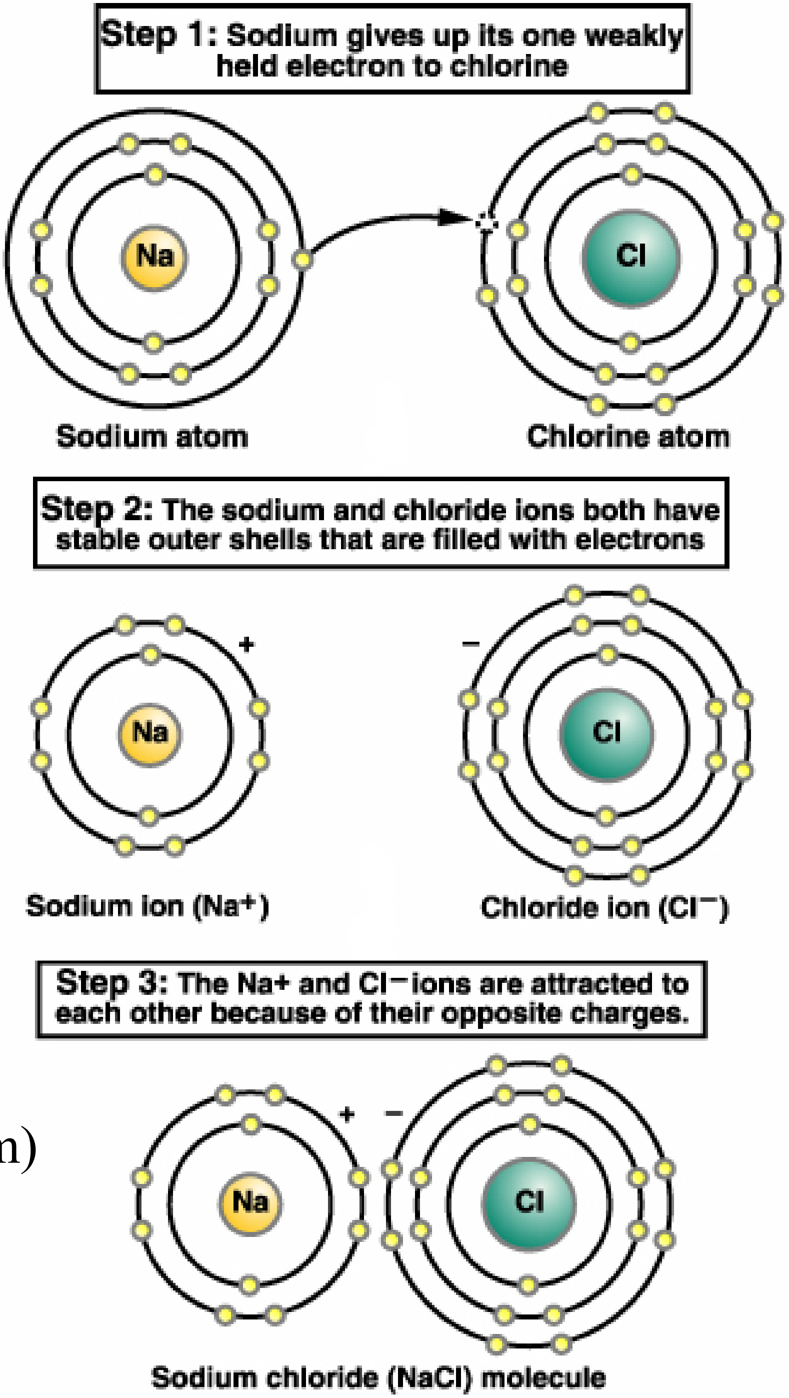
Ionic Bonding

- **Ion**: an atom or molecule that *gains* or *loses* electrons (acquires an electrical charge). Atoms form **cations** (+charge), when they lose electrons, or **anions** (-charge), when they gain electrons.
- **Ionic bonds** are *strong bonds* formed when *oppositely charged ions are attrac to each other.*
- Ionic bonds are **non-directional** (ions may be attracted to one another in any direction)

Example:

Atomic Radius: Na (r = 0.192nm) Cl (r = 0.099nm)

Ionic Radius : Na (r = 0.095nm) Cl (r = 0.181nm)



Step 1: Sodium gives up its one weakly held electron to chlorine

Step 2: The sodium and chloride ions both have stable outer shells that are filled with electrons

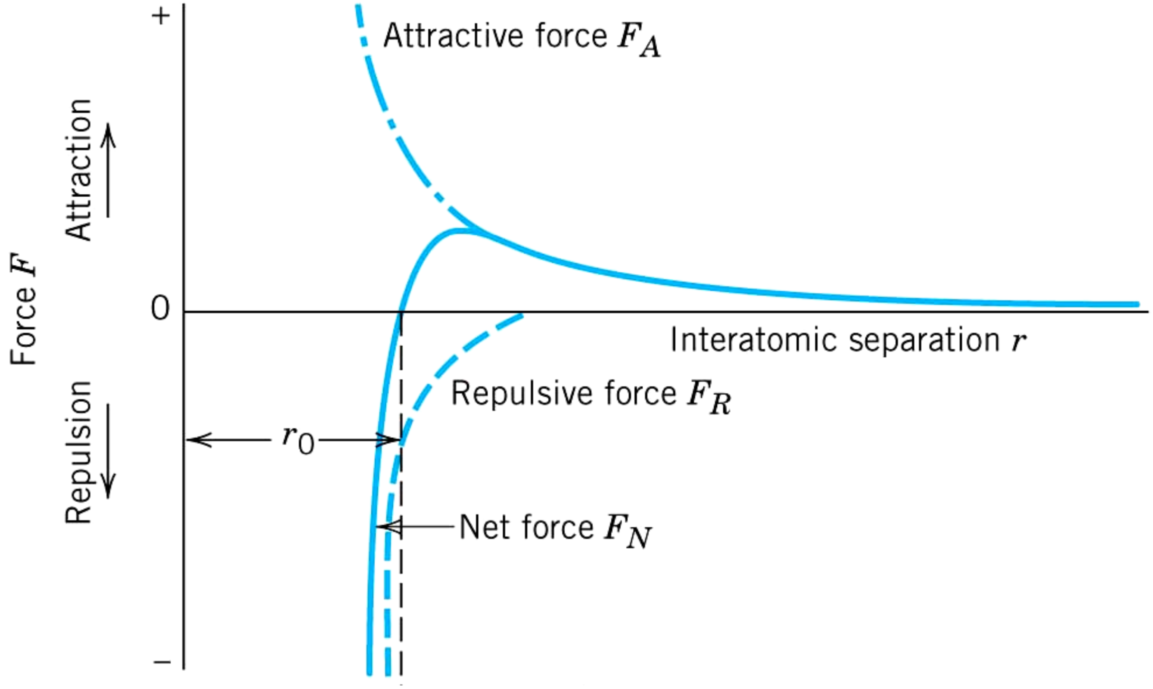
Step 3: The Na+ and Cl− ions are attracted to each other because of their opposite charges.

Inter-ionic Forces for an Ion Pair

$$F_{attr} = -\frac{(z_1 \cdot z_2)e^2}{4\pi\varepsilon_o a^2}$$

$$F_{rep} = -\frac{nb}{a^{n+1}}$$

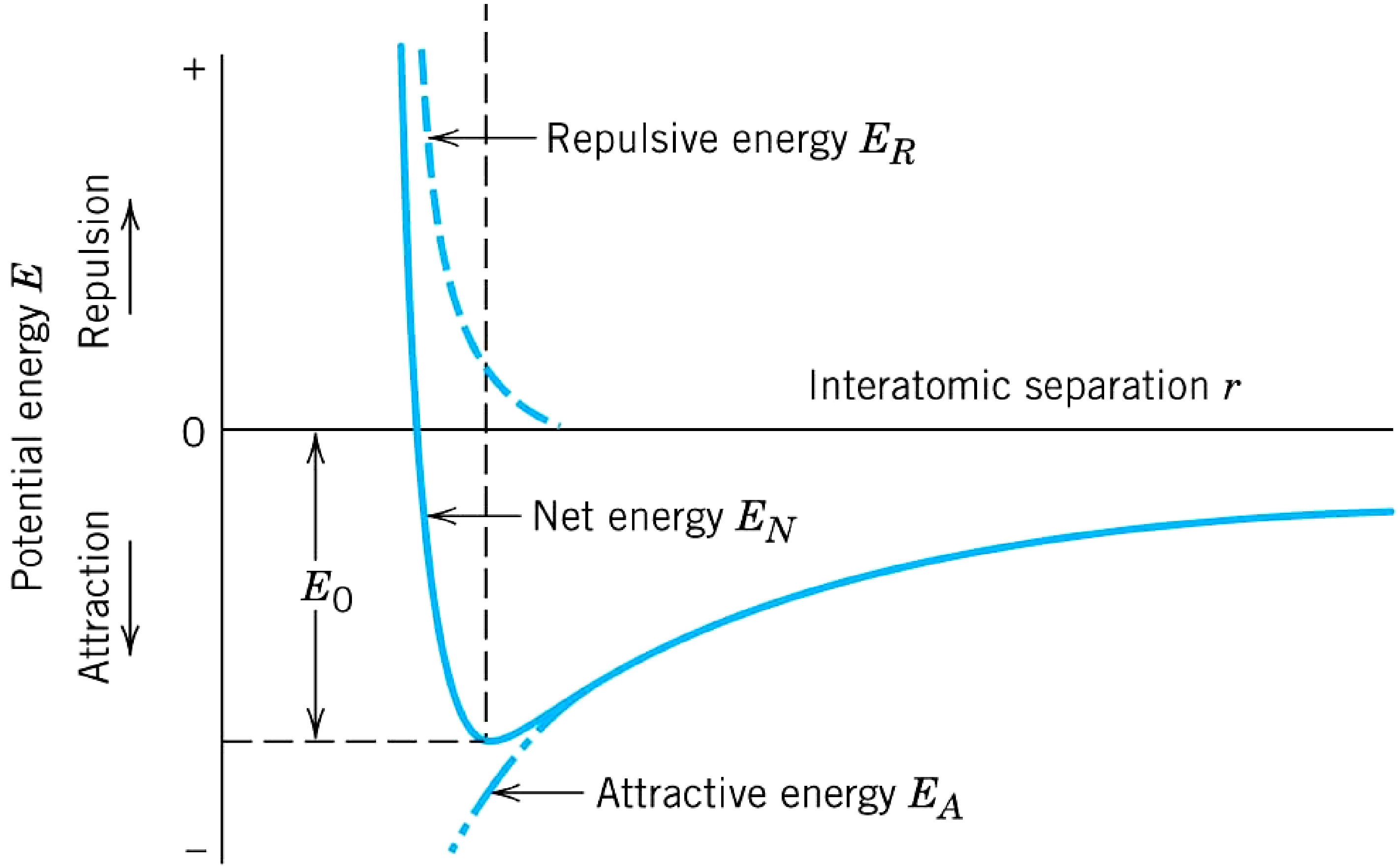
$$F_{net} = -\frac{(z_1 \cdot z_2)e^2}{4\pi\varepsilon_o a^2} - \frac{nb}{a^{n+1}}$$



Where z_1 and z_2 are the number of electrons added or removed from the atoms during the ion formation; ***e*** is the electron charge ($1.6\text{x}10^{-19}$ C); ***a*** is the interionic separation distance; ε_o is the permittivity of free space ($8.85\text{x}10^{-12}$ $C^2/(N.m^2)$) and ***b*** and ***n*** are constants.

Inter-ionic Energies for an Ion Pair

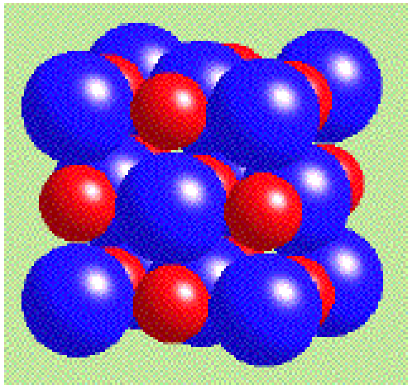
$$E_{net} = +\frac{z_1 z_2 e^2}{4\pi\varepsilon_o a} + \frac{b}{a^n}$$



Geometric Arrangement of Ions in an Ionic Solid

Because the ionic bond is nondirectional the ions pack together in a solid in ways which are governed by their relative sizes.

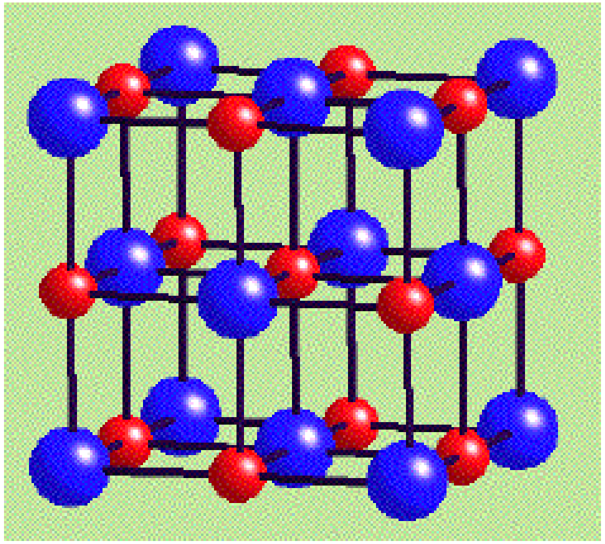
Another important factor is that the ions must be arranged so that their is local charge neutrality. [Note the structure of NaCl.]

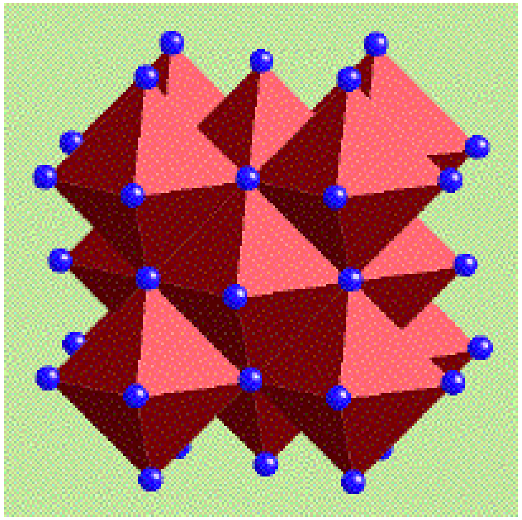


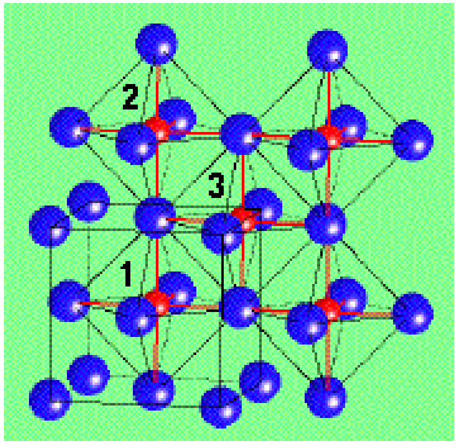
NaCl

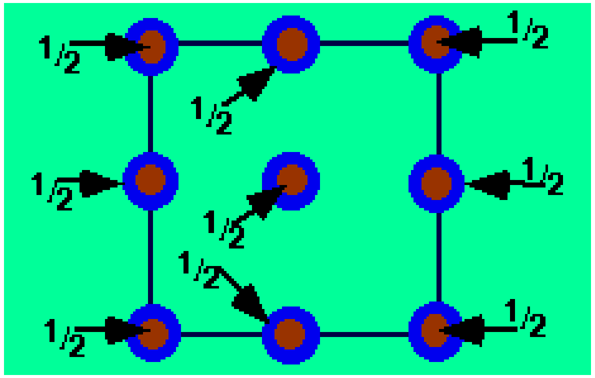
Rock Salt

(Halite)









Ionic Solids - Properties

- Formed by Coulombic attraction between ions.
  - Examples include Na+ plus Cl- (table salt).
- Large cohesive energy (2-4 eV/ atom).
  - Leads to high melting and boiling points.
- Low electrical conductivity.
  - No “free” electrons to carry current.
- Transparent to visible light.
  - Photon energy too low to “free” electrons.
- Soluble in polar liquids like water.
  - Liquid dipole of water attracts ions.

Covalent Bonding

Covalent bonding involves the ***sharing*** of one or more electrons pairs between atoms. Elements that tend to form covalent bonds are those that are:

- **strongly electronegative,**
- **not strongly electropositive, or**
- **have similar electronegativities**

Covalent bonds can be formed not only between identical atoms but also between different atoms.

By sharing electrons, the atoms completely fill their valence shell and achieve a stable-octet arrangement of electrons.

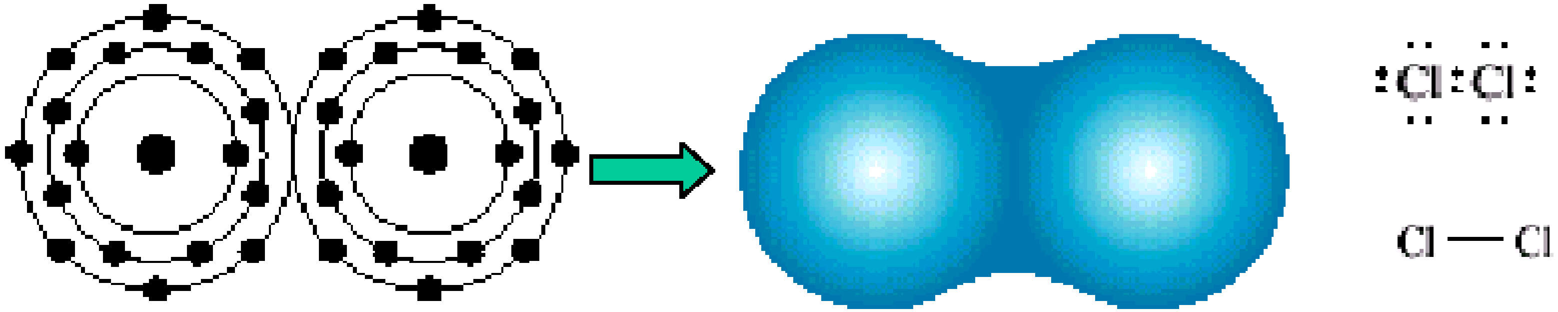
It forms a strong **localized** and **directional** bond (in the direction of the greatest orbital overlap).

If the atoms in a covalent bond are different from one another, **the electron pair may not be shared equally between them. Such a bond is call a *polar covalent bond*.**

The atoms that are linked will carry a partial negative or positive charge.

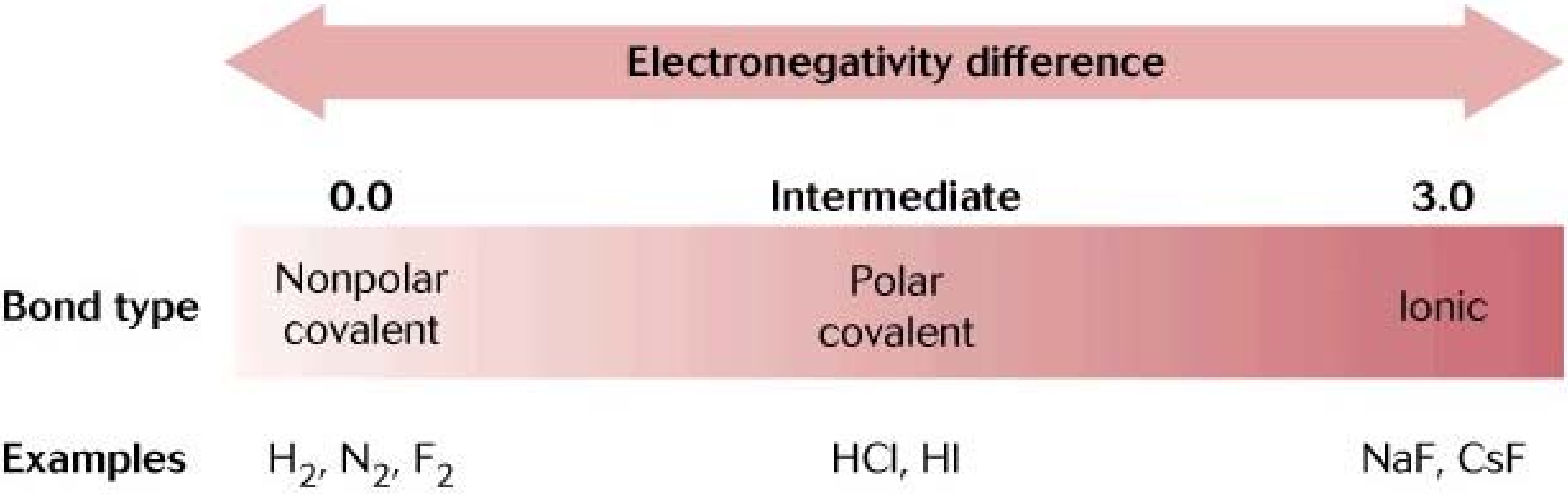
Example: Cl_2 molecule. $Z_{Cl}=17$ ($1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^5$)

N' = 7, 8 - N' = 1 → can form only one covalent bond



$$H_{\times}^{\bullet}\ddot{\underset{\bullet\bullet}{C}}l\colon \quad \text{or} \quad {}^{\delta+}H-\ddot{\underset{\bullet\bullet}{C}}l\colon^{\delta-}$$

Polar bonds are distributed along a continuum,

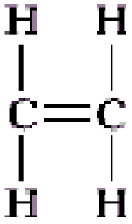


	0.0	Intermediate	3.0
Bond type	Nonpolar covalent	Polar covalent	Ionic
Examples	H_2, N_2, F_2	HCl, HI	NaF, CsF

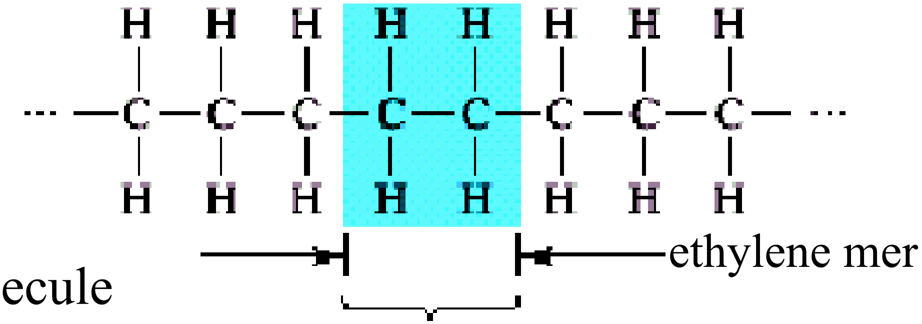
Covalent Solids - Properties

- Examples include group IV elements (C, Si) and III-V elements (GaAs, InSb).
- Formed by strong, localized bonds with stable, closed-shell structures.
- Larger cohesive energies than for ionic solids (4-7 eV/atom).
  Leads to higher melting and boiling points.
- Low electrical conductivity.
  Due to energy band gap that carriers must "jump," where larger gaps give insulators and smaller gaps give semiconductors.

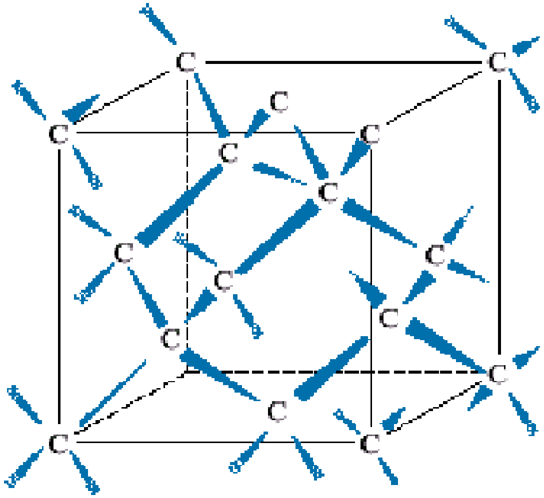
Example: Carbon materials. $Z_C = 6$ ($1S^2\ 2S^2\ 2P^2$)
N’ = 4, 8 - N’ = 4 → can form up to four covalent bonds



ethylene molecule



polyethylene molecule



diamond: (each C atom has four covalent bonds with four other carbon atoms)

Covalent Bonding by Carbon

- Ground State: Electron configuration $1s^2\ 2s^2\ 2p^2$.
- This electron arrangement indicates that carbon should form **two covalent** bonds with its two half-filled ***2p*** orbitals.
- In many cases carbon forms **four covalent** bonds of equal strength.
- Hybridization: one of the ***2s*** orbitals is promoted to a ***2p*** orbital so that four equivalent ***sp³*** hybrid orbitals are produced

Hybrid orbitals

Carbon: ↑↓ | ↑↓ | ↑ ↑ → ↑↓ | ↑ ↑ ↑ ↑

1s 2s 2p 1s $2(sp^3)$

$2(sp^3)$ is tetrahedrally shaped (energy is identical)

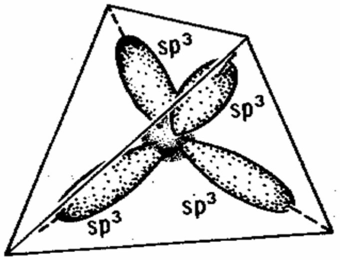
Larger overlap → stronger

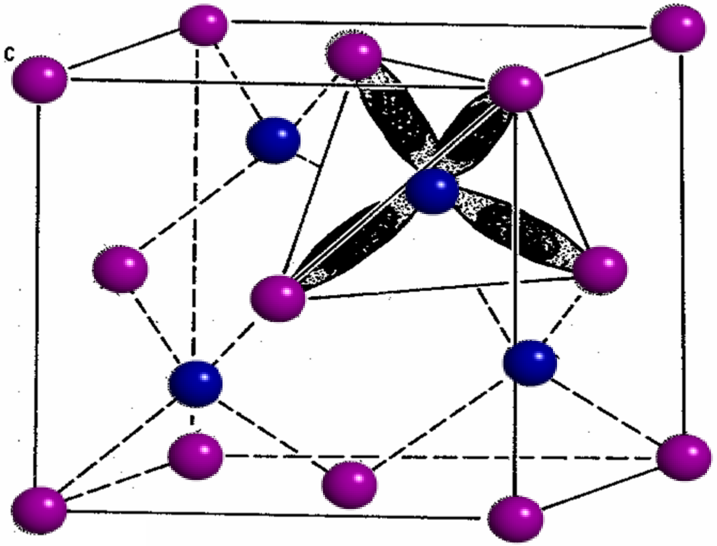
Directional: each C is tetrahedrally coordinated with 4 others (& each of them with 4 others...)

C-C-C bond angle fixed at 109° 28' (max. overlap). It is also known as *σ-bond*

Note Face-centered Cubic lattice (Diamond – very hard)

The directional character → lower coordination & symmetry, density.





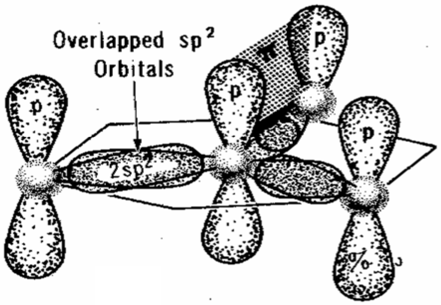
Hybrid Orbitals

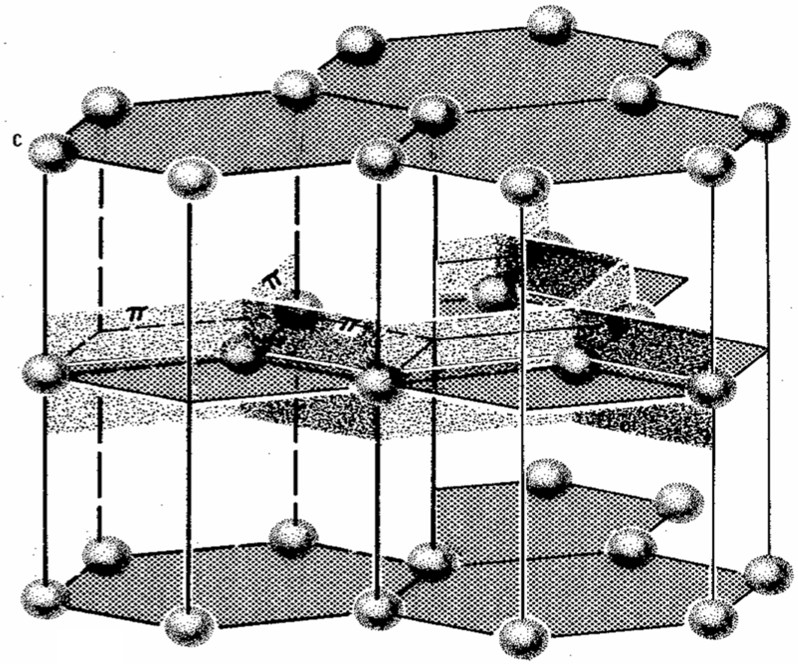
Alternatively:

Carbon: ↑↓ | ↑↓ | ↑ ↑ → ↑↓ | ↑ ↑ ↑ | ↑

1s 2s 2p 1s 2(sp2) 2p

The ***3 - 2(sp^2)*** orbitals are coplanar & 120^o apart
Graphite structure (***sp^2*** Hexagonal Crystal Class) Overlap similar to diamond w/in sheets (strong too!). Note ***π****-bonding* (vertical bonding) between remaining ***2p's.*** This results in delocalized ***e$^-$*** 's in ***2p*** which results in electrical conductivity only within sheets. Good lubricant





Covalent/Ionic mixed bonding

Different atoms widely spaced on the periodic table form mainly ionic bonds.

Different atoms which are closer together form mixed covalent/ionic bonds.

Fraction can be predicted pretty well by electronegativity.

$$\% \text{ ionic} = \{1 - \exp[-(0.25)(X_a - X_b)^2]\} \times 100$$

where X's are electronegativities of the two atoms.

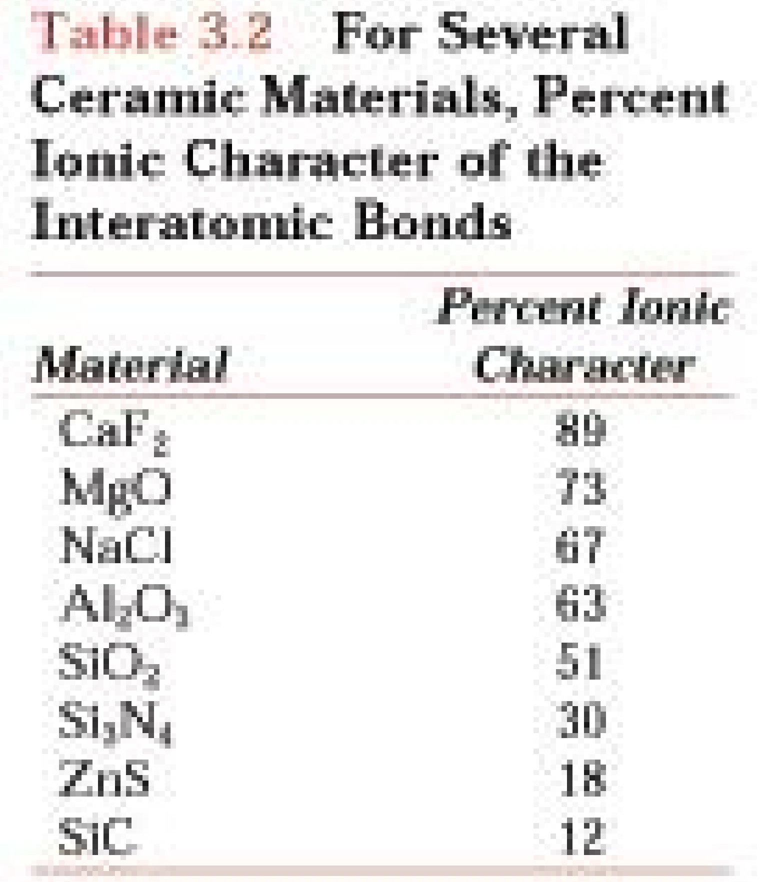


Table 3.2 For Several Ceramic Materials, Percent Ionic Character of the Interatomic Bonds

Material	*Percent Ionic Character*
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

Example

Calculate the percentage ionic character of rock salt NaCl (electronegativities 0.9 and 3.0 respectively)

$$\% \text{ ionic} = \{1 - \exp[-(0.25)(3.0 - 0.9)^2]\} \times 100 = (1 - 0.33) \times 100$$

$$\% \text{ ionic} = 67\%$$

Metallic Bonding

Atoms of similar electron negativity and toward left side of PT

Metallic bonds are directionless bonds → high symmetry and density

Pure metals have same sized atoms

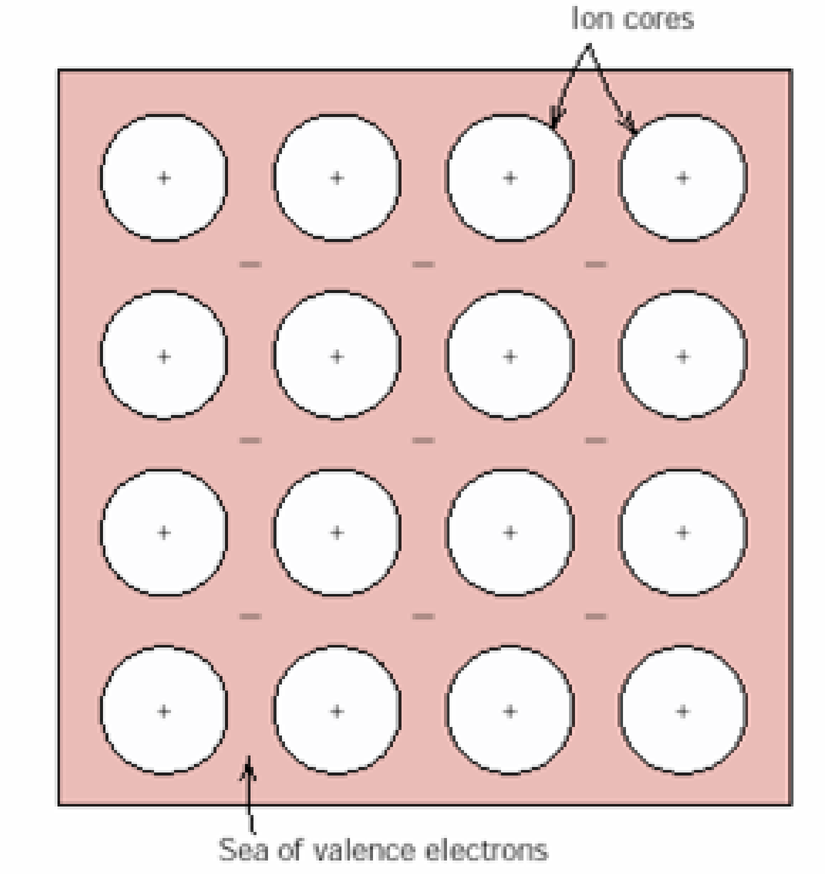
Closest packing → 12 nearest mutually-touching neighbors

Cubic Closest Packing (CCP) ***ABCABCABC = FCC cell***

Hexagonal Closest Packing (HCP) ***ABABABAB = hexagonal cell***

Also BCC in metals, but this is not close-packed (CP) (VII coordination)

Most metals readily give up their valence electrons when they bond to other metals. Result is positive ion cores in a “sea” of electrons. (this is why metals conduct heat and electricity.) Covalent and ionic bonds lock up electrons, which is why ceramics are electrical and thermal insulators.



Metallic Solids - Properties

•Formed by Coulombic attraction between (+) lattice ions and (–) electron “gas.”

•Metallic bond allows valence electrons to move freely through lattice (i.e. e^- gas).

•Smaller cohesive energy (1-4 eV).

•High electrical conductivity.

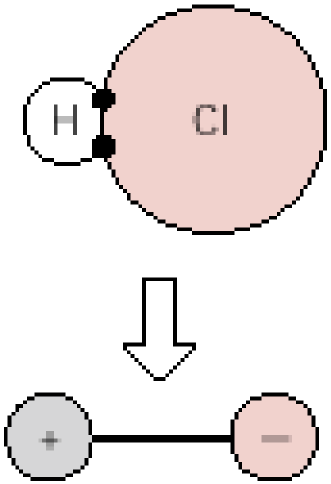
•Absorbs visible light (non-transparent, “shiny” due to re-emission).

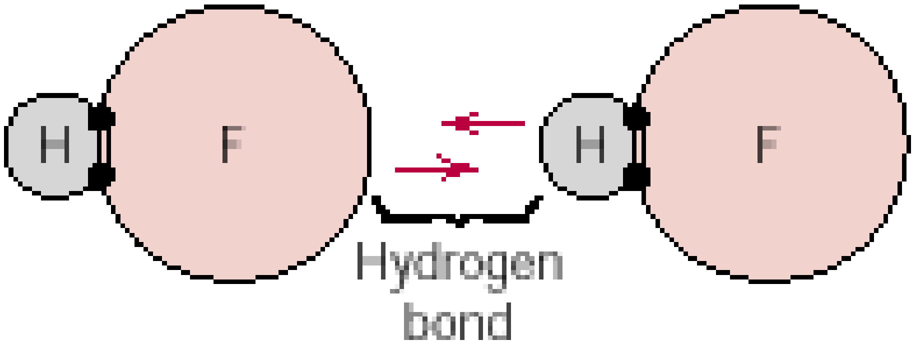
•Good alloy formation (due to non-directional metallic bonds).

Secondary Bonding

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.

Occur due to electrostatic attraction between dipoles. Dipoles form when regions on molecules have charges concentrated in different areas. H_2O is a common example.

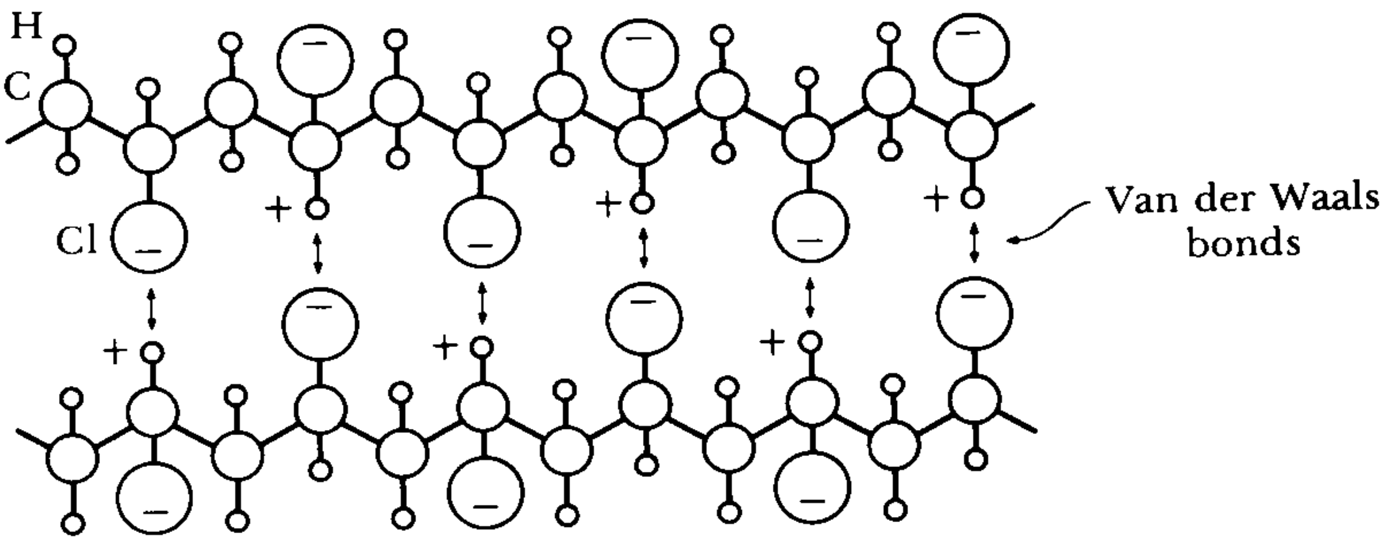




Permanent dipole moments exist in some molecules (called **polar molecules**) due to the asymmetrical arrangement of positively and negatively regions (HCl, H_2O). Bonds between adjacent polar molecules – **permanent dipole bonds** – are strongest among secondary bonds.

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 induce a dipole momentum in this atom. **This bond due to fluctuating induced dipoles is the weakest (inert gases, H_2, Cl_2).**



Permanent Dipole Bonds

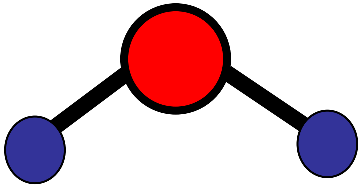
- Weak intermolecular bonds are formed between molecules which possess permanent dipoles. (Example: methane, PVC)
- A dipole exists in a molecule if there is asymmetry in its electron density distribution.

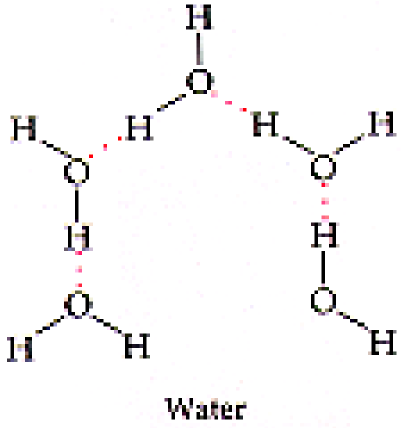
Fluctuating Dipole Bonds

- Weak electric dipole bonding can take place among atoms due to an instantaneous asymmetrical distribution of electron densities around their nuclei. (Example: atoms in noble gases)
- This type of bonding is termed fluctuation since the electron density is continuously changing.

Hydrogen Bond

- Permanent dipole-dipole interaction between polar molecules. Example: water, ***2H*** and ***1O*** form a polar covalent bond with an asymmetrical structure (105° angle).
- Hydrogen bonding forms a weak bond with either Fluorine, Nitrogen, Oxygen

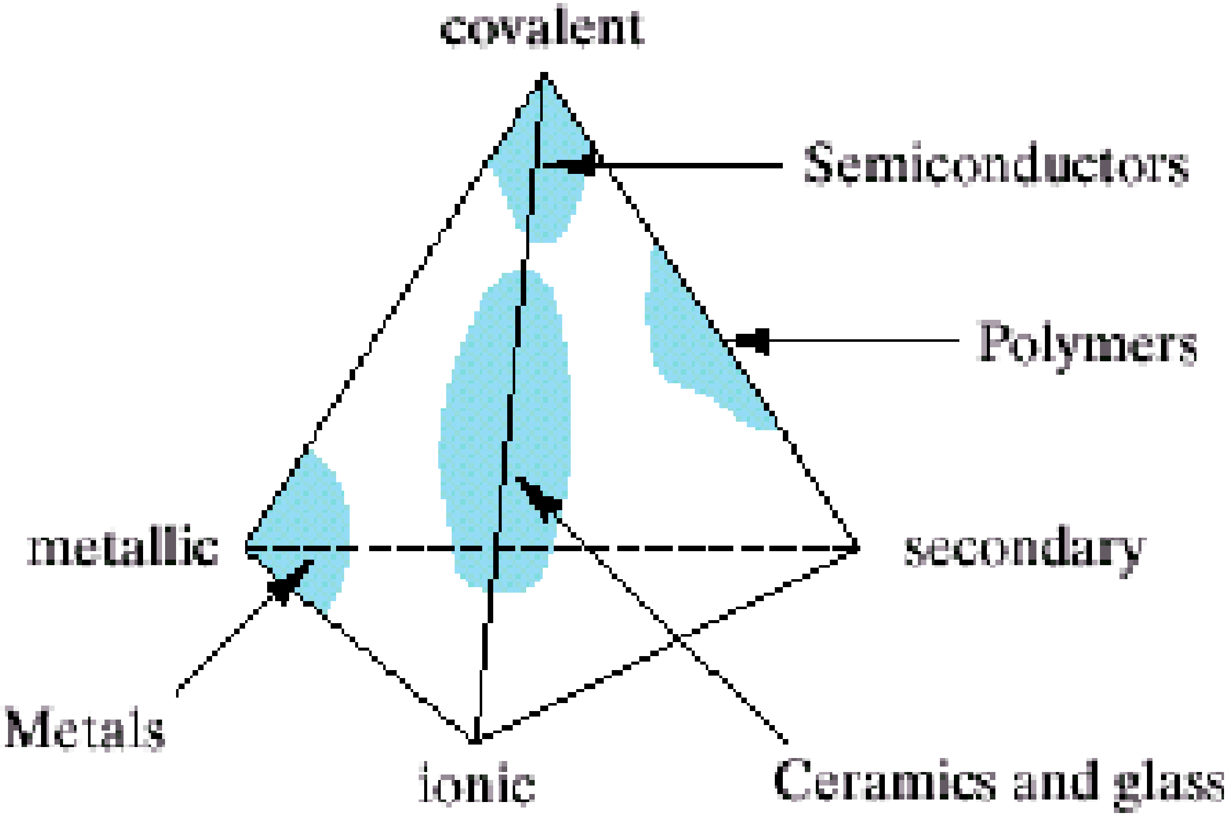




"***Hydrogen bond***" – secondary bond formed between two **permanent dipoles** in adjacent water molecules.

Mixed Bonding

- ❑Metallic-Covalent Mixed Bonding: The *Transition Metals* are an example where *dsp* bonding orbitals lead to high melting points.
- ❑Ionic-Covalent Mixed Bonding: Many oxides and nitrides are examples of this kind of bonding. [Values in the table below were calculated from Pauling Equation.

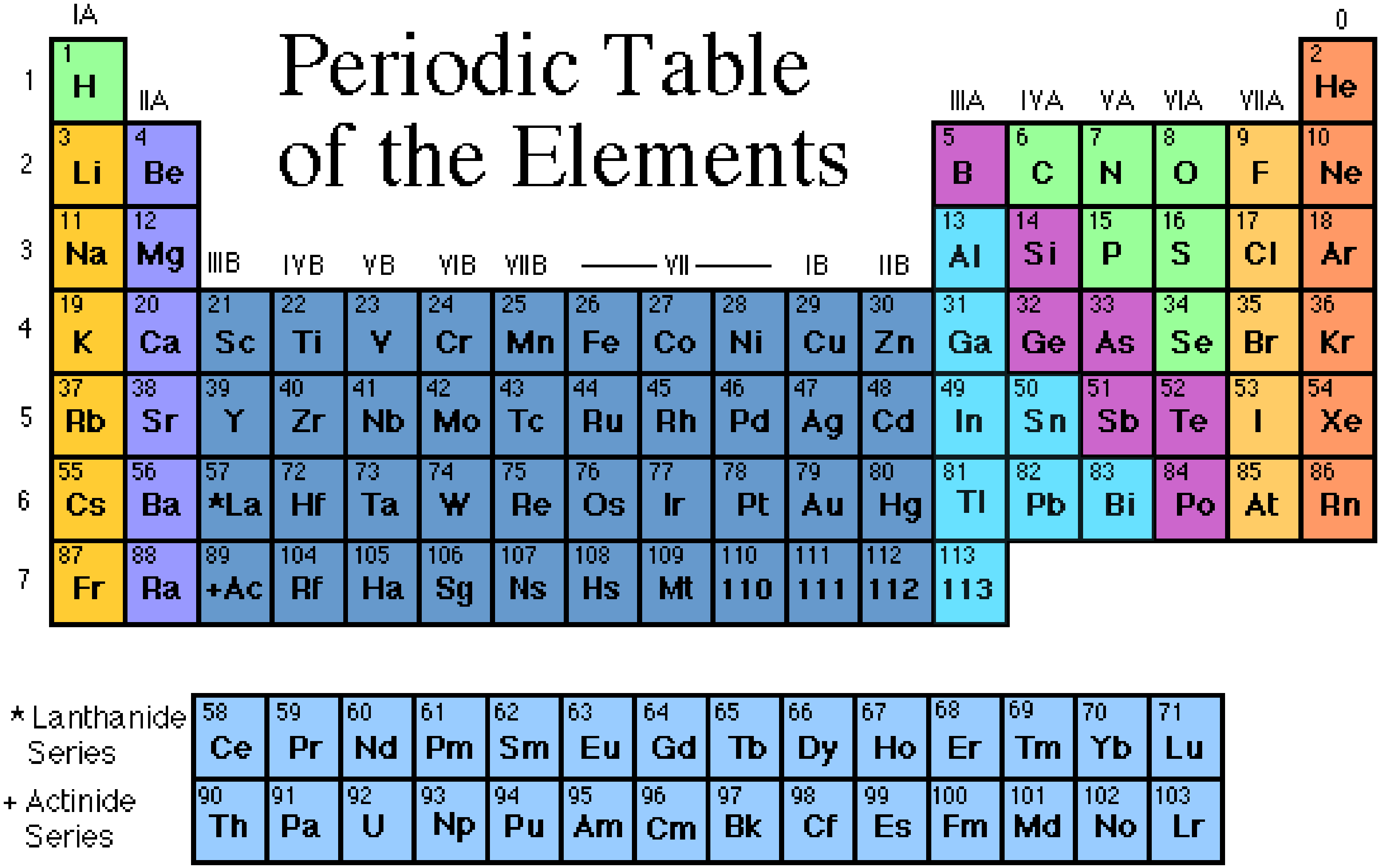


Elements are classified as:

Metals w/ e-neg < 1.9 thus lose e^- and → **cations**

Nonmetals > 2.1 thus gain e^- and → **anions**

Metalloids intermediate (B, Si, Ge, As, Sb, Te, Po..)



Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

		Bonding Energy		*Melting Temperature (°C)*
Bonding Type	*Substance*	*kJ/mol (kcal/mol)*	*eV/Atom, Ion, Molecule*	
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl_2	31 (7.4)	0.32	−101
Hydrogen	NH_3	35 (8.4)	0.36	−78
	H_2O	51 (12.2)	0.52	0