Bonding
Polymers and Glasses

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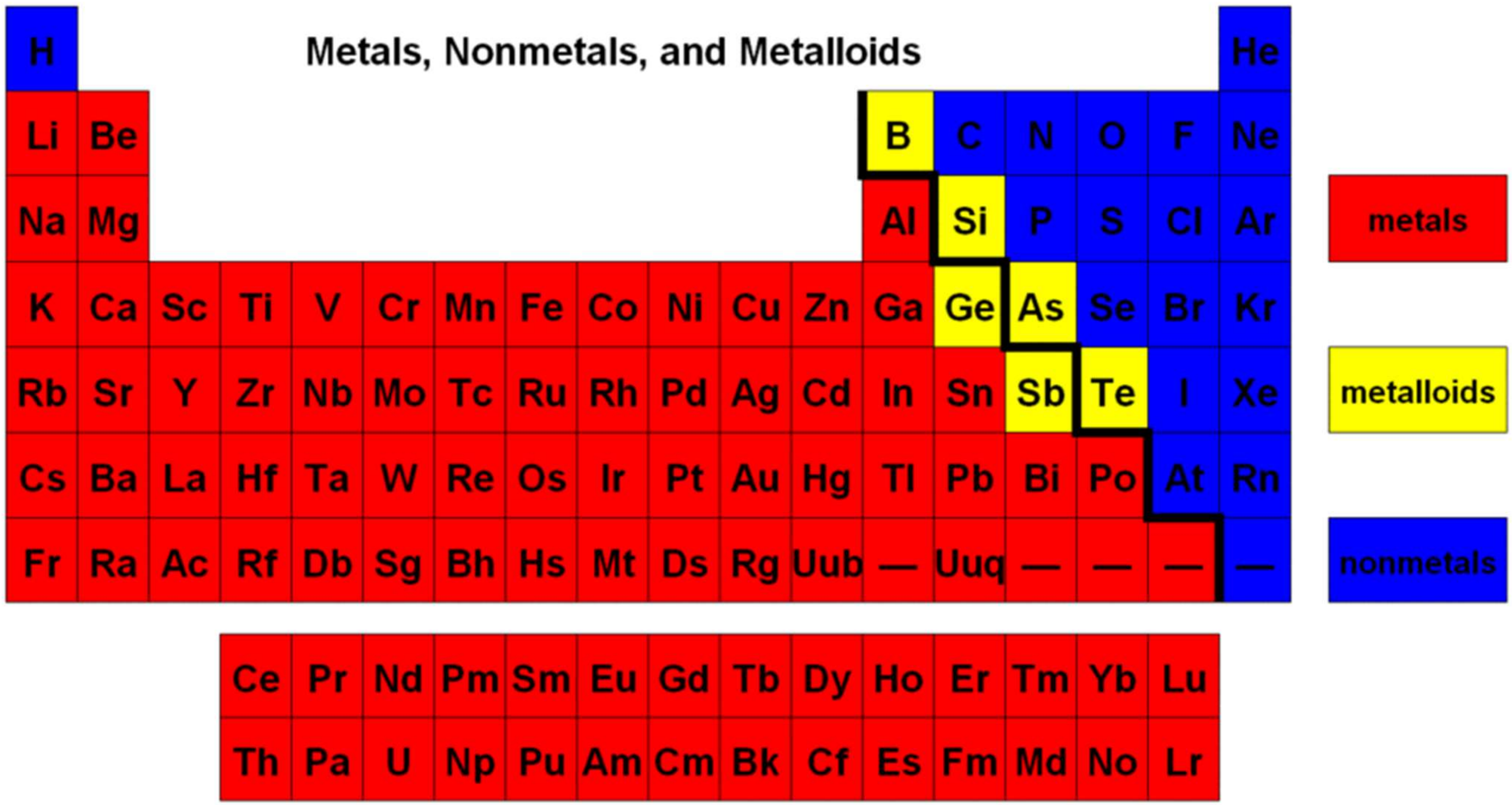
The elemental palette

Elements and their structure

H																	He
453.69 Li bcc	1560 Be hcp											B	C	N	O	F	Ne
370.87 Na bcc	923 Mg hcp											933.47 Al fcc	Si	P	S	Cl	Ar
336.53 K bcc	1115 Ca fcc	1814 Sc hcp	1941 Ti hcp	2183 V bcc	2180 Cr bcc	1519 Mn	1811 Fe bcc	1768 Co hcp	1728 Ni fcc	1357.8 Cu fcc	692.68 Zn	301.91 Ga	Ge	As	Se	Br	Kr
312.46 Rb bcc	1050 Sr fcc	1799 Y hcp	2128 Zr hcp	2750 Nb bcc	2896 Mo bcc	2430 Tc hcp	2607 Ru hcp	2237 Rh fcc	1828 Pd fcc	1235 Ag fcc	594 Cd	430 In	505 Sn	904 Sb	Te	I	Xe
302 Cs bcc	1000 Ba bcc	*	2506 Hf hcp	3290 Ta bcc	3422 W bcc	3186 Re hcp	3306 Os hcp	2446 Ir fcc	1768 Pt fcc	1337.33 Au fcc	234.32 Hg	577 Tl hcp	600.61 Pb fcc	544.7 Bi	527 Po	At	Rn
Fr	973 Ra bcc	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo



https://www.angelo.edu/faculty/kboudrea/periodic/physical_metals.htm

Metals

- Usually solid at room temperature (mercury is an exception)
- High luster (shiny) Metallic appearance
- Good conductors of heat and electricity
- Easy forming (can be bent and pounded into thin sheets)
- Readily lose electrons

https://www.thoughtco.com/metals-nonmetals-and-metalloids-periodic-table-608867#:~:text=The%20line%20begins%20at%20boron,are%20termed%20metalloids%20or%20semimetals.

Metalloids

- Dull or shiny
- Usually conduct heat and electricity, though not as well as metals
- Often make good semiconductors

Metalloids

- Often exist in several forms
- May gain or lose electrons in reactions

Non metals

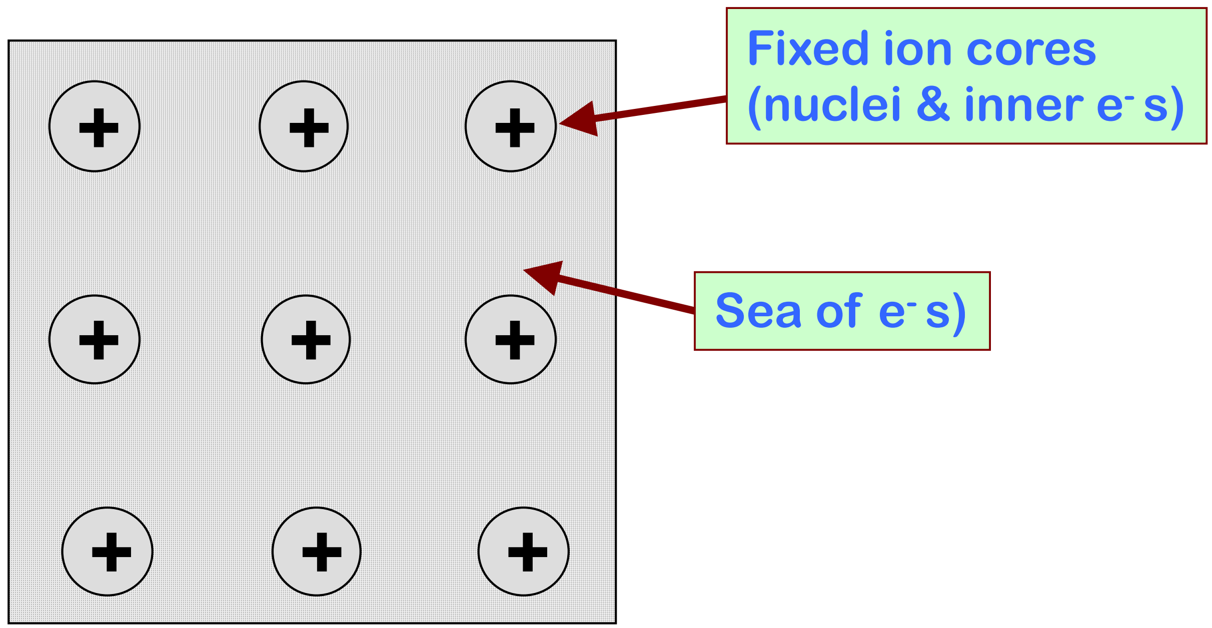
- Dull appearance
- Usually brittle
- Poor conductors of heat and electricity
- Usually less dense, compared to metals
- Usually low melting point of solids, compared with metals
- Tend to gain electrons in chemical reactions

Bonding

- Solid state matter comprises of atoms attached by a bond
- Different type of bonds
- Most elements are metallic in the periodic table
- Compounds contain more than one element
- Different size, electronegativity and electronic structure
- Balls of different sizes
- Springs of different type and strength

Metallic Bonding

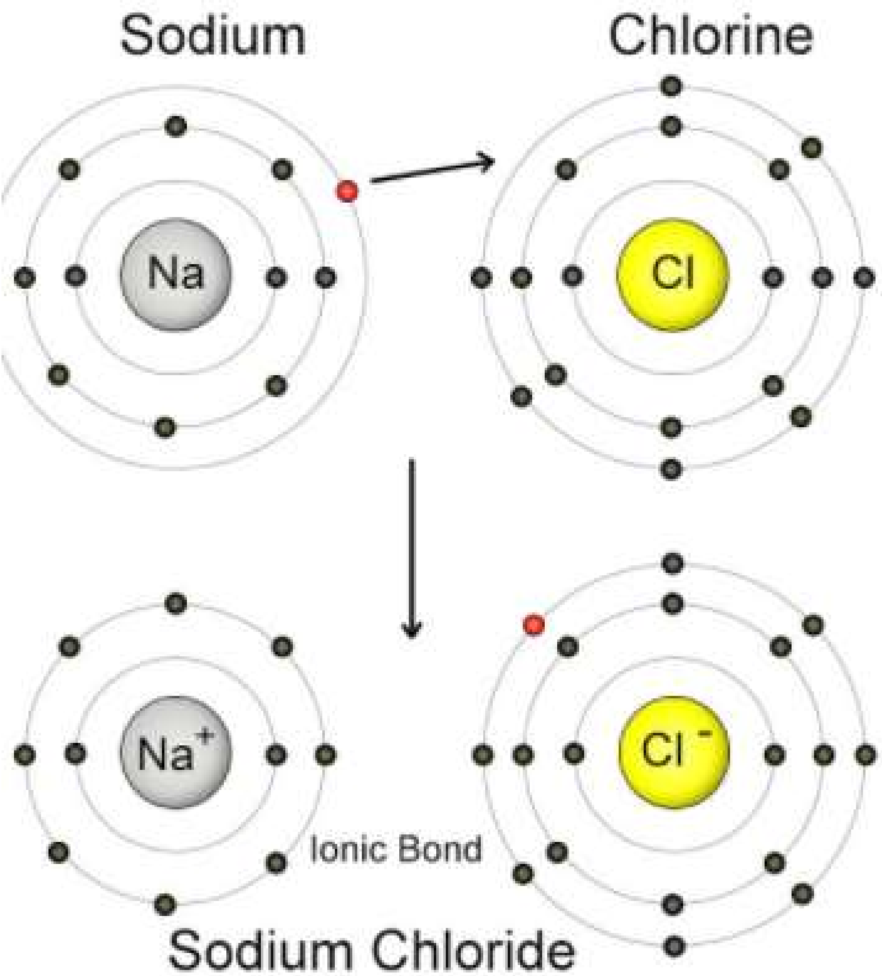
- Metals contain free electrons
- Metal ions in a sea of electron (electron cloud)
- Non directional close packing
- Metals and alloys



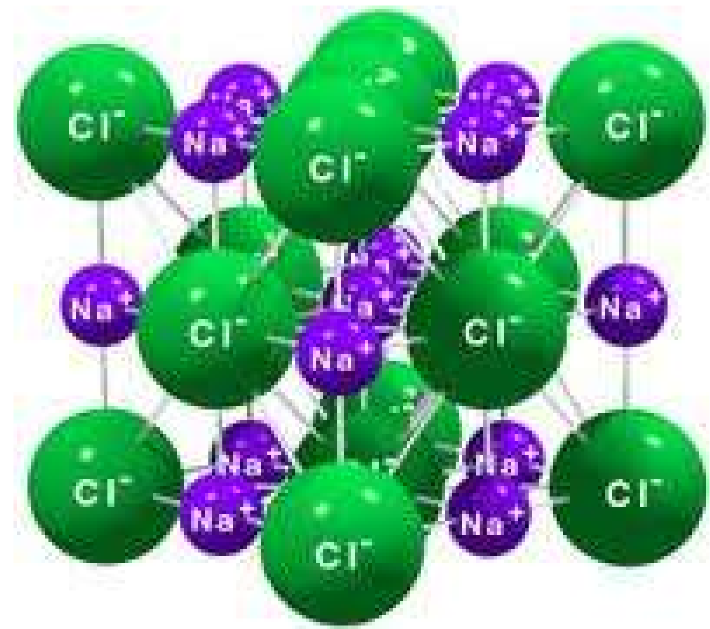
Adapted from Fig. 2.11, *Callister 6e.*

Ionic Bonding

- Bonds between ions instead of atoms
- Electron transfer
- Positive and negative ions
- Cations and anions Na^+ and Cl^-
- Large difference in electronegativity leads to electron transfer
- Sodium is a metal and chlorine a non metal
- Different sizes of ions



https://gardenandplate.com/sodiumchloride.html



Space group Fm-3m
Cl^- at FCC and Na^+ at octahedral

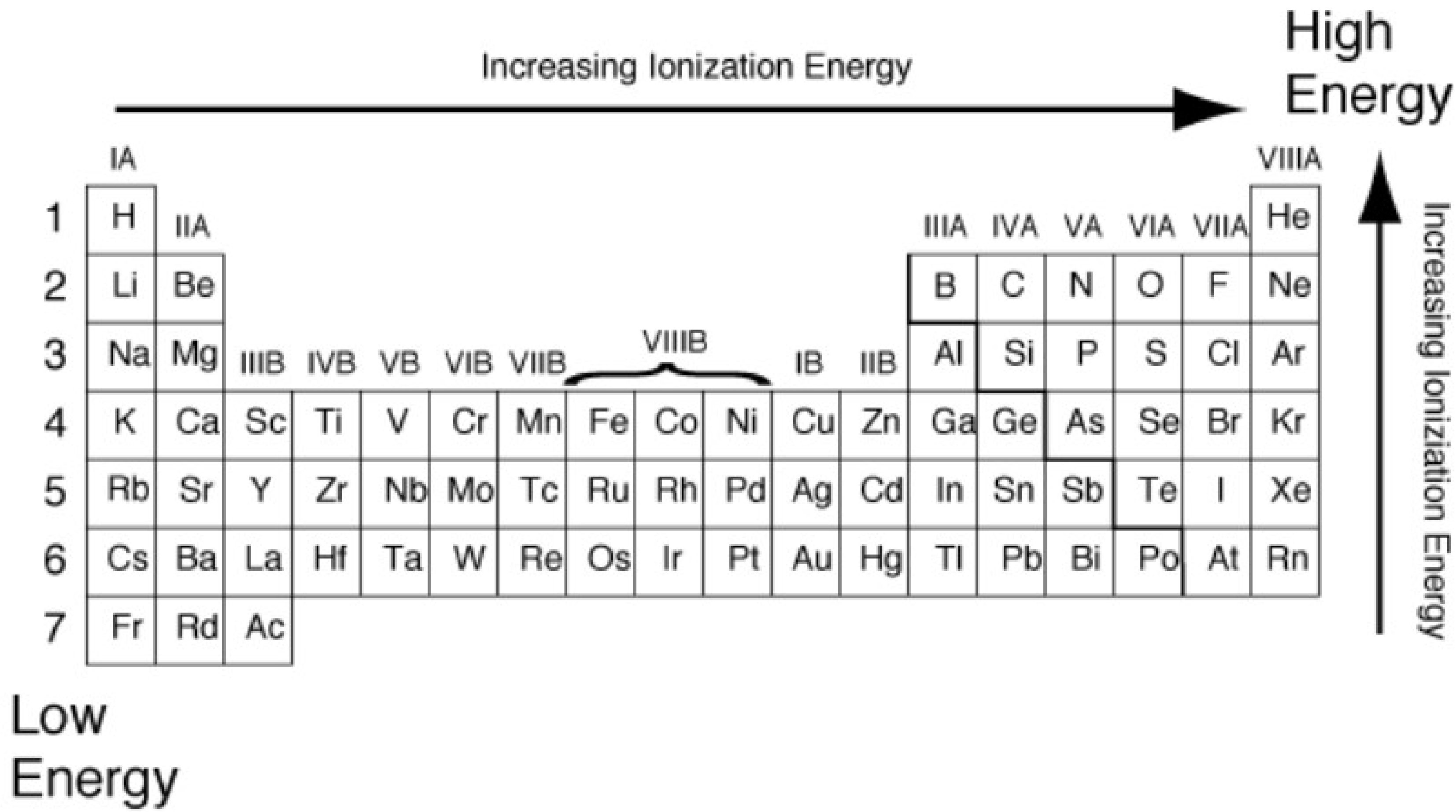
http://www.chemistry.wustl.edu/~edudev/LabTutorials/Water/PublicWaterSupply/PublicWaterSupply.html

- Energy required to remove an electron from its orbital and bring to free-space i.e. not a part of any atom is known as Ionization energy or Ionization potential

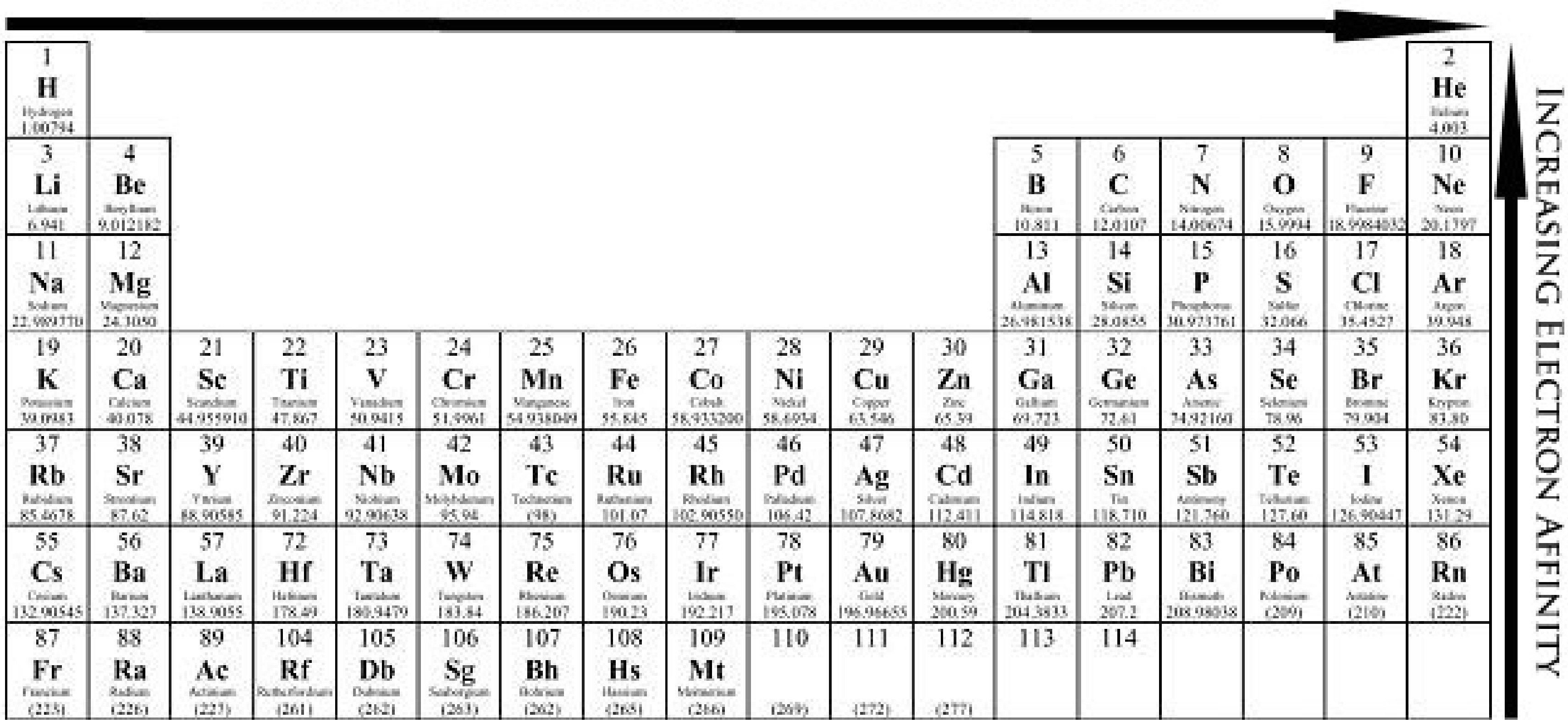
- First ionization energy is energy required to remove the outermost electron i.e. the electron in the outermost orbital of a neutral atom

- Energy required to take a free-electron and place it into the outer-orbital of a neutral atom is known as electron affinity

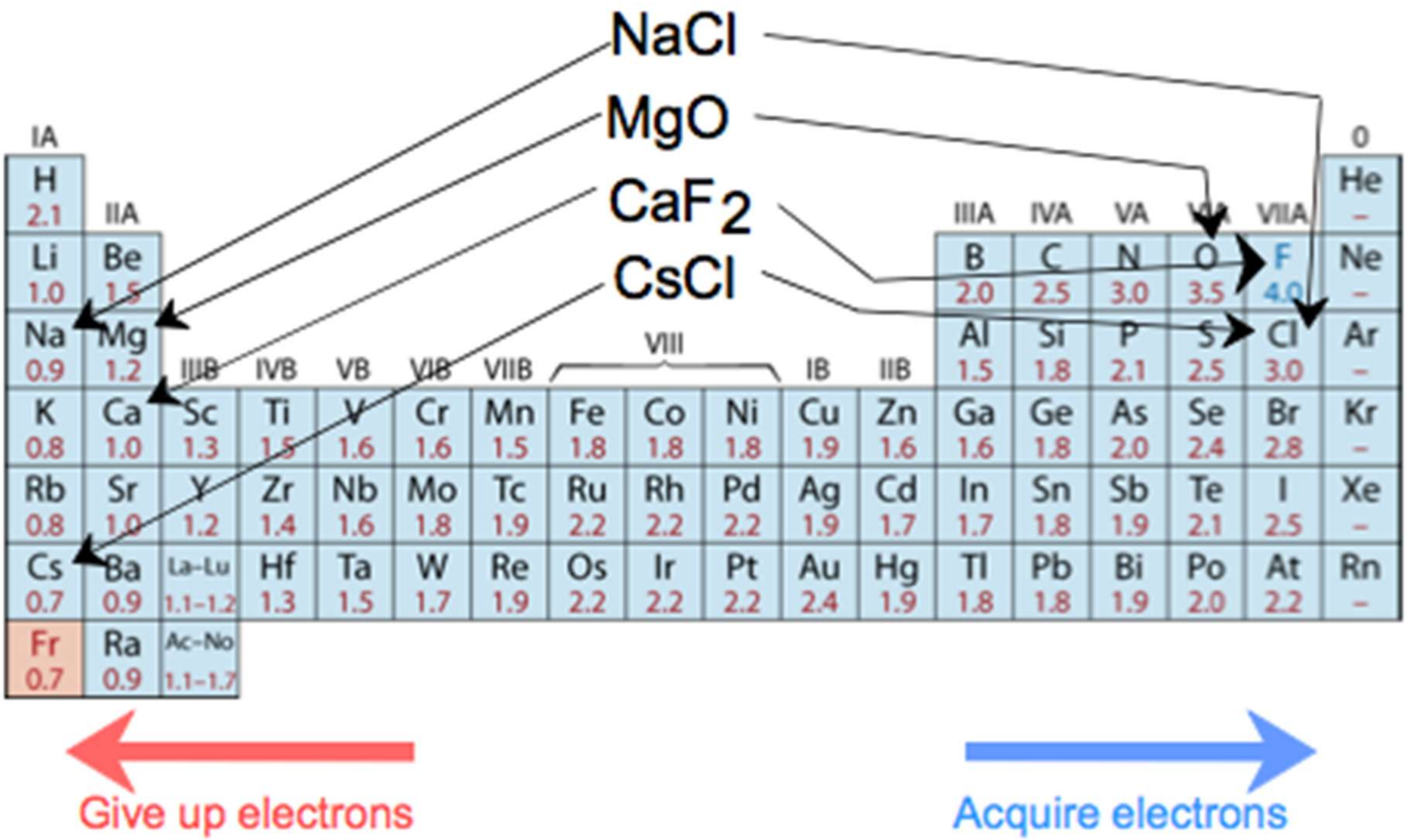
- Ionic bonds are formed between elements with small ionization energy and high electron affinity or, between electropositive and electronegative elements


Increasing Ionization Energy
High Energy
IA
VIIIA
IIA
IIIA IVA VA VIA VIIA
IIIB IVB VB VIB VIIB VIIIB IB IIB
1 H He
2 Li Be B C N O F Ne
3 Na Mg Al Si P S Cl Ar
4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
6 Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
7 Fr Rd Ac
Increasing Ionization Energy
Low Energy

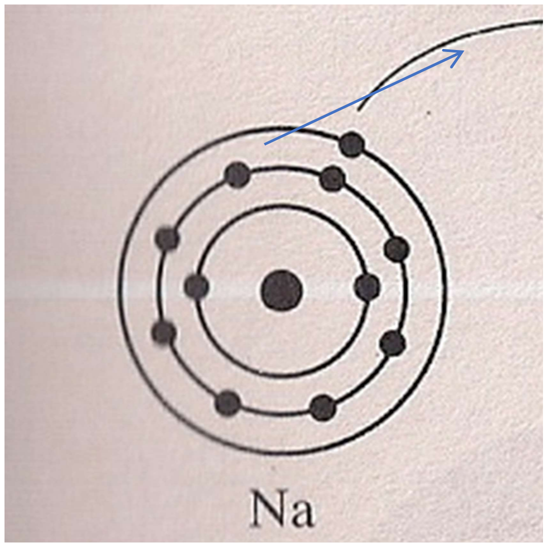
INCREASING ELECTRON AFFINITY

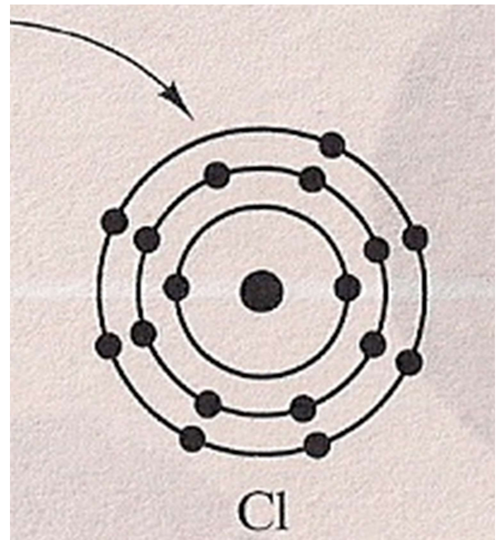


- Predominant bonding in Ceramics



Adapted from Fig. 2.7, *Callister & Rethwisch 8e*. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

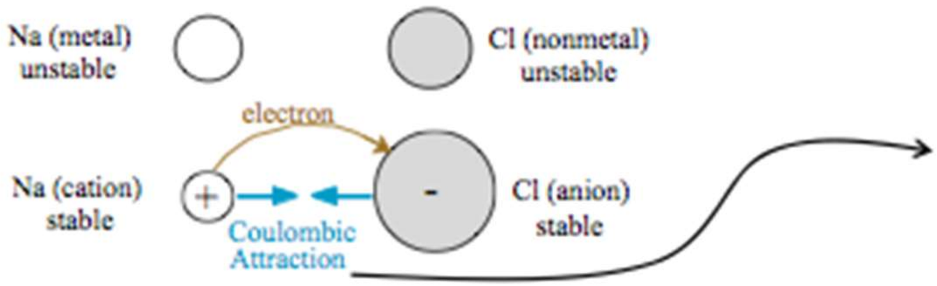




energy required to
Remove and electron
from an electropositive
atom

+

energy gained as
An electron is accepted
by an electronegative
atom



$$E_A = \frac{z_1 z_2 e^2}{4\pi\varepsilon_o r}$$

Since $z_1 = +1$ for Na^+ and $z_2 = -1$ for Cl^-

$$E_A = -\frac{e^2}{4\pi\varepsilon_o r} = -\frac{A}{r}$$

Negative energy means attraction only.
Will the atoms collapse on themselves?

No, there is also repulsive energy (e.g. e-e repulsion)

$$E_R = \frac{B}{r^n}$$

B and *n* depend on atoms involved.
In many cases *n* ~ *8.*

16

$$W = \frac{-Az_1z_2e^2}{r} + \frac{B}{r^m} + \Delta E$$

Coulombic attraction

Coulombic repulsion
(a short range force)

Difference between the energy spent in removing an electron and energy gained by putting an extra electron, or difference between ionization energies.

A condition of $\frac{\partial W}{\partial r} = 0$ is used to find the equilibrium distance and bond-energy

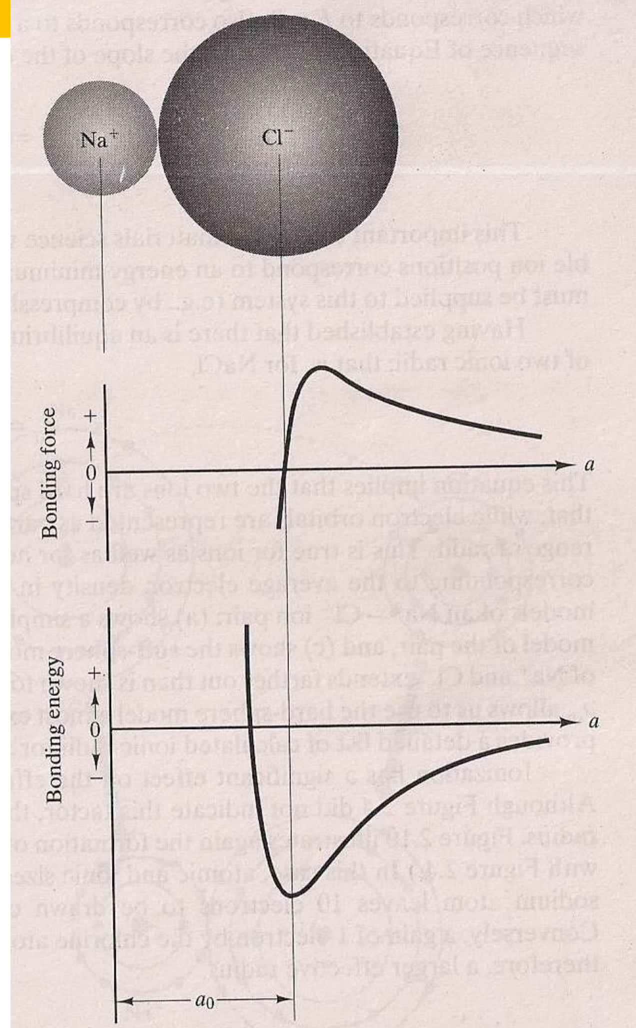


Figure 2.8 *Comparison of the bonding force curve and the bonding energy curve for a $Na^+ - Cl^-$ pair. Since $F = dE/da$, the equilibrium bond length (a_0) occurs where $F = 0$ and E is a minimum (see Equation 2.5).*

The potential energy of the crystal having one mole of NaCl is given by

$$W = \left[\frac{-Az_1z_2e^2}{r}\alpha + \frac{B}{r^m} + \Delta E \right] N_A$$

Madelung constant

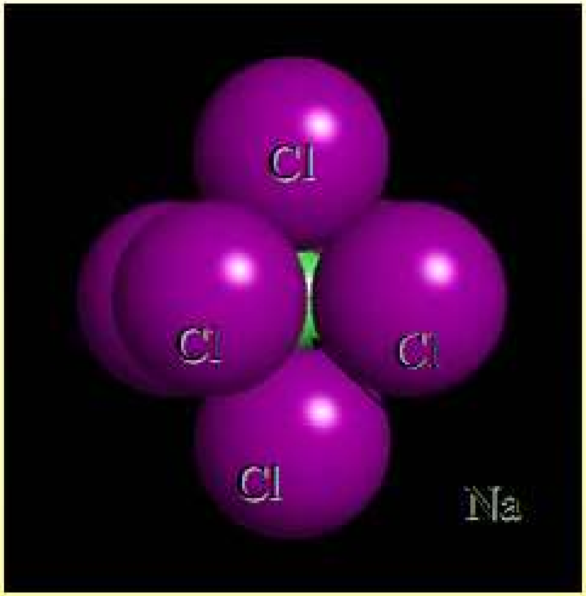
- Ceramics have ionic bonding
- Oxides, carbides, borides
- Extremely important class of engineering materials
- Much more than a grain of salt !

Pauling’s rules

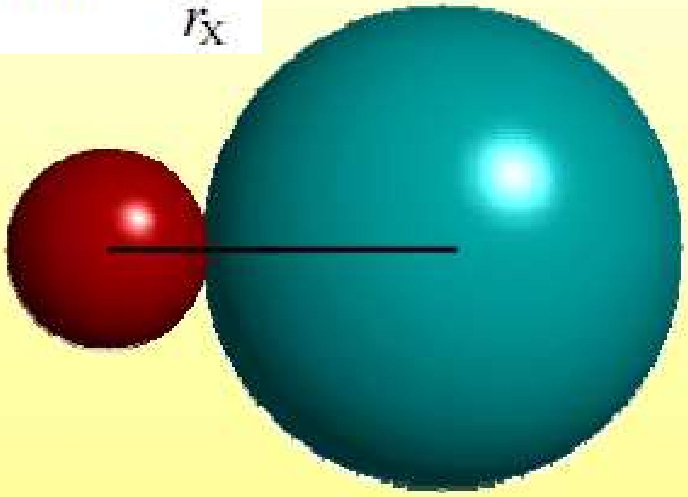
- Ionic bond between cations and anions of different size and charge
- Anions are generally bigger than cations
- Co-ordination number is important for charge neutrality
- Prof. Linus Pauling came up with 5 rules

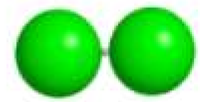
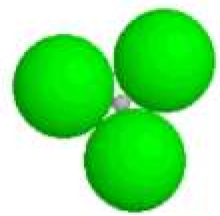
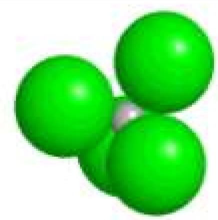
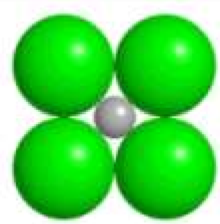
Rule 1

A coordination polyhedron of anions is formed about each cation. The cation-anion distance equaling the sum of their characteristic packing radii and their radius ratio determining both the nature of the coordination polyhedron and therefore the coordination number of the cation.

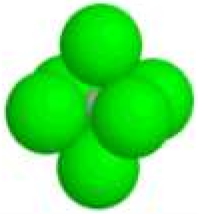
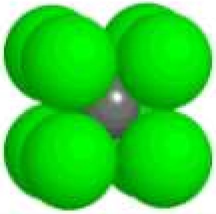
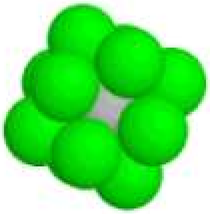


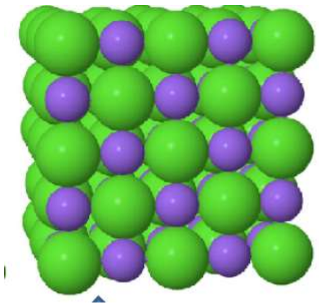
$$\text{Radius ratio} = \frac{r_M}{r_X}$$

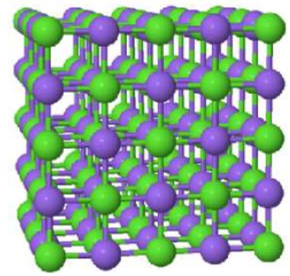


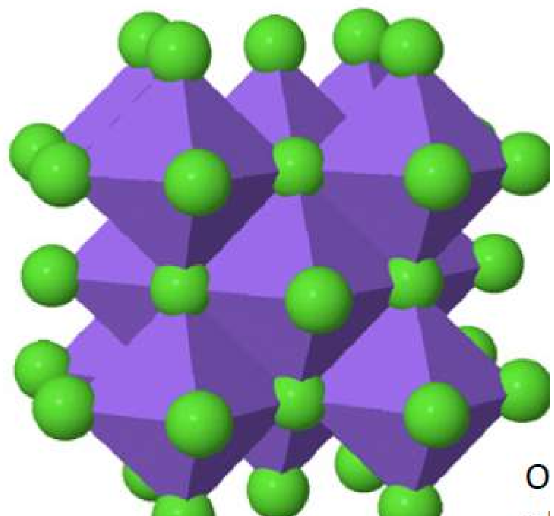
r_C/r_A	Coord. #	Angle	Config.	Image	Example
0.000-0.155	2	180°	Linear		$(HF_2)^{-1}$
0.155-0.225	3	120°	Trigonal planar		$(CO_3)^{-2}$
0.225-0.414	4	109.47°	Tetrahedral		$(SiO_4)^{-4}$
0.414-0.732	4	90°	Square planar		$(CuO_4)^{-6}$

https://www.geo.arizona.edu/xtal/geos306/geos306-6.htm

0.414-0.732	6	90°	Octahedral		$(NaCl_6)^{-5}$
0.732-1.000	8	70.53°	Square - bipyramid		$(CsCl_8)^{-7}$
1.000	12	60°	Closest-packed		$(KO_{12})^{-23}$



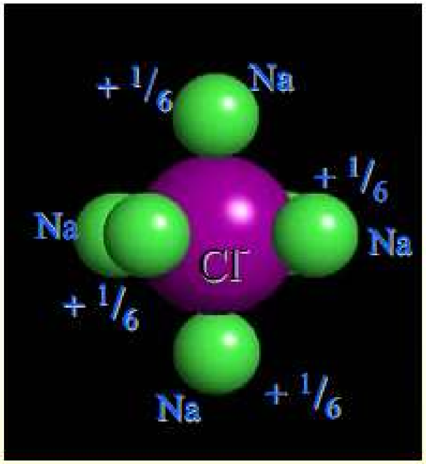




ıttp://mrsec.wisc.edu/Edetc/pmk/pages/why.html

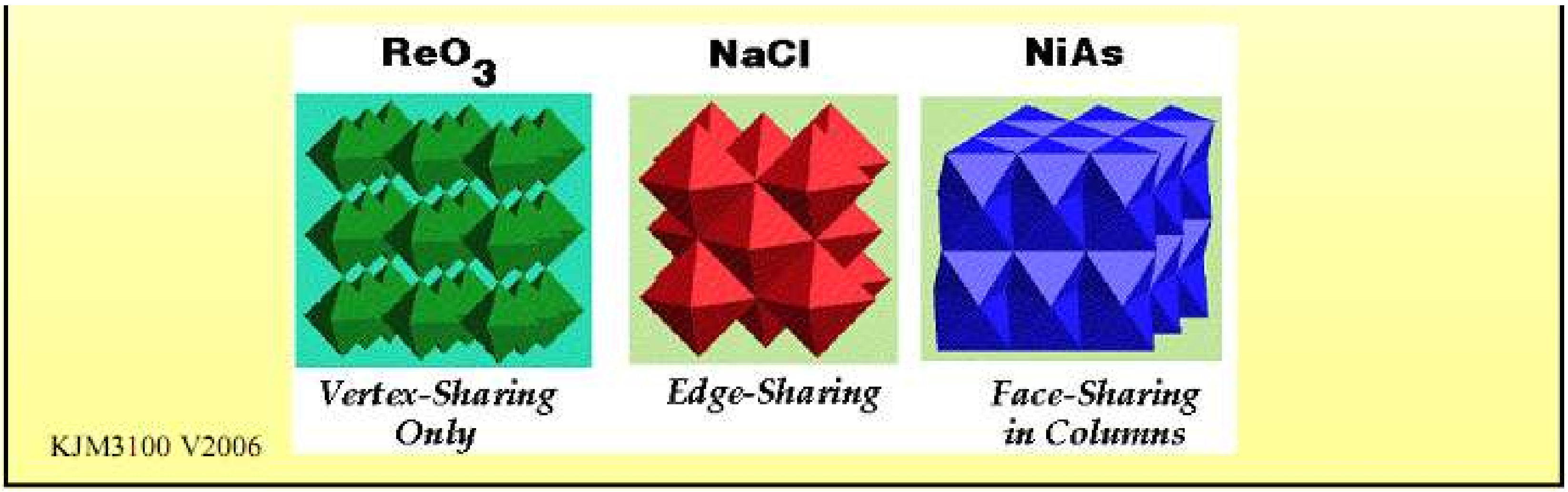
Rule 2

- An ionic structure will be stable to the extent that the sum of the strengths, S, of the electrostatic bonds that reach an anion from adjacent cations equals the charge, Z_A, on that anion
- $Z_A = \sum S$ (Strength of an electrostatic bond $S = Z_C/CN$).
- Z_C is valence of the cation and CN is the co-ordination number of the cation



Rule 3

- Polyhedra sharing and stability of structures
- Vertex sharing > Edge sharing > Face sharing
- Severe for cations with larger charge and low co-ordination number



Rule 4 to 6

4. In a crystal structure containing different cations, those of high valency and small coordination number tend not to share polyhedron elements with each other

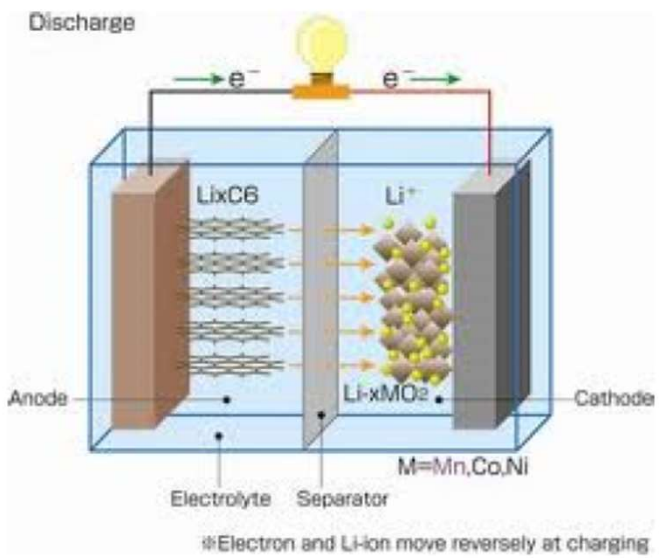
5. The number of essentially different kinds of constituents in a crystal tends to be small

6. Prewitt's addendum: Given that the chemical formula for a crystal is charge balanced, then the sum of the coordination numbers of the cations must equal the sum of the coordination numbers of the anions

From Bloss, Crystallography and Crystal Chemistry

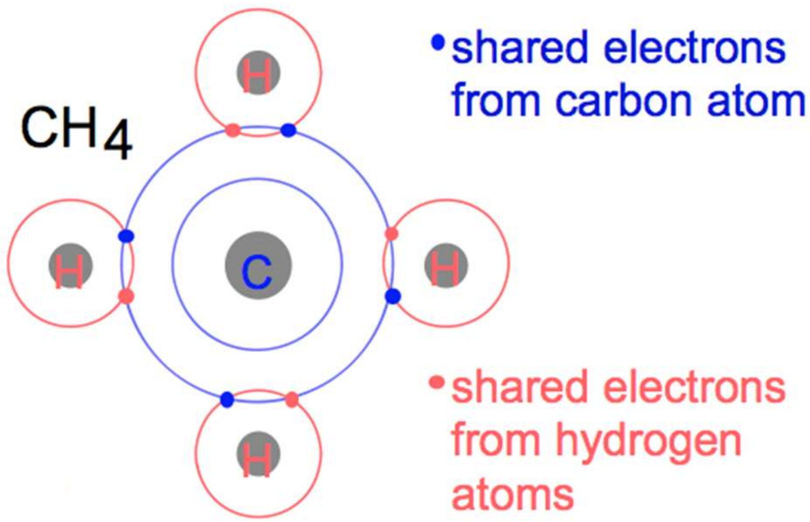
Properties and applications

- High melting point and brittle
- Ionic solids have structural and functional applications
- Furnace refractory to sensors and fuel cells



Covalent bonding

- Sharing of electrons
- Similar or comparable electronegativities
- Directional in nature
- Formed along the direction of orbital (sigma bond) or perpendicular to it (pi bond)



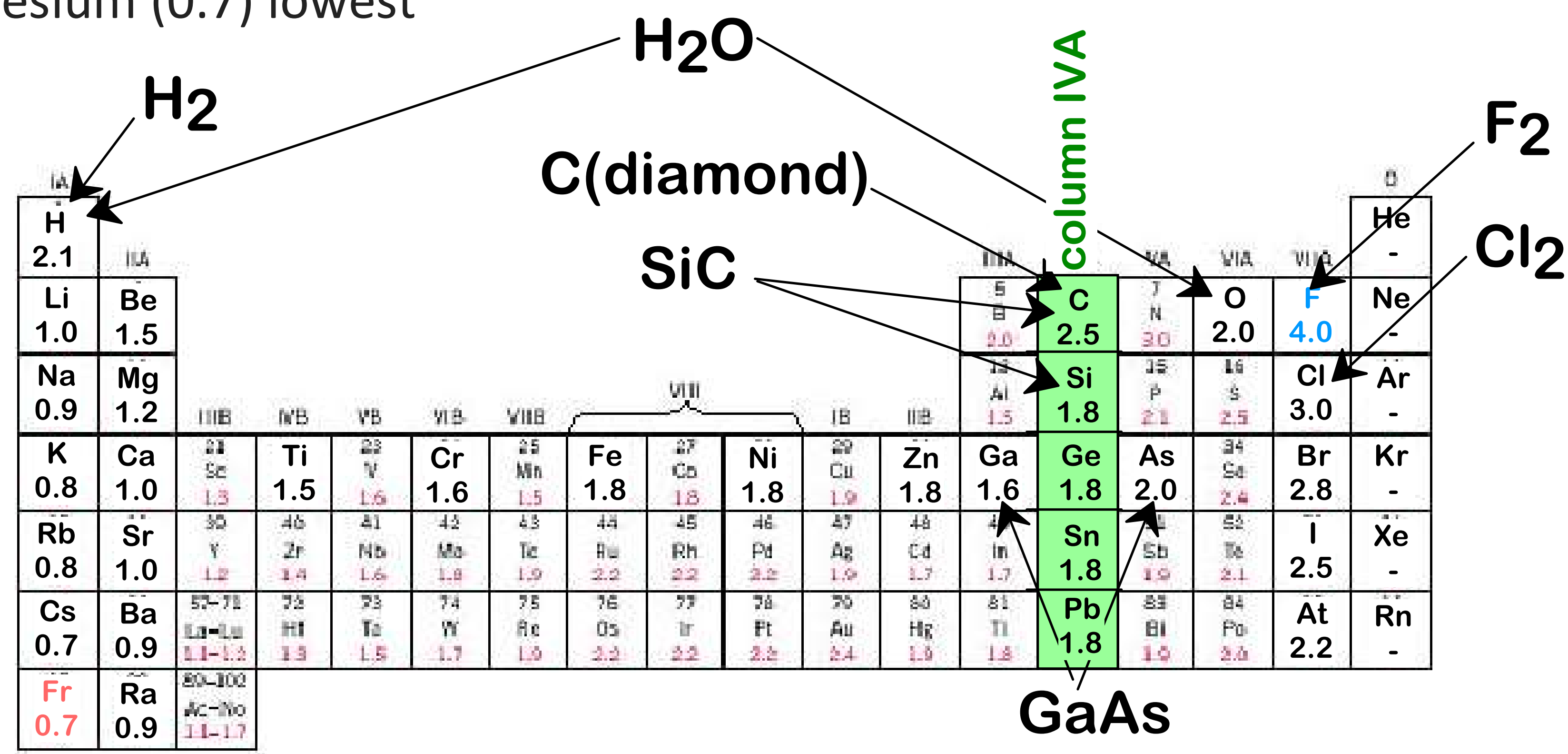
- Silicon, Gallium Arsenide drive semiconductor industry
- Diamond as abrasive

Adapted from Fig. 2.10, *Callister 6e.*

Pauling electronegativity

- Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons

- Fluorine has a value of 4 on the Pauling scale (highest) while Cesium (0.7) lowest



- Very few compounds show pure ionic or covalent bonding. Usually the bonds are of mixed nature

% ionic character = $\{ 1- \exp[-(0.25)(\chi_A-\chi_B)^2]\}x100$

χ_A& χ_B are electronegativities of the atoms forming that bond.

Important as electronic properties affected by $ ionic character

- Metallic-covalent mixed bonding: example, transition metals involving *dsp*bonding orbitals.
- Metallic-ionic mixed bonding: example, intermetallic compounds such as $NaZn_{13}$

Electronegativity and Electron affinity

Comparison basis	Electronegativity	Electron Affinity
Define	The ability of atoms to attract electrons from outside	The amount of energy liberated when a molecule or neutral atom acquires an electron from outside
Applied to	Single-atom	Either an atom or molecule
Measured	Pauling units	Kj/mol or eV
Property	Qualitative	Quantitative
Example	Fluorine	Chlorine

Secondary or Physical bonds

- In these bonds electron transfer or sharing does not take place

- van der Waals bonds
  - London forces (Induced dipoles)
  - Debye interaction(Induced – permanent dipole)
  - Hydrogen bonds (between permanent dipoles)

Van der Waals

- **Dipole-dipole interaction**: secondary bond between molecules with permanent dipole moments

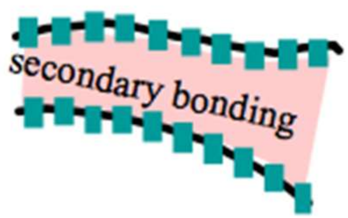
-general case:

Adapted from Fig. 2.14, *Callister 6e.*

-ex: liquid HCl

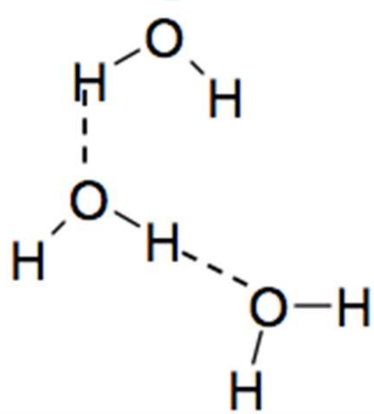
Adapted from Fig. 2.14, *Callister 6e.*

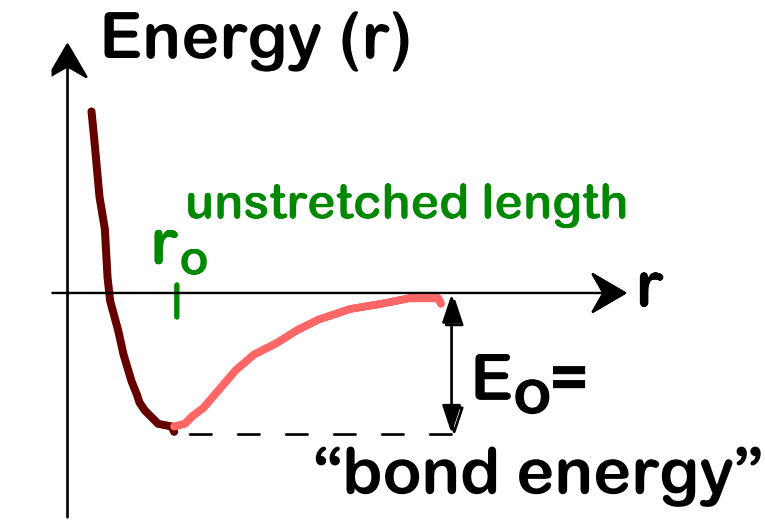
-ex: polymer



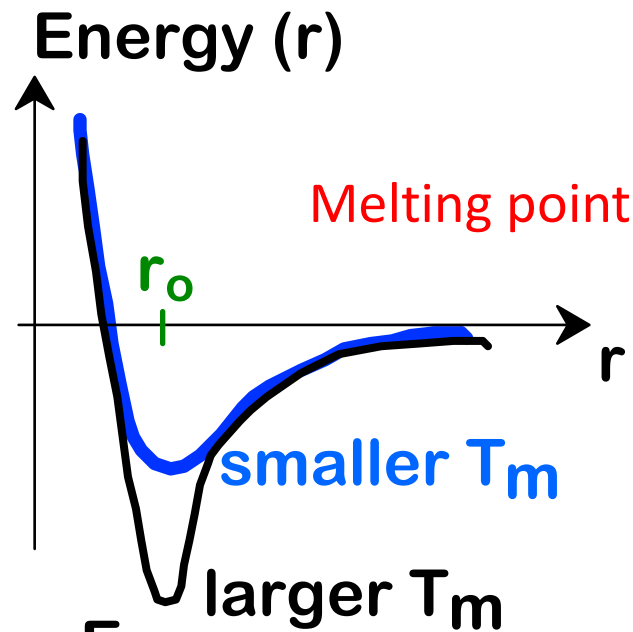
From Callister 6e resource CD.

- **Hydrogen bonding**

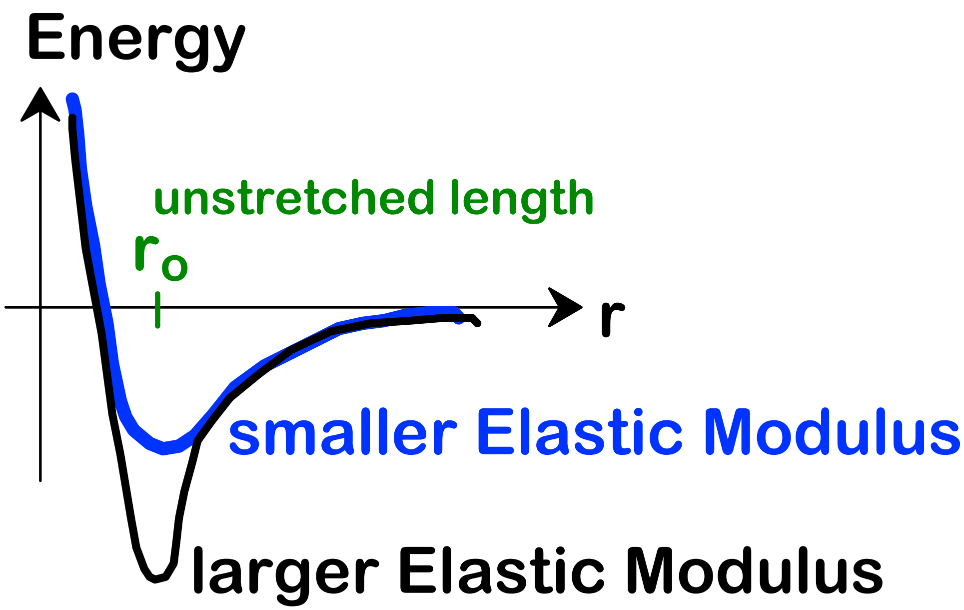




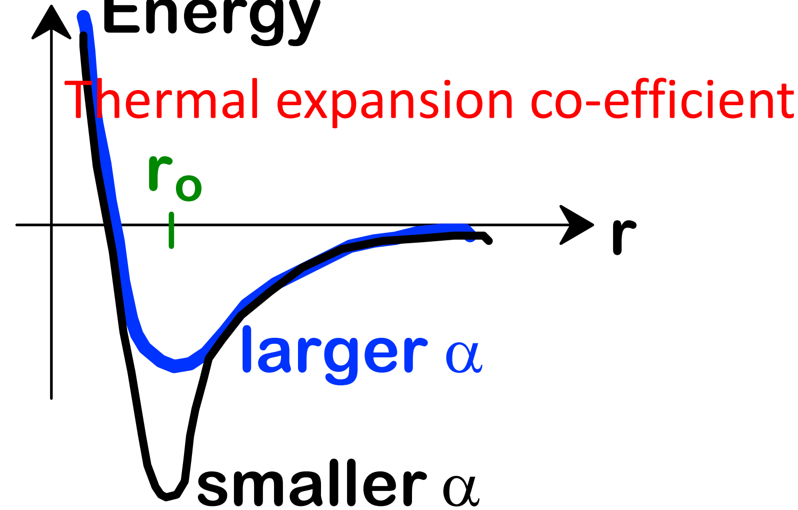
Energy (r)
unstretched length
r o
r
Eo=
"bond energy"



Energy (r)
Melting point
r o
r
smaller Tm
larger Tm



Energy
unstretched length
r o
r
smaller Elastic Modulus
larger Elastic Modulus



Energy
Thermal expansion co-efficient
r o
r
larger α
smaller α

Type	Bond Energy	Comments
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional semiconductors, ceramics polymer chains)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Confluence of PHY, CHM, MAT. SCI.

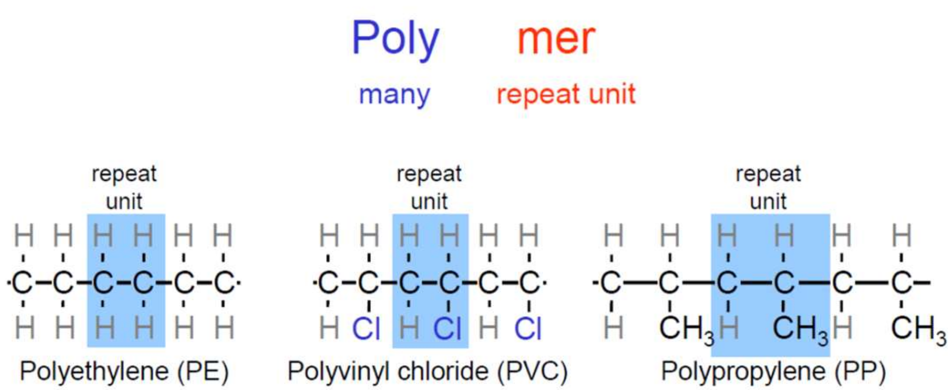
- Symmetry and bonding decides properties at the atomistic scales
- Atomistic simulations using First principles
- Molecular dynamics and statics
- Solve newtons equation at atomic level
- Develop potential from electronic structure
- Employ in molecular dynamics
- Computational materials science

Polymers

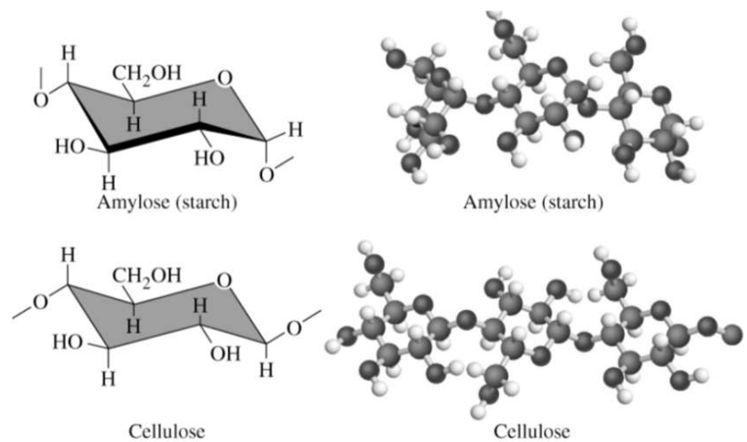
- Polymers are high molecular weight compounds obtained by repeated union of simple molecules

- Poly means many mer means unit

- Macromolecules

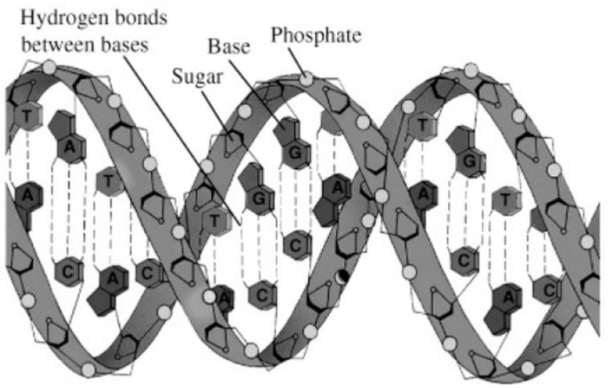


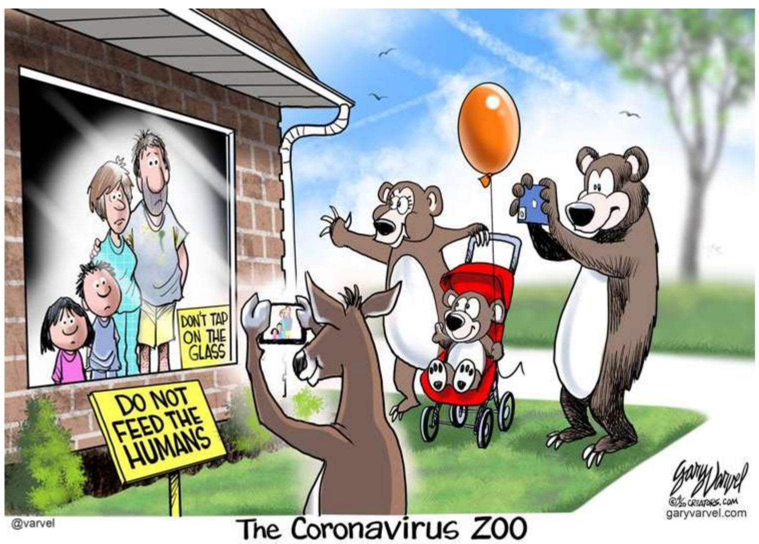
From Fig. 13.2
Callister's Materials Science and Engineering, Adapted Version.

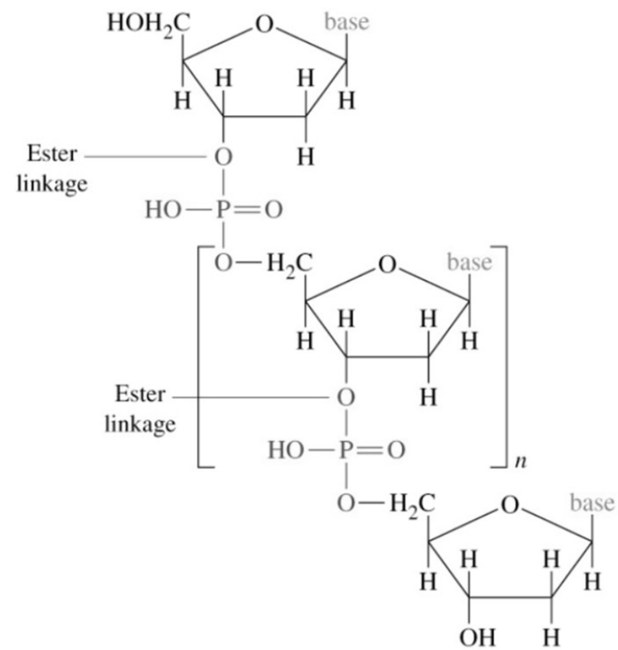


- Produced by polymerization of monomers
- Natural and synthetic polymers
- Wood, rubber, polysaccharides, proteins are natural
- Polyethylene, Styrene, polymers are everywhere
- Recycling is an issue
- Biodegradable polymers

Humans don’t mess with things you can’t fix !







https://www.goshennews.com/opinion/the-latest-editorial-cartoon/image_82f1c6d8-7fe4-11ea-961e-f7a1a3154d1c.html

As you sow, so shall you reap

My car is costlier and bigger than yours …….

My car or well bicycle is environmentally better than yours……

"A developed country is not a place where the poor have cars. It's where the rich use public transportation" – Gustavo Petro, Mayor of Bogotá

Semester over, course completed, degree obtained, job done, let me photobomb my FB, Twitter and Insta with my big bad mean machine

Fulfilled my parent’s wish to get ahead of the our neighbour but what about the Earth, well who cares ?

- Polymerization
    - Addition
    - Condensation
    - Copolymerization
- Biodegradable polymers

Addition polymerization

- Addition polymerization comprises of addition of monomers to each other such that the product contains all atoms of the starting monomers

- Comprises of three steps

  Initiation mostly through free radicals

  Propagation radicals join to form a large radical

  Termination after formation of a macromolecule without an unpaired electron

Initiation

$$R_2 \longrightarrow 2R\cdot$$

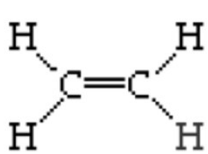
Propagation

$$R\cdot + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2\cdot$$

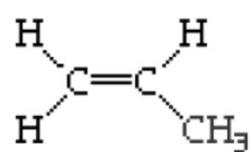
$$R{-}CH_2{-}CH_2\cdot + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}CH_2\cdot$$

Termination

$$R{+}CH_2\text{-}CH_2{+}_n CH_2CH_2\cdot + R{+}CH_2\text{-}CH_2{+}_m CH_2CH \longrightarrow R{+}CH_2\text{-}CH_2{+}_n CH_2CH_2\text{-}CH_2CH_2{+}CH_2\text{-}CH_2{+}_m R$$



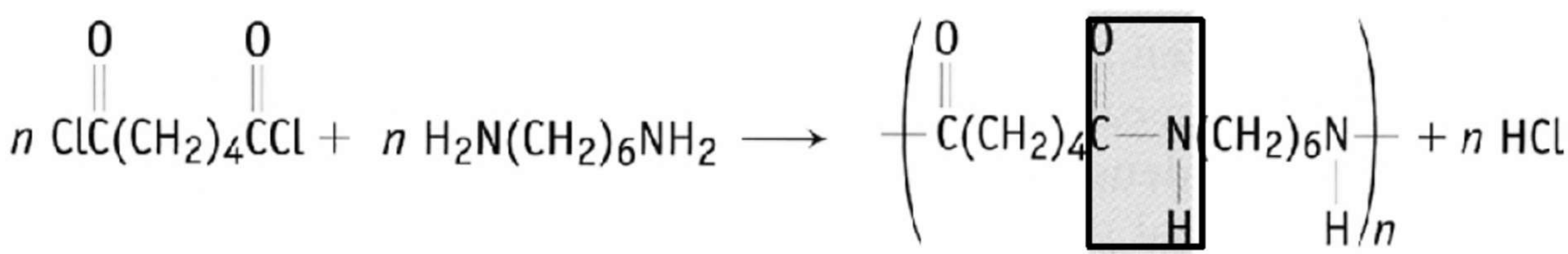
Ethylene to Polyethylene



Propylene to Polypropyline

Condensation polymerization

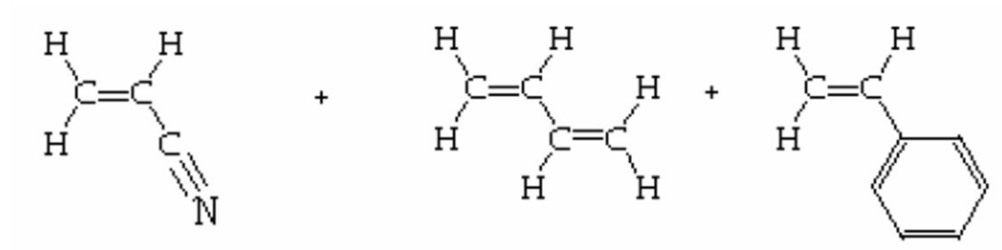
- A small portion of the monomer molecule is not incorporated in the final product in condensation polymerization
- Monomers are held by certain bonds (like amide) and a molecule is eliminated
- Polyester, polyamide nylon 66



adipoyl chloride hexamethylenediamine amide link in nylon-66, a polyamide

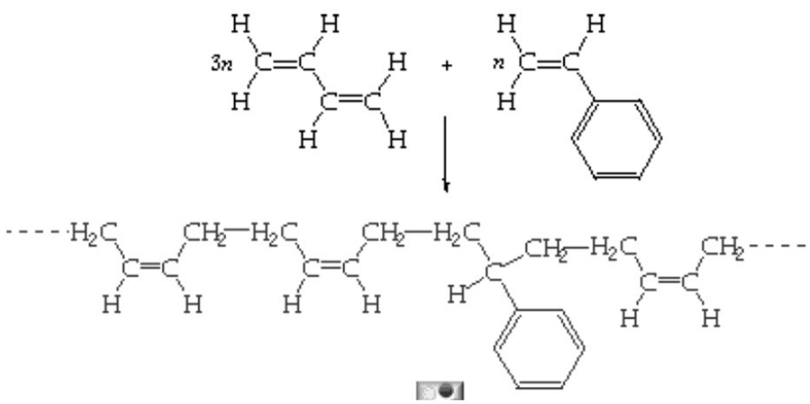
Coolymerization

- Copolymerization is a process in which mixture of two different monomers forms a product that contains both the monomers as building blocks



Acrylonitrile Butadiene Styrene
ABS

ng



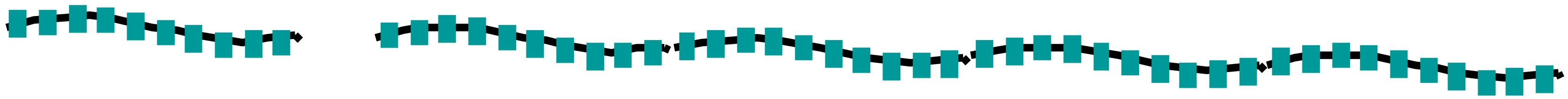
Styrene butadiene rubber

Slide 46

ng1 nilesh guao, 20-09-2020

Molecular weight

- Molecular weight, M_i: Mass of a mole of chains.



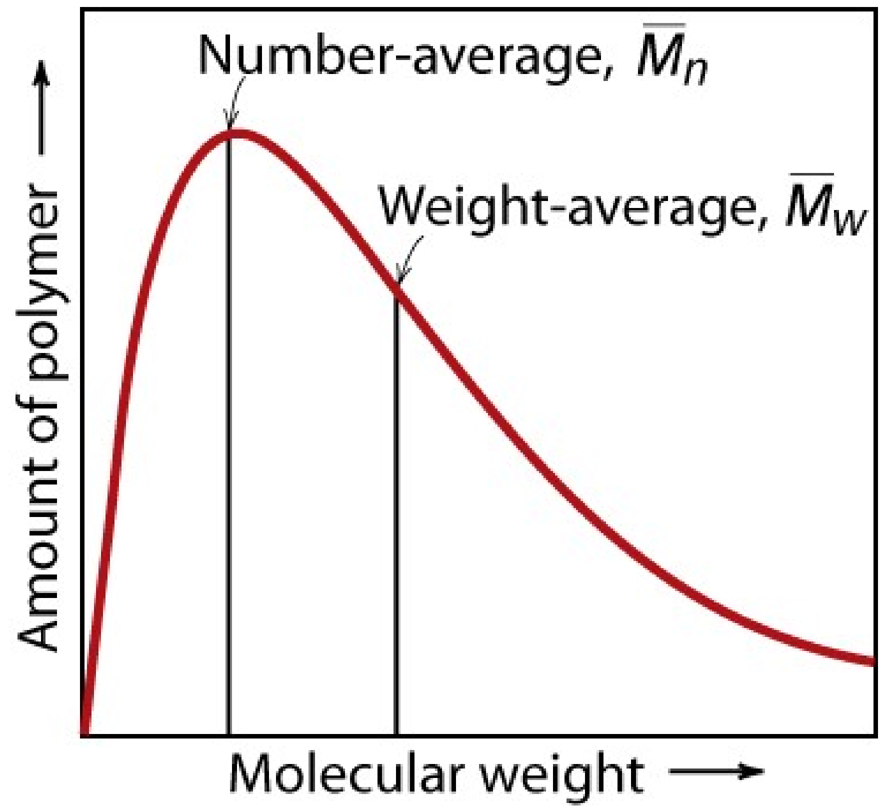
Lower M higher M

$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

$$\overline{M}_n = \Sigma x_i M_i$$

$$\overline{M}_w = \Sigma w_i M_i$$

$\overline{M}_w$ is more sensitive to higher molecular weights



From Fig. 13.4, *Callister's Materials Science and Engineering, Adapted Version.*

Molecular weight calculation

Example: average mass of a class

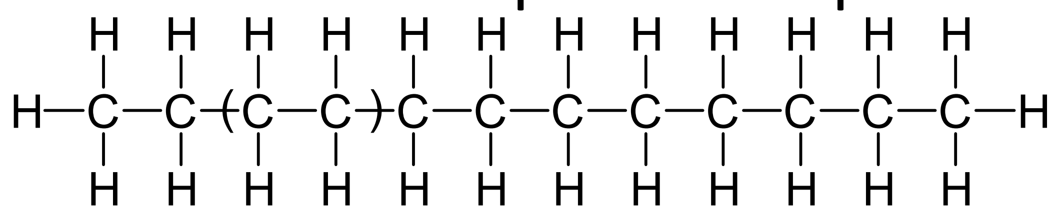
N_i	M_i	x_i	w_i
# of students	mass (lb)		
1	100	0.1	0.054
1	120	0.1	0.065
2	140	0.2	0.151
3	180	0.3	0.290
2	220	0.2	0.237
1	380	0.1	0.204
		$\overline{M}_n$	$\overline{M}_w$
		186 lb	216 lb

$$\overline{M}_n = \sum x_i M_i$$

$$\overline{M}_w = \sum w_i M_i$$

Degree of polymerization, n

n = number of repeat units per chain

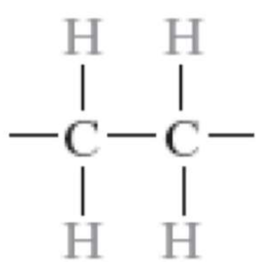


$n_i = 6$

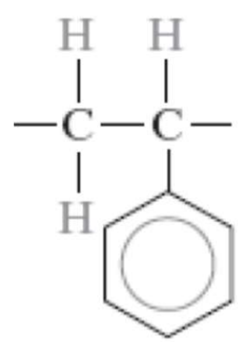
$$DP = \frac{\overline{M}_n}{m}$$

Thermoplastic polymers

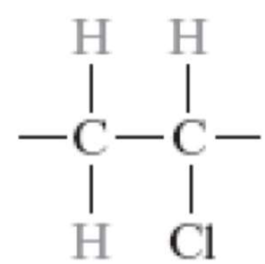
- Long chain molecules held together by secondary bonds
- Secondary bonds become weaker, the material softens
- Easy to mould
- Not suitable for high temperature applications
- Lower strength at room temperature



Polyethylene



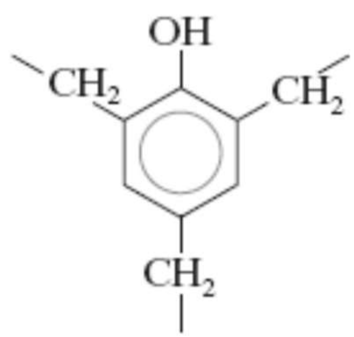
Polystyrene

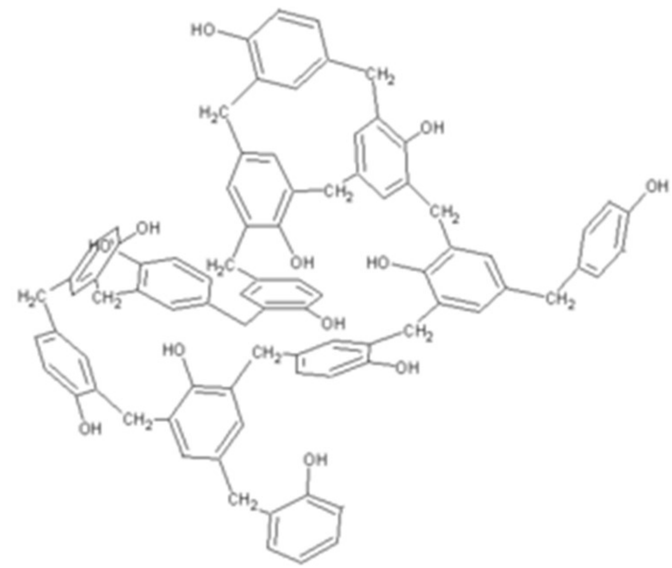


Polyvinyl chloride

Thermoset polymers

- 3 dimensional network of covalent bonds
- Do not soften at high temperature
- React with atmospheric oxygen and degrade
- These are relatively hard & rigid at RT
- Example Bakelite





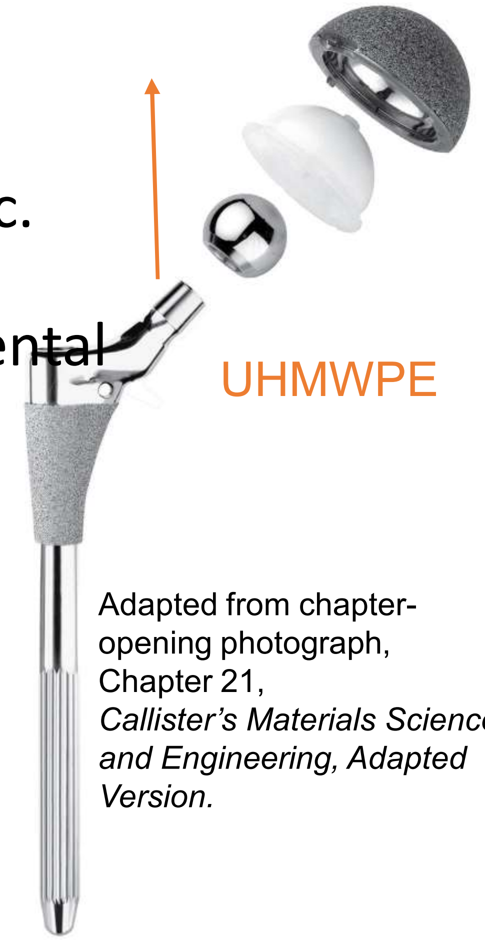
Advanced polymers

- Ultrahigh molecular weight polyethylene (UHMWPE)
  Molecular weight ~4 x 10^6 g/mol

- Excellent properties for variety of applications
  bullet-proof vest, golf ball covers, hip joints, etc.

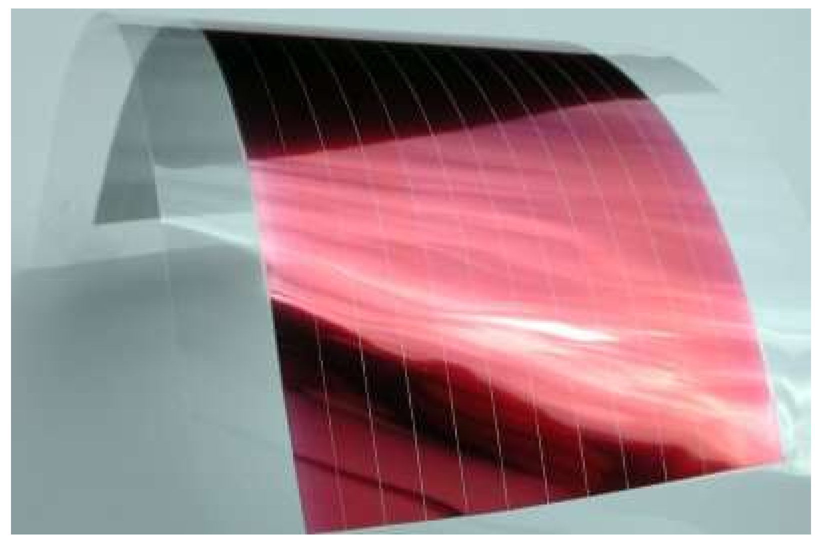
- Polymethylmethacrylate (PMMA): bone and dental cement, contact lenses

- Polytetrafluoroethylene (PTFE), Polyurethane, Polyvinylchloride (PVC)



Adapted from chapter-opening photograph, Chapter 21, *Callister's Materials Science and Engineering, Adapted Version.*

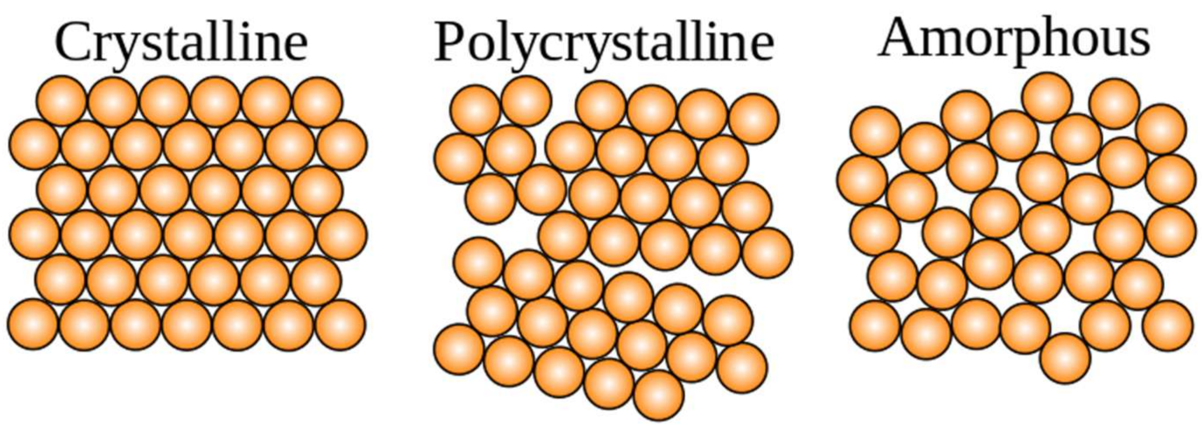
- Organic light emitting diodes
- Organic solar cells
- Conducting polymers



- Crystalline: Long range order
  - Single crystal
  - Polycrystalline

- Amorphous: Absence of long range order

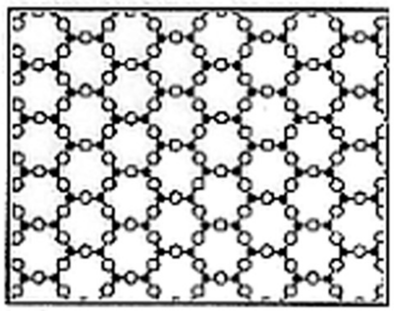
- Semi-crystalline: Crystalline + Amorphous



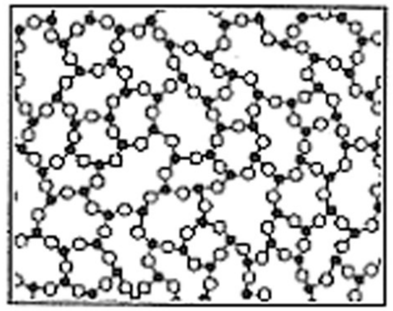
- Crystalline materials like metals, alloys, ionic solids and covalent compounds in solid state have anisotropic properties
- Polycrystals have lower anisotropy
- Amorphous materials can be truly isotropic
- Solar cell of silicon
- Crystalline or amorphous
- Engineering of defects

Glasses

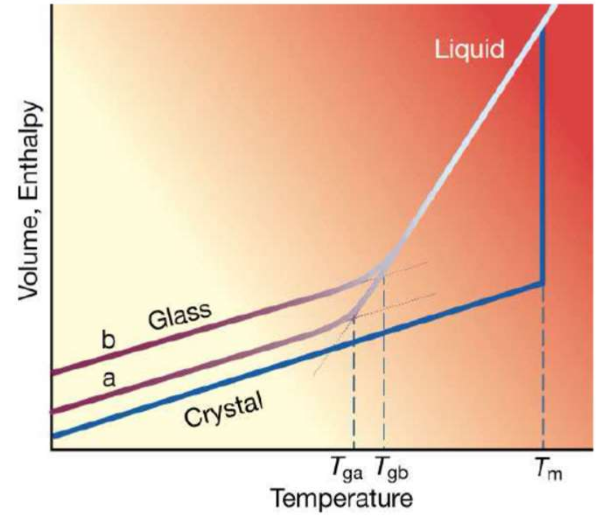
- From chai ki pyali to Gorilla glass on your mobile
- Absence of long range order
- Amorphous phase
- Supercooled liquid
- Nucleation and growth of crystals in solid state
- Avoid nucleation
- Possible to obtain Metallic glasses



quartz



glass

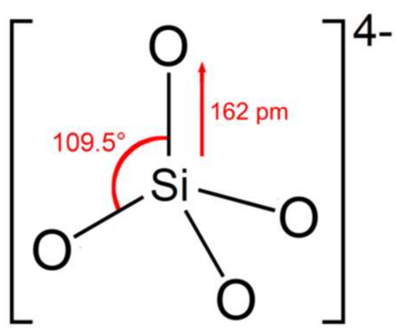


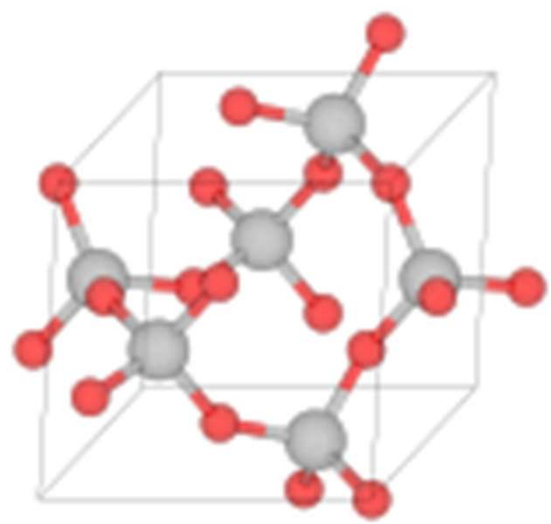
- Range of melting point

- Kinetic definition of glass is T_g, the glass transition temperature

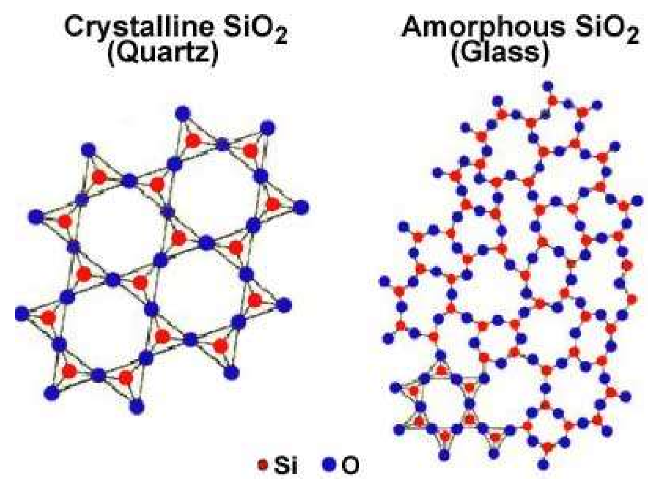
- The glass–liquid transition, or glass transition, is the gradual and reversible transition in amorphous materials) from a hard and relatively brittle "glassy" state into a viscous or rubbery state as the temperature is increased

- Crystalline silicon dioxide is quartz
- Quartz is crystalline
- $(SiO_4)^{4-}$ tetrahedron in chiral stacking



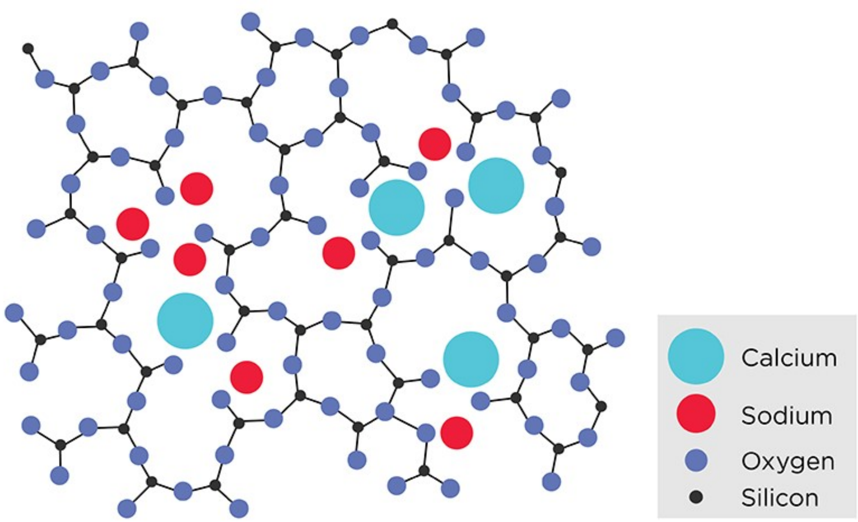


Alpha Quartz



https://en.wikipedia.org/wiki/Quartz

- Silicate glasses made of sand ($SiO_{2)}$
- Amorphous SiO4 tetrahedral network
- Borosilicate B_2O_3 and SiO_2
- Soda lime glass Na_2O_3, CaO, SiO_2



https://en.wikipedia.org/wiki/Quartz

- Glasses have isotropic properties and are an important class of amorphous materials
- Metallic glasses like CuZr offer excellent isotropic mechanical properties like high strength
- Possible to achieve higher cooling rate for larger cross sections
- Bulk metallic glasses for structural applications