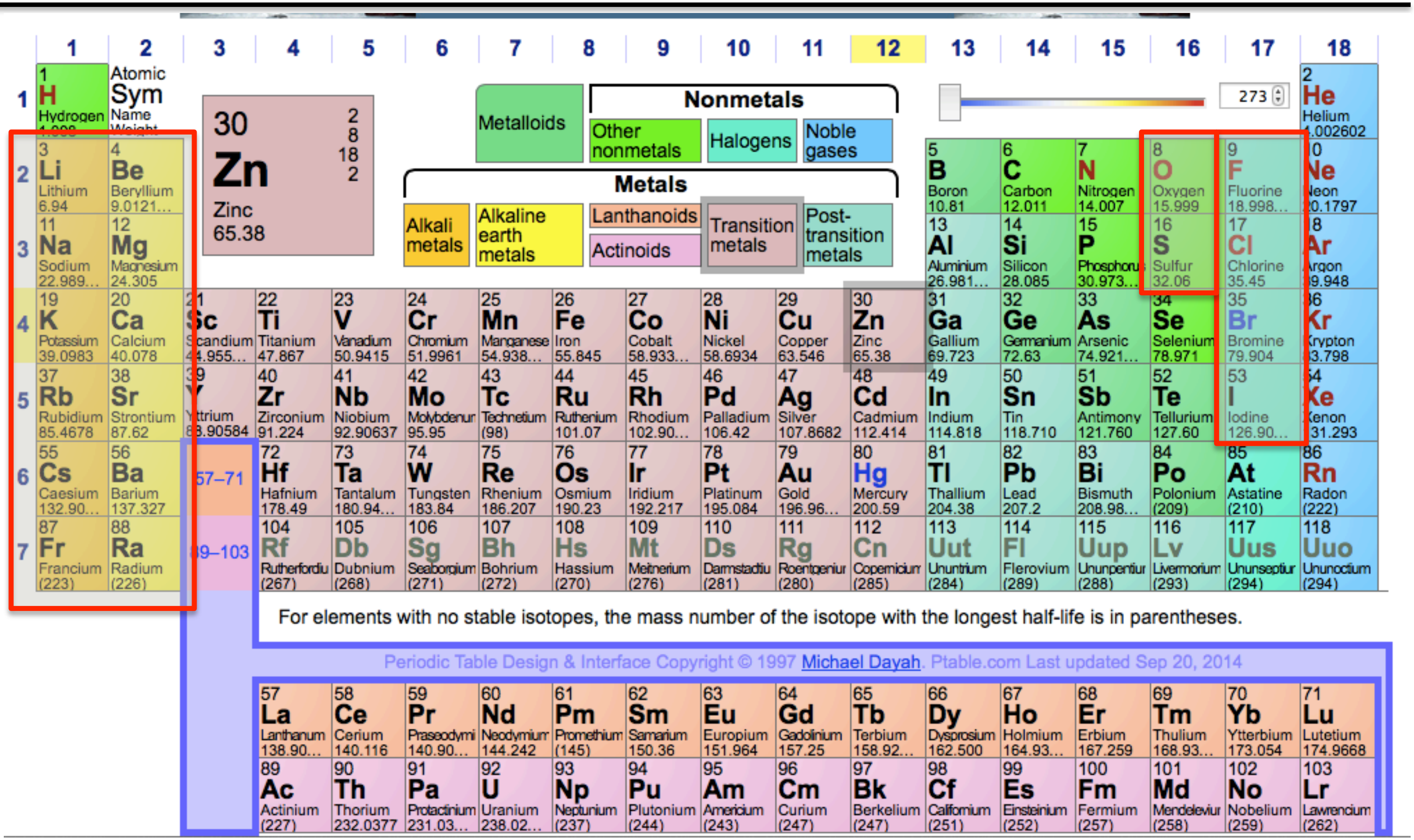
low electrical conductivity

in solid state, brittle, hard





Ionic bonds



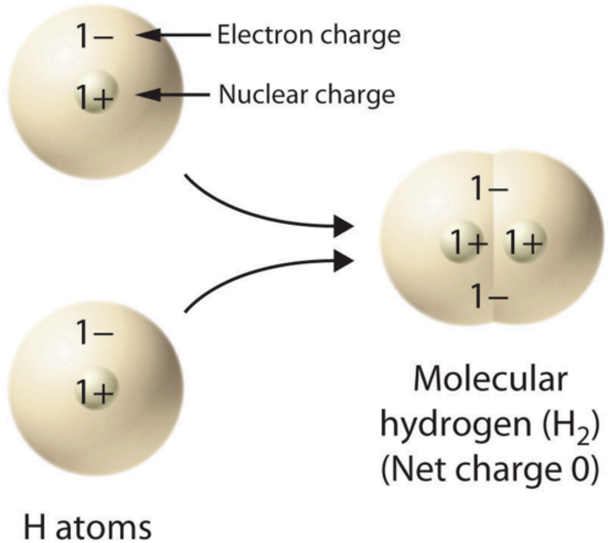
Usually between metals from column IA and IIA and non metals from VIA and VIIA

Examples: KCl, LiCl, LiBr, NaBr, BaS, CaO, CaF_2, Na_2S,CsF, MgS, …

http://www.ptable.com

Primary interatomic bonds

2 - Covalent bonds – due to sharing of valence electrons (usually between non metals)



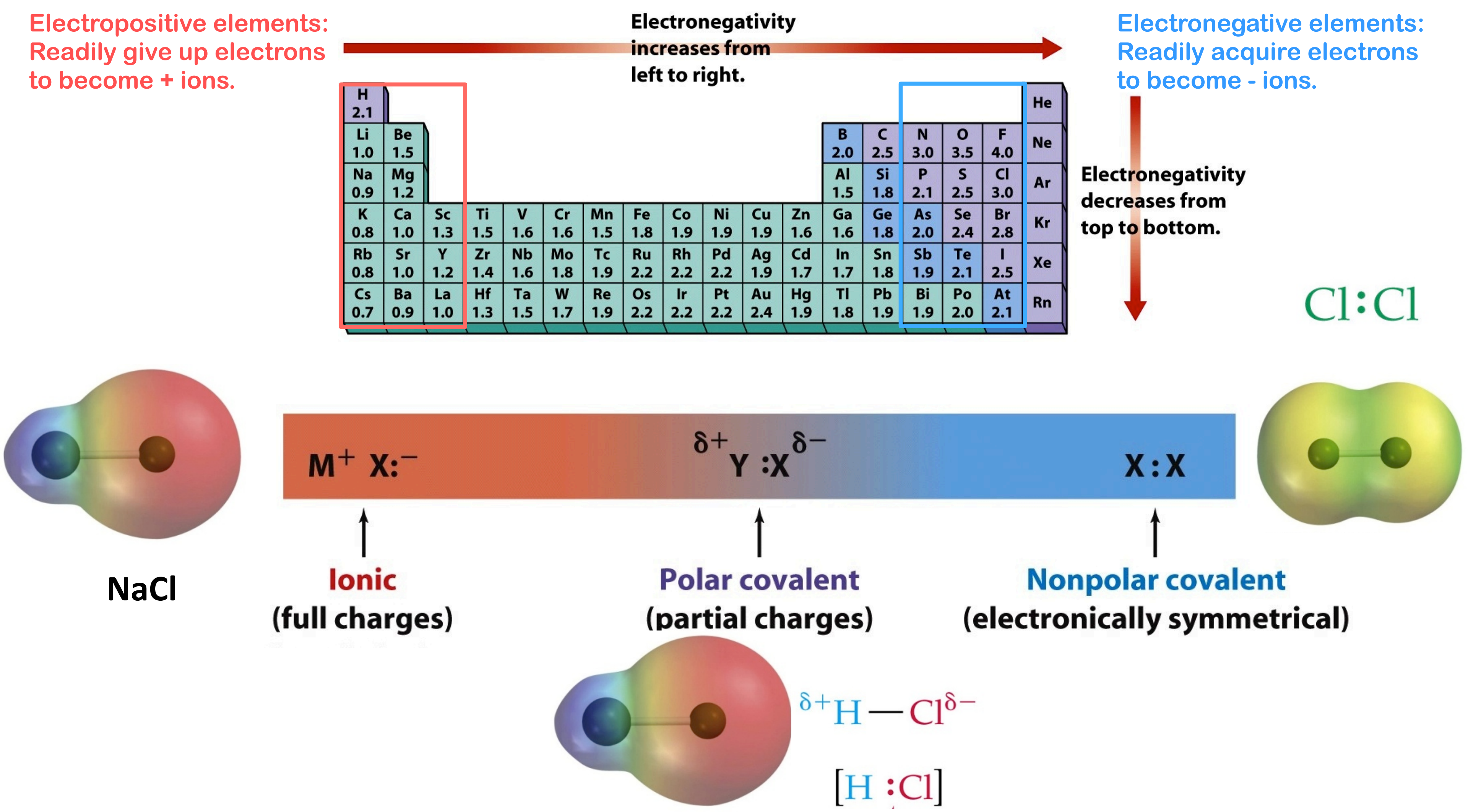
(a) Covalent bonding

Cl_2, H_2, F_2, N_2
CH_4, H_2O, HNO_3
Diamond
SiC
Most polymers (along carbon chains)

These materials can be very hard (like diamond) and can have very high melting T
They can also be weak and have low melting T

Polar covalent bonds: electronegativity

ELECTRONEGATIVITY: The ability of an atom in a molecule to attract the shared electrons in a covalent bond.



Primary interatomic bonds

3 - Metallic bonds – consists of metal cores (net positive charge) in a sea of free electrons – this bond is non-directional

Properties (nature of metallic bonding in solids):

- Electrically and thermally conductive (because of free electrons)
- They exists between all metals in the P-table
- Ductile (can deform significantly before fracturing (but ionic bonds are brittle))

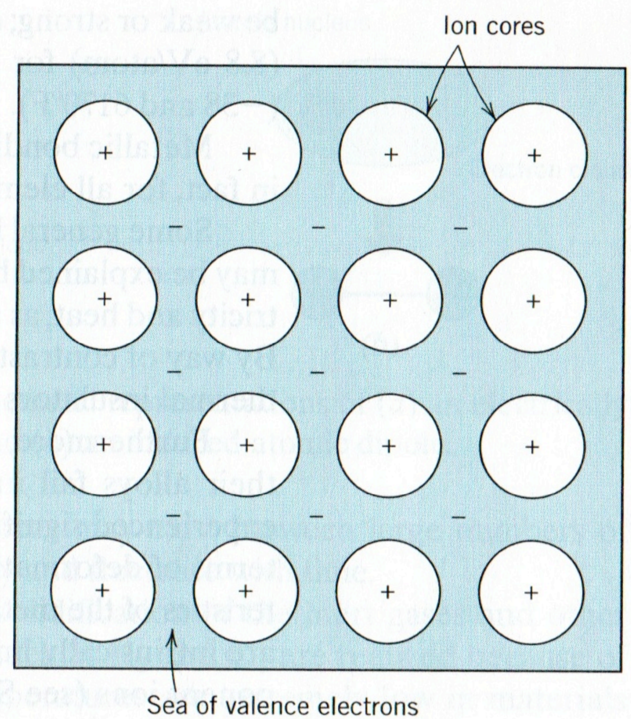


Figure 2.11 Schematic illustration of metallic bonding.

Summary:
Primary interatomic bonding
(between atoms)

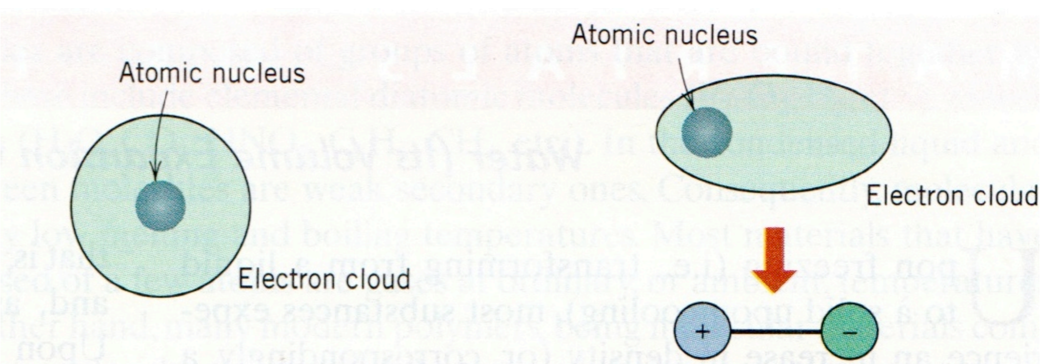
1. Ionic (electrostatic between cation & anion)
2. Covalent (electron sharing, stable electronic structure)
3. Metallic (positively charged ions, shielded from each other, kept together by a sea of e^-)

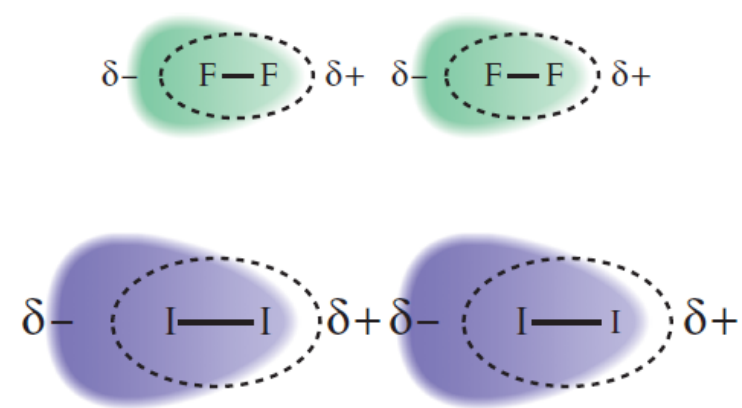
Secondary bonding (between molecules)

Secondary bonding

1. **Van der Waals bonds: Fluctuating induced dipole bonds** – an electrically symmetric molecule (non-polar) may loose its symmetry instantaneously and becomes dipole and induces this to its neighbor – then there will be attraction between these molecules (like noble gases, Cl_2, H_2)

Melting T and boiling T are very low; the weakest type of bonding

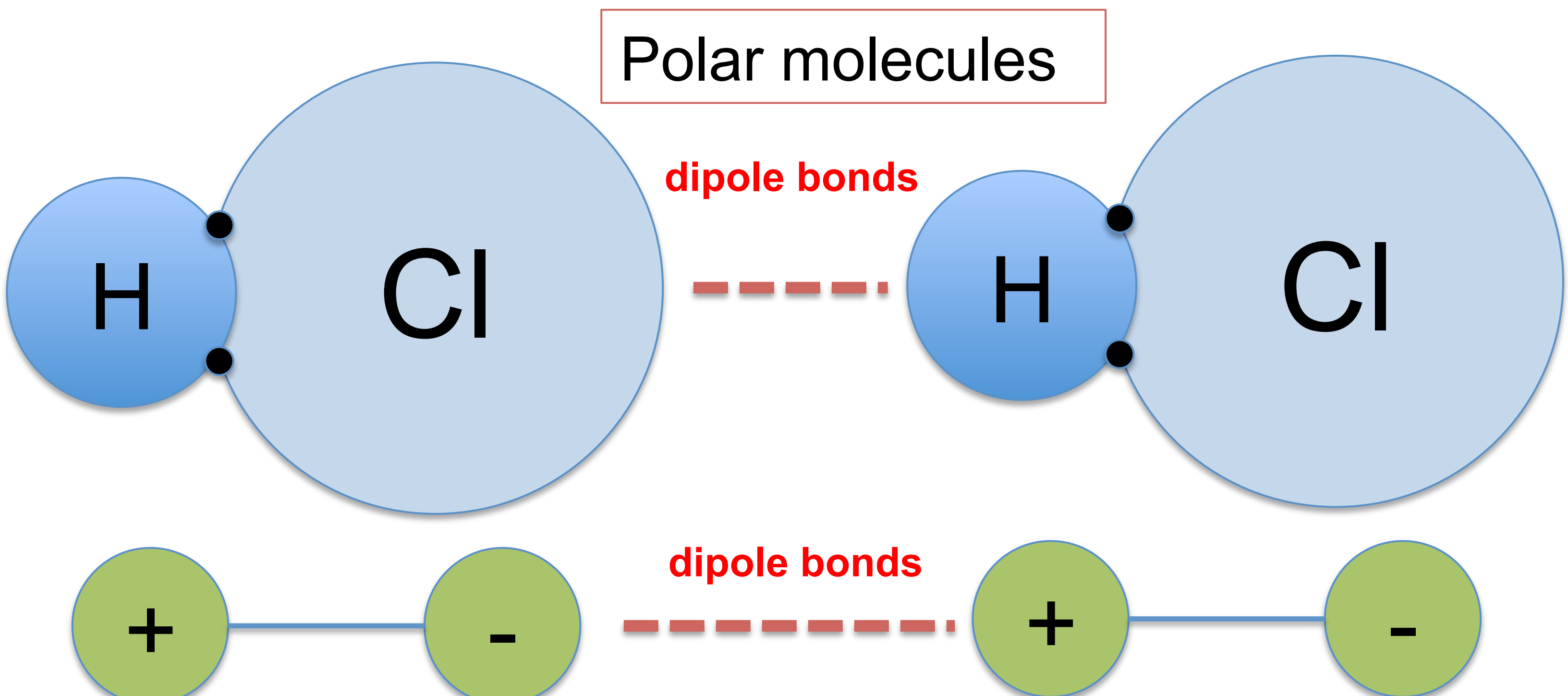




Secondary bonding

2. Polar molecules – dipole bonds – between molecules that are polar (have negative and positive poles due to electronegativity difference)

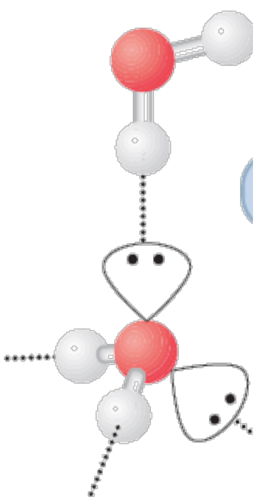
Polar molecules consist of atoms with different electronegativity like HCl, H_2S, SO_2

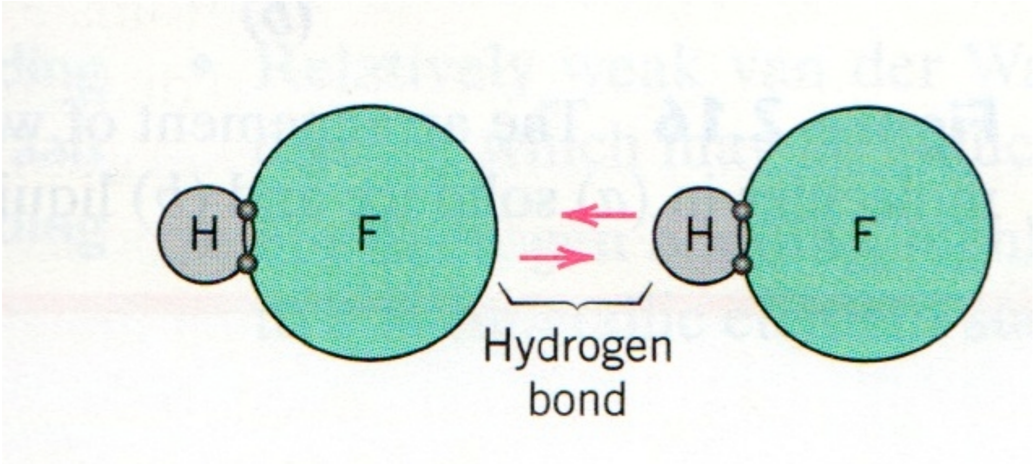


Secondary bonding

3. Hydrogen bonding– between molecules in which hydrogen is bonded with F, O, or N (H – F) (H – O) (H – N) (Example: HF, H_2O, NH_3)

Hydrogen is highly positively charged in these molecules and it can accept an electron pair from the negative end of an adjacent molecule → each proton is like a bridge between two negatively charged atoms.

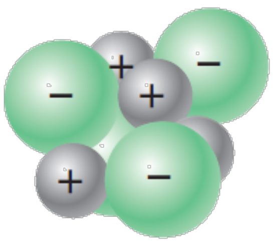




Summary:
Secondary bonding
(between molecules)

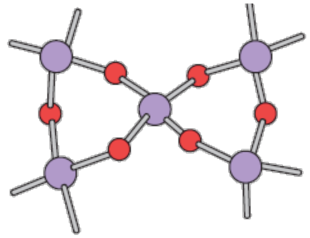
1. Van der Waals bonds (Fluctuating induced dipole bonds) (weakest)
2. Dipole bonds (between polar molecules) (intermediate)
3. Hydrogen bonds (strongest)

Various types of solids



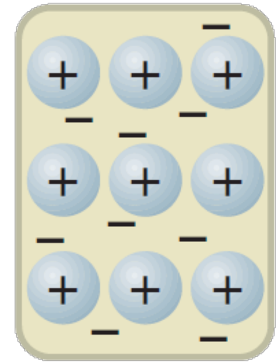
Ionic solid

KCl, NaI



Network solid

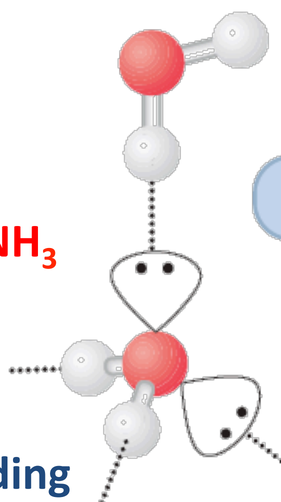
Diamond, SiO_2



Metallic solid

Au, Fe, Ba, …

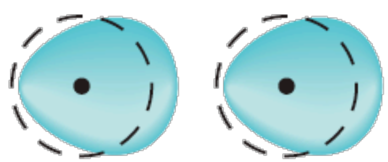
HF, H_2O, NH_3



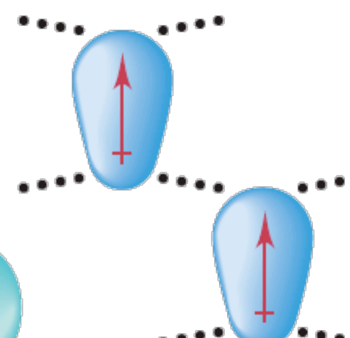
Hydrogen bonding

Molecular solid

O_2, Noble gases



Van der Waals bonds



dipole bonds

HCl, CO_2

Strength of the bonds

- If you make covalent solids (atoms with covalent bonds between them, like diamond, SiO_2); they form a "*solid network*" and they have the highest melting point.
- After that, we have *ionic solids*, and then *metallic solids*. Sometimes metallic solids has higher melting point, it is case by case.
- Then we have secondary bonding; hydrogen bonding is the highest, then dipole bonding (between polar molecules), and then van der Waals bonds (between non polar molecules). They all make *molecular solids*.

Case by case

- Network solids > "ionic solids > metallic solids" > "hydrogen bonds > dipole > van der Waals"

Molecular solids

Example

Indicate what type of solid (ionic, network, metallic, or molecular) each of the following forms on solidification:

(a) Br_2 (b) KBr (c) Ba (d) SiO_2 (e) CO_2

A. molecular
B. ionic
C. metallic
D. network
E. molecular

Example: compare melting points of following compounds

HF, HCl, NaCl, diamond, SiO_2, CH_3OH, CH_4

Answer:

Diamond > SiO_2 > NaCl > HF > CH_3OH > HCl > CH_4

Example: type of bonding in the following materials

- Brass (Copper-zinc alloy) metallic — Metallic solid
- BaS ionic — Ionic solid
- Xenon Van der Waals
- HF Hydrogen bonding between molecules, (covalent between atoms)
- HCl Dipole-dipole between molecules, (covalent between atoms)
- F_2 Van der Waals between molecules, (covalent between atoms)

Molecular solids

Properties of the Major Classes of Solids

Network solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous
***Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.**			

The general order of increasing strength of interactions in a solid is molecular solids < ionic solids ≈ metallic solids < network solids.

Comparison of bond types and typical properties (general trends)

	Typical Solids	Bond Energy eV/atom	Melt. Temp. (°C)	Elastic Modulus (GPa)	Density (g cm^{-3})	Typical Properties
Ionic	NaCl, (rock salt) MgO, (magnesia)	3.2 10	801 2852	40 250	2.17 3.58	Generally electrical insulators. May become conductive at high temperatures. High elastic modulus. Hard and brittle but cleavable. Thermal conductivity less than metals.
Metallic	Cu Mg	3.1 1.1	1083 650	120 44	8.96 1.74	Electrical conductor. Good thermal conduction. High elastic modulus. Generally ductile. Can be shaped.
Covalent	Si C (diamond)	4 7.4	1410 3550	190 827	2.33 3.52	Large elastic modulus. Hard and brittle. Diamond is the hardest material. Good electrical insulator. Moderate thermal conduction, though diamond has exceptionally high thermal conductivity.
van der Waals: Hydrogen bonding	PVC, (polymer) H_2O, (ice)	- 0.52	212 0	4 9.1	1.3 0.917	Low elastic modulus. Some ductility. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.
van der Waals: Induced dipole	Crystalline Argon	0.09	−189	8	1.8	Low elastic modulus. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.

From *Principles of Electronic Materials and Devices, Second Edition* , S.O. Kasap (© McGraw Hill, 2002)

http://Materials.Usask.Ca