Chapter 2
Atomic Structure

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Outline

1- Review of Atomic Structure

- Electrons, Protons, Neutrons.
- Atomic Bonding in Solids.
- Periodic Table.
- Primary Interatomic Bonds .
- Secondary Bonding (Van der Waals).

2- Molecules and Molecular Solids

Review of Atomic Structure

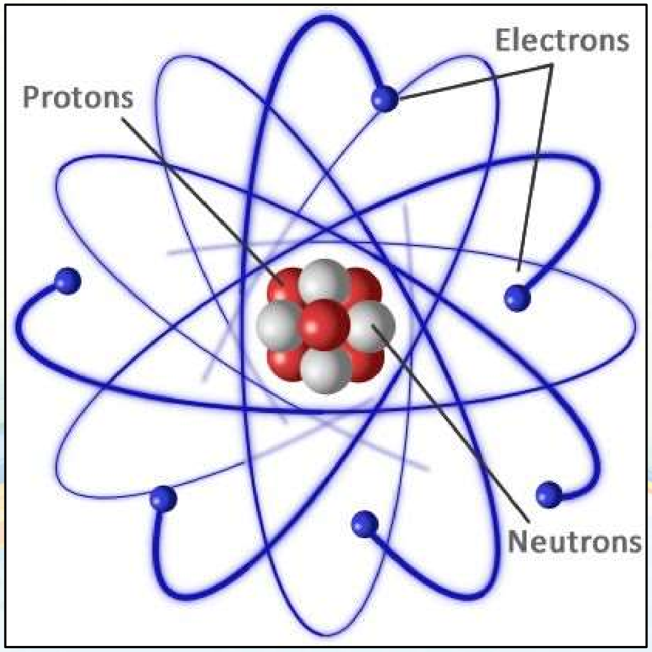
What are atoms?

- Atoms are the basic building blocks of matter that make up everyday objects.
- Atoms are made out of three basic particles:

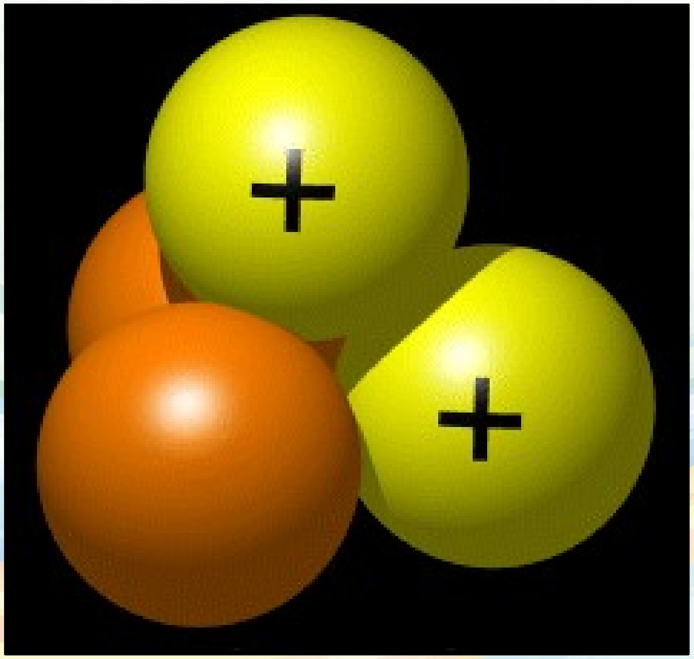
1. Protons – carry a positive charge
2. Neutrons – carry no charge

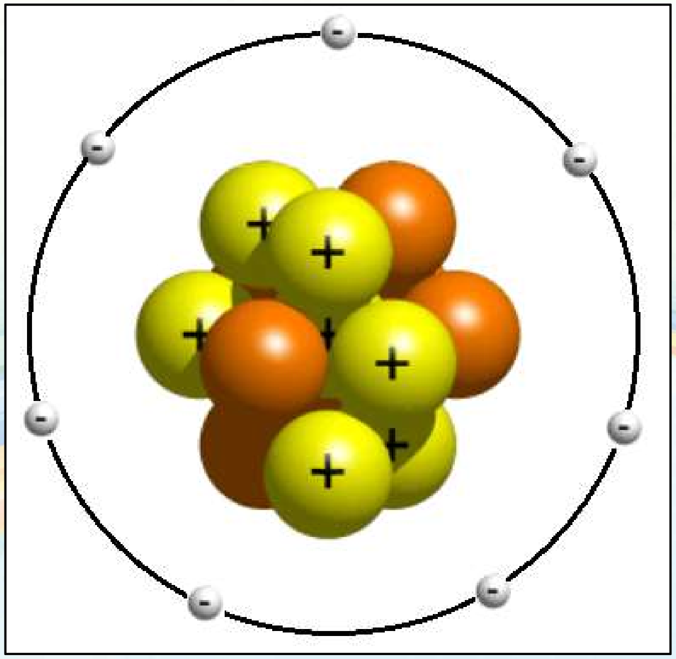
✓ Protons and Neutrons join together to form the Nucleus – the central part of the atom

3. Electrons – carry a negative charge and circle the nucleus



- *The nucleus is the massive center of the atom. It was discovered in 1911, but it took scientists another 21 years of experimenting to identify its parts.*





Atomic Weight

Protons + Neutrons

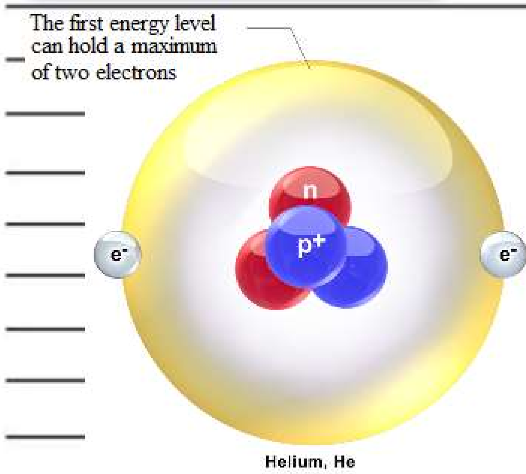
Element's Symbol

$${}^{A}_{Z}X_{N}$$

Atomic Number

Protons = Electrons

Number of Neutrons



Atomic number: 2 Mass number: 4

(2 protons + 2 neutrons) 2 electrons

$\therefore N = A - Z$

As an example: Helium atom ${}^{4}_{2}He_{2}$

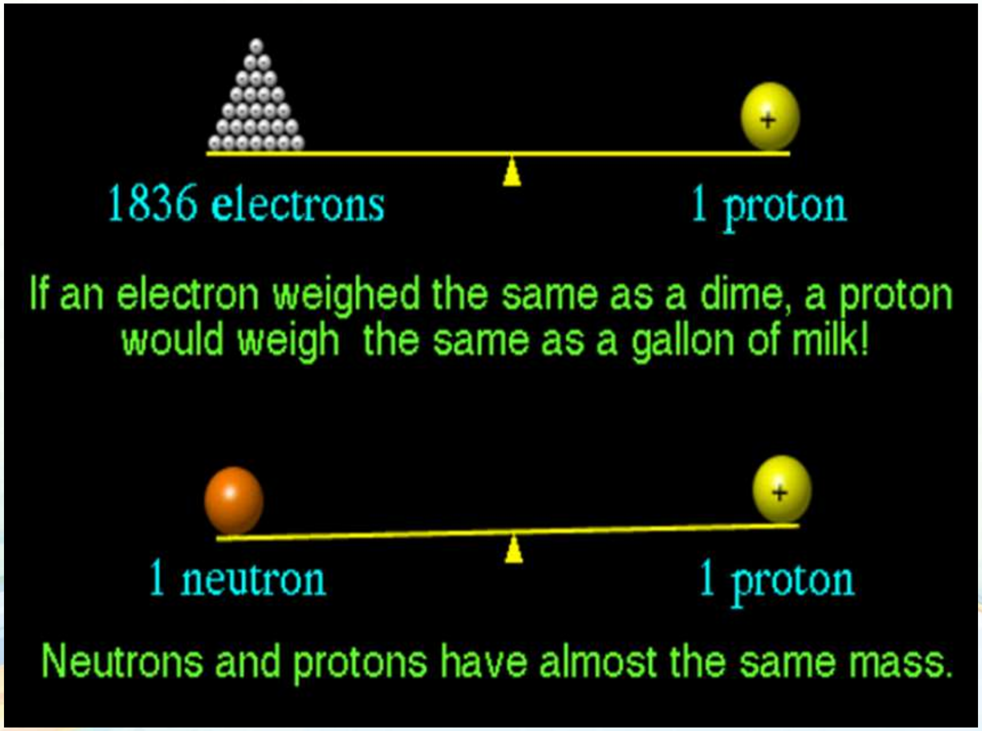
- Protons
- Neutrons
- Electrons

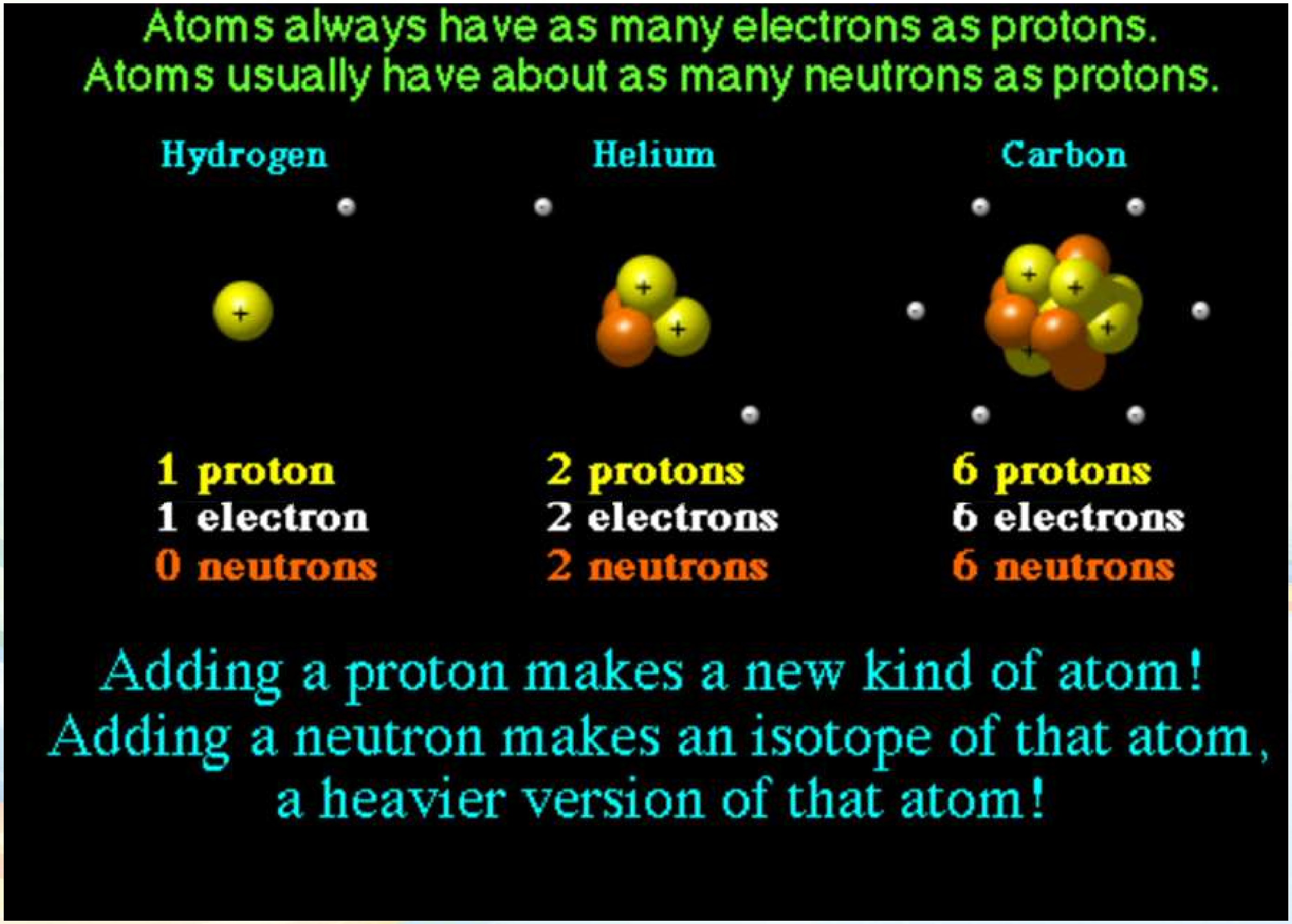
Charges:

- *Electron's and Proton's charges are of the same magnitude, 1.602 × 10^{-19} Coulombs.*

Masses:

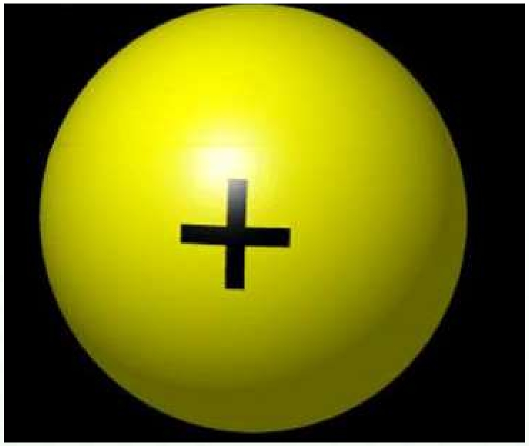
- *Protons and Neutrons have the same mass, 1.67 × 10^{-27} kg.*
- *Mass of an electron is much smaller, 9.11 × 10^{-31} kg and can be neglected in calculation of atomic mass.*

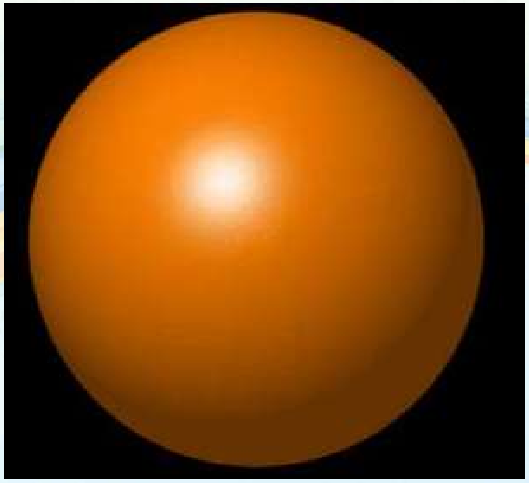



Atoms always have as many electrons as protons.
Atoms usually have about as many neutrons as protons.
Hydrogen
Helium
Carbon
1 proton
1 electron
0 neutrons
2 protons
2 electrons
2 neutrons
6 protons
6 electrons
6 neutrons
Adding a proton makes a new kind of atom!
Adding a neutron makes an isotope of that atom,
a heavier version of that atom!

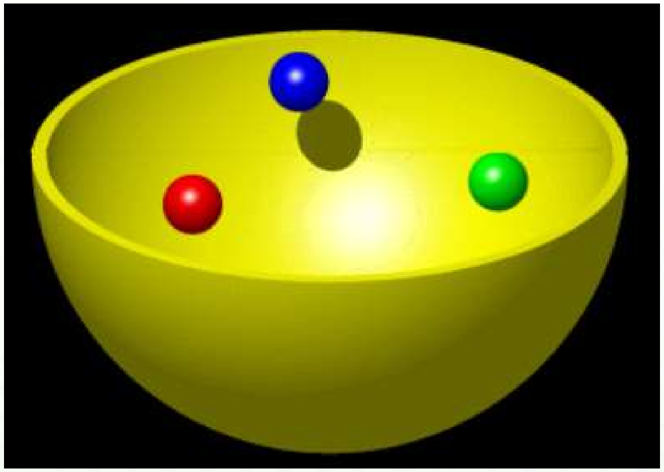
- *Scientists thought there was nothing smaller than the proton in the nucleus of the atom.*

- *Scientists discovered the neutron in 1932. They thought that there was nothing smaller in the atom's nucleus?*

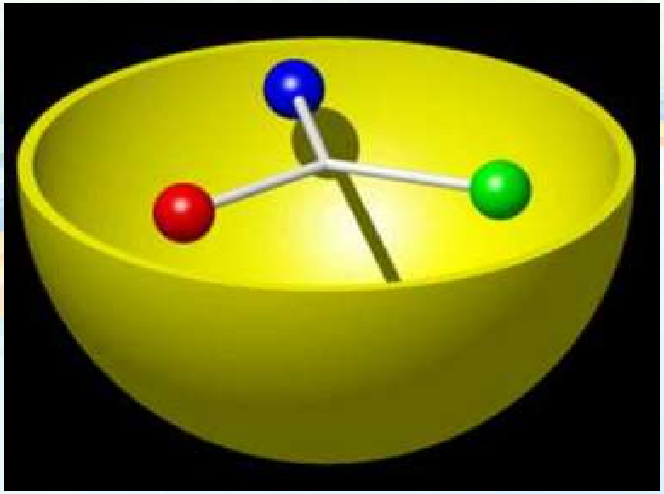




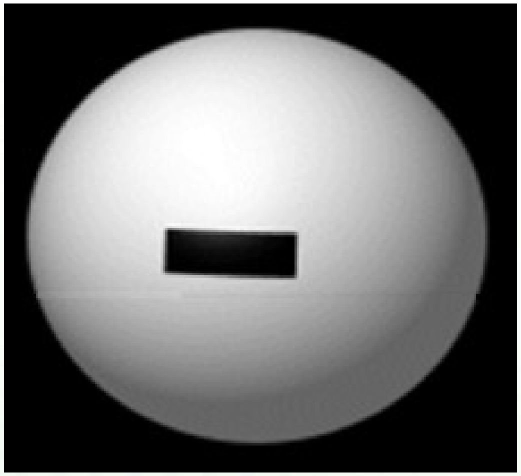
- *In 1968, scientists discovered new particles inside the proton. They called these particles quarks.*

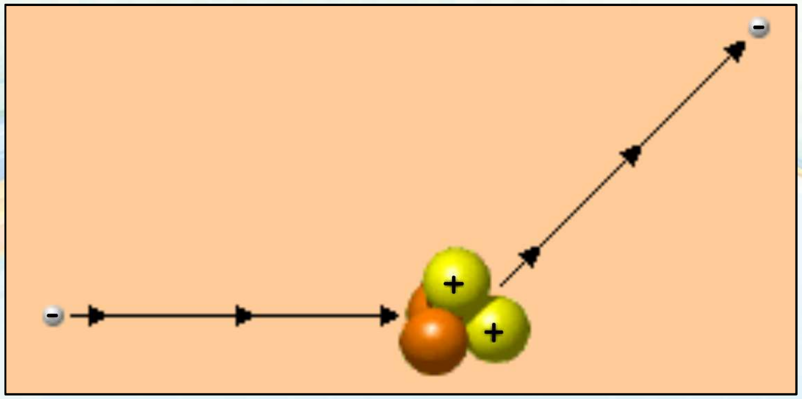


- *There are three quarks in each proton. The quarks are held to each other by other particles called gluons.*



- *Electrons are extremely small and very light.*
- *It is easy to strip off electrons of atoms and use them for electrical power and in devices like television sets.*
- *Electrons can be used to probe inside of atoms. Higher energy electrons can detect smaller features inside of atoms. Scientists learn about the inside of atoms by watching how electrons bounce off the atom, and by how the atom changes as a result of being hit by an electron.*





Number of Atoms

- The number of atoms per cm³, n, for material of density d (g/cm³) and atomic mass M (g/mol) is:

$$n = \frac{N_{av} d}{M}$$

where N_{av} is Avogadro's number = 6.022×10^{23} atms/mol

- Mean distance between atoms

$$L = \left(\frac{1}{n}\right)^{1/3}$$

Example:

Diamond (carbon): $d = 3.5$ g/cm³, $M = 12$ g/mol

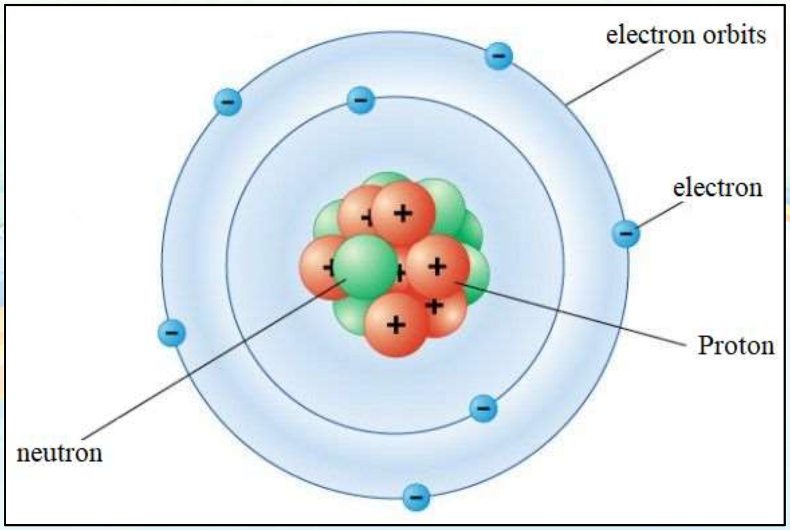
$n = 6 \times 10^{23}$ atoms/mol $\times$ 3.5 g/cm³/12 g/mol

$= 17.5 \times 10^{22}$ atoms/cm³

$L = (1/(17.5 \times 10^{22}))^{1/3} = 0.179$ nm

Electrons in Atoms

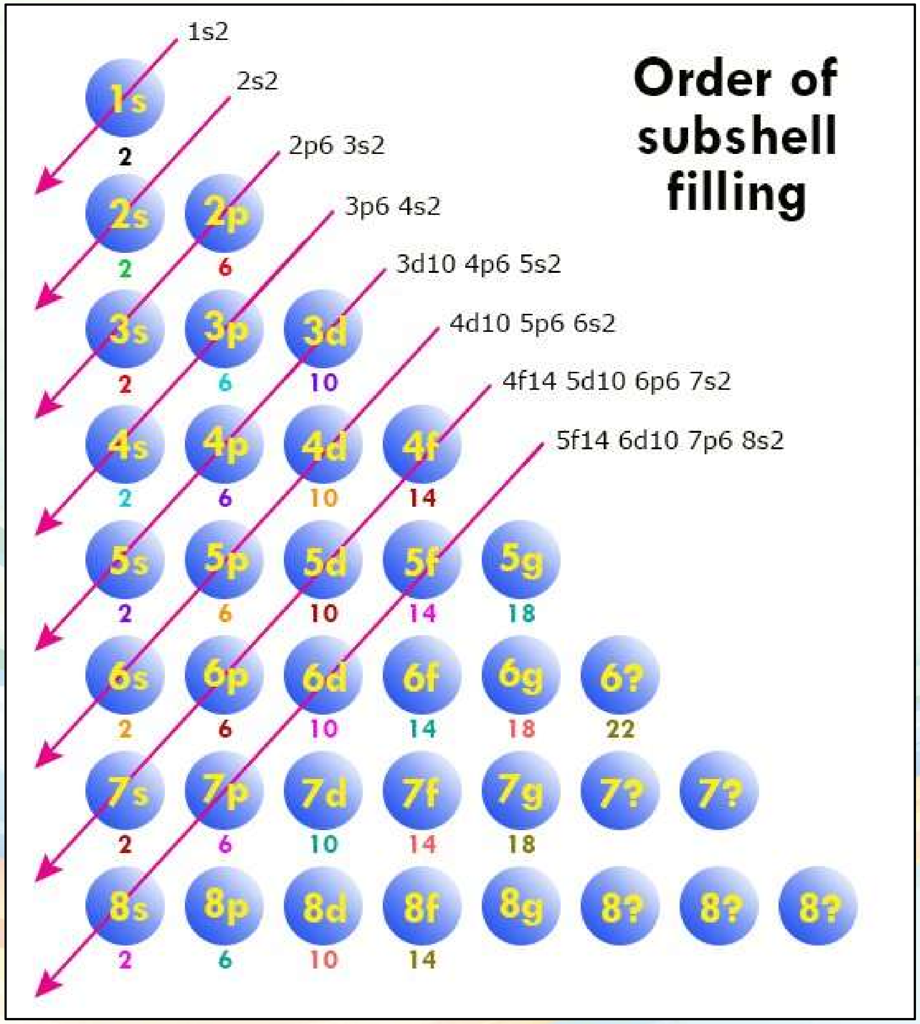
- The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.
- This "Bohr" picture looks like a mini planetary system. But quantum mechanics tells us that this analogy is not Correct.
- Electrons move not in circular orbits, as in popular drawings, but in 'fuzzy' orbits.



- *One cannot tell how it moves, but only say what is the probability of finding it at some distance from the nucleus.*
- *Valence electrons determine all of the following properties:*
  - ✓ *Chemical.*
  - ✓ *Electrical.*
  - ✓ *Thermal.*
  - ✓ *Optical.*
- *Each orbital at discrete energy level determined by quantum numbers.*

- The number of available electron states in some of the electron shells and subshells

Principal Quantum number n	Shell designation	Subshells	Number of States	Electrons per Subshell	Electrons per Shell
1	K	S	1	2	2
2	L	S	1	2	8
		P	3	6	
3	M	S	1	2	18
		P	3	6	
		D	5	10	
4	N	S	1	2	32
		P	3	6	
		D	5	10	
		F	7	14	



Subshells by energy:

1s,2s,2p,3s,3p,4s,3d,4p,5s,4d,5p,6s,4f,…

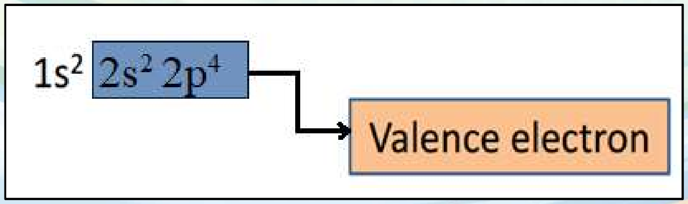
- *Most elements: Electron configuration not stable.*

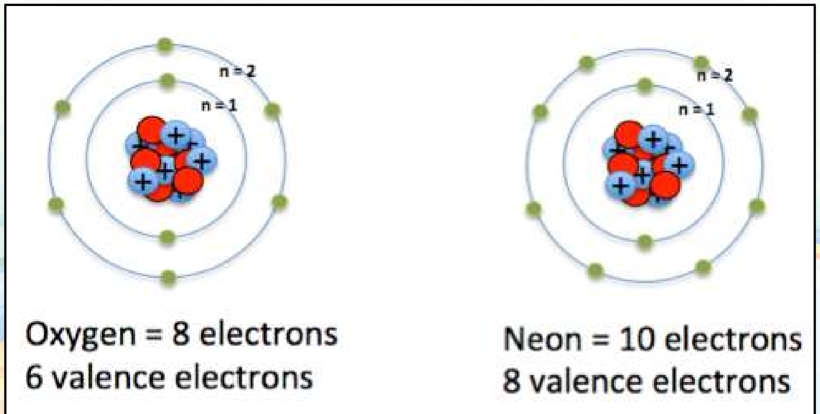
Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
...		...	
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	(stable)
...	...	...	
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$	(stable)

Valence Electron

- Valence electrons – those in unfilled shells.
- Filled shells more stable.
- Valence electrons are most available for bonding and tend to control the chemical properties.

Example: O (atomic number = 8)

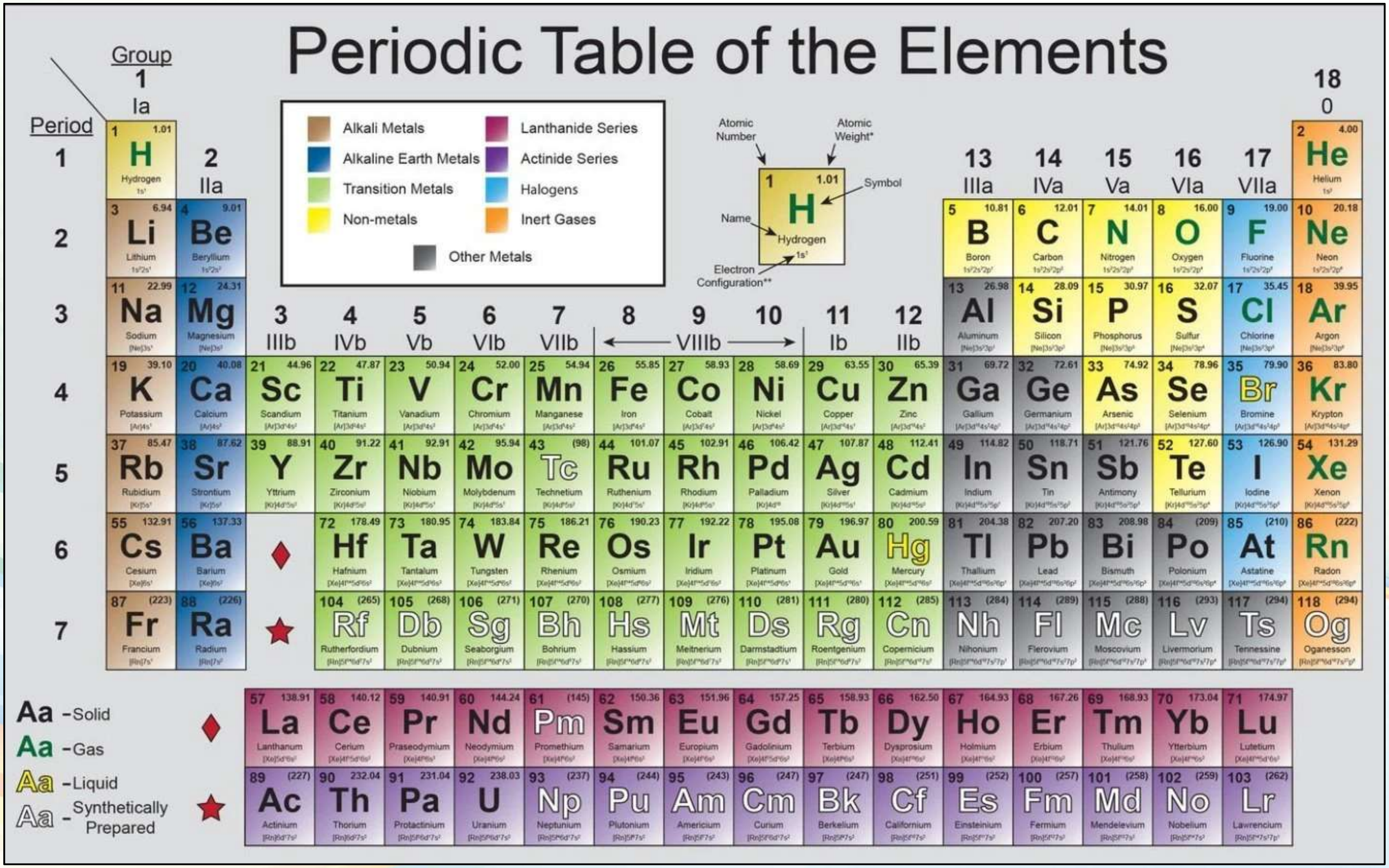




Valence Electrons of Oxygen and Neon

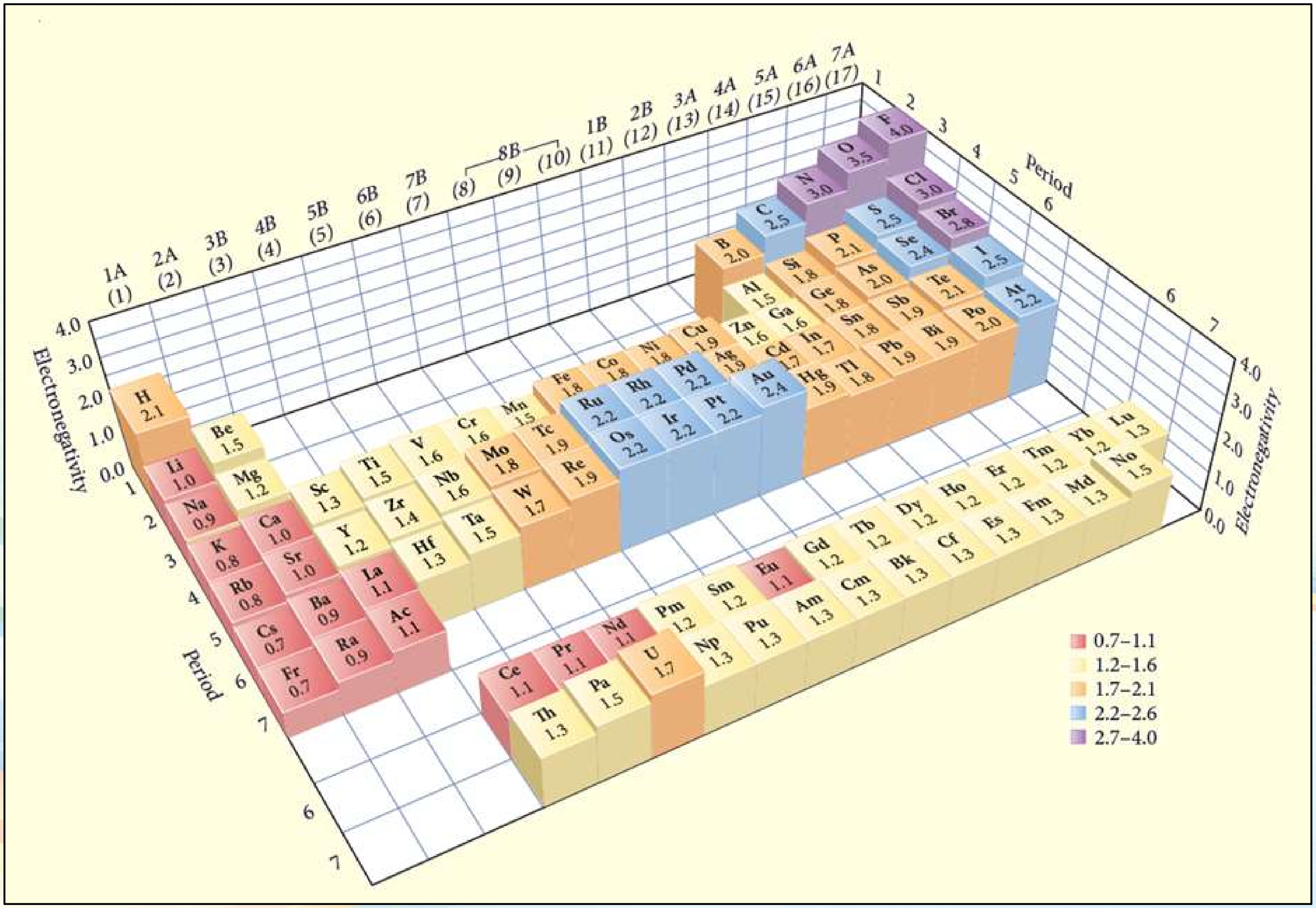
The Periodic Table

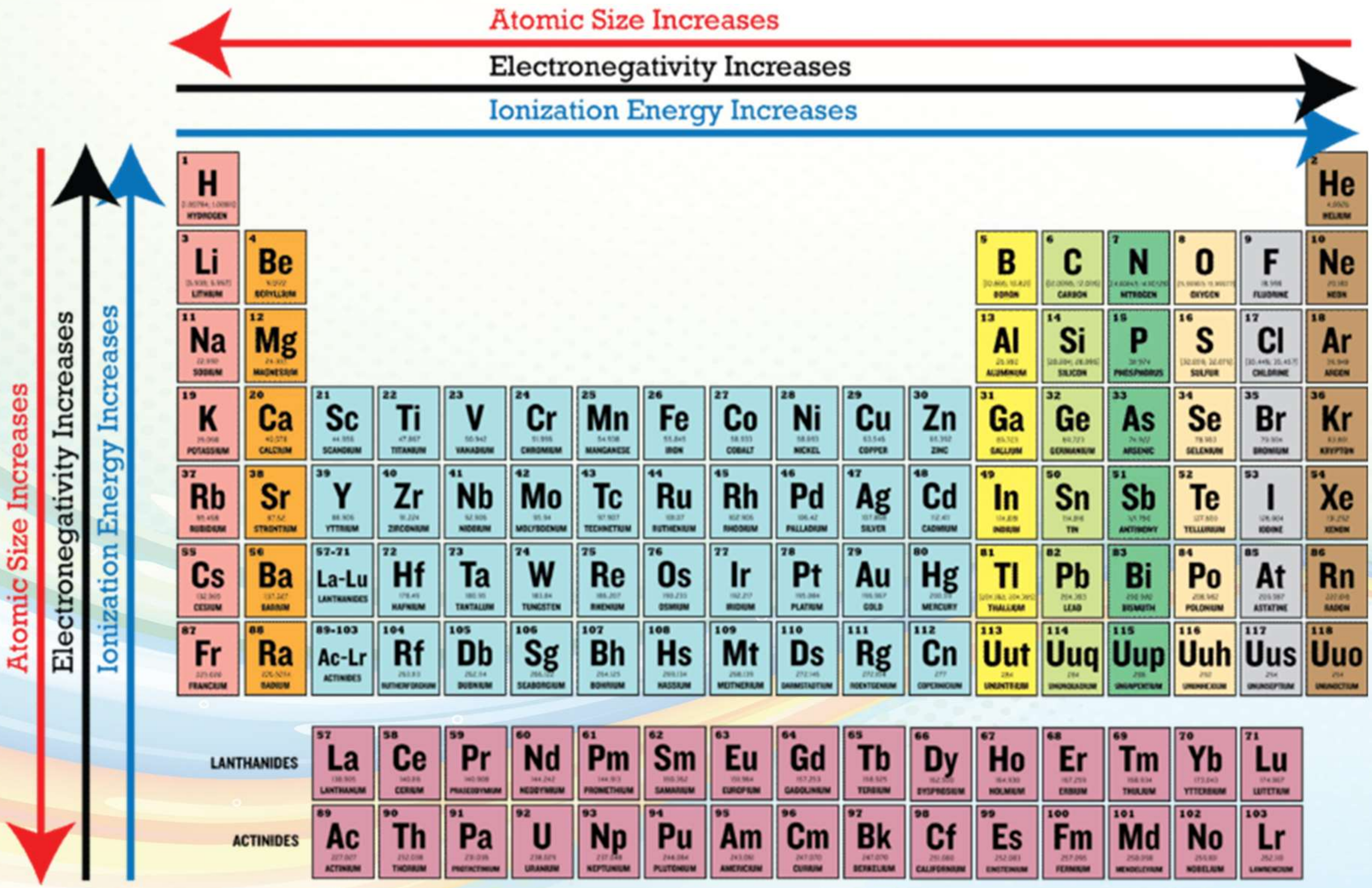
- Electrons that occupy the outermost filled shell (the valence electrons) they are responsible for bonding.
- Electrons fill quantum levels in order of increasing energy (due to electron penetration).
- Example: Iron, Fe = 26: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. Elements in the same column (Elemental 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.


Periodic Table of the Elements
Group
Period
Alkali Metals
Alkaline Earth Metals
Transition Metals
Non-metals
Other Metals
Lanthanide Series
Actinide Series
Halogens
Inert Gases
Atomic Number
Atomic Weight*
Symbol
Name
Electron Configuration**
Aa -Solid
Aa -Gas
Aa -Liquid
Aa - Synthetically Prepared

The Electronegativity Values

- **Electronegativity** - a measure of how willing atoms are to accept electrons.
  - Subshells with one electron - low electronegativity
  - Subshells with one missing electron – high electronegativity.
  - Electronegativity increases from left to right in the periodic table.
  - Metals are electropositive – they can give up their few valence electrons to become positively charged ions.
  - Electronegativity ranges from 0.7 to 4.0


1A (1)
2A (2)
3B (3)
4B (4)
5B (5)
6B (6)
7B (7)
8B
(8) (9) (10)
1B (11)
2B (12)
3A (13)
4A (14)
5A (15)
6A (16)
7A (17)
Electronegativity
4.0
3.0
2.0
1.0
0.0
Period
1
2
3
4
5
6
7
H 2.1
Li 1.0
Be 1.5
Na 0.9
Mg 1.2
K 0.8
Ca 1.0
Sc 1.3
Ti 1.5
V 1.6
Cr 1.6
Mn 1.5
Fe 1.8
Co 1.8
Ni 1.8
Cu 1.9
Zn 1.6
Ga 1.6
Ge 1.8
As 2.0
Se 2.4
Br 2.8
Rb 0.8
Sr 1.0
Y 1.2
Zr 1.4
Nb 1.6
Mo 1.8
Tc 1.9
Ru 2.2
Rh 2.2
Pd 2.2
Ag 1.9
Cd 1.7
In 1.7
Sn 1.8
Sb 1.9
Te 2.1
I 2.5
Cs 0.7
Ba 0.9
La 1.1
Hf 1.3
Ta 1.5
W 1.7
Re 1.9
Os 2.2
Ir 2.2
Pt 2.2
Au 2.4
Hg 1.9
Tl 1.8
Pb 1.9
Bi 1.9
Po 2.0
At 2.2
Fr 0.7
Ra 0.9
Ac 1.1
B 2.0
C 2.5
N 3.0
O 3.5
F 4.0
Al 1.5
Si 1.8
P 2.1
S 2.5
Cl 3.0
Ce 1.1
Pr 1.1
Nd 1.1
Pm 1.2
Sm 1.2
Eu 1.1
Gd 1.2
Tb 1.2
Dy 1.2
Ho 1.2
Er 1.2
Tm 1.2
Yb 1.2
Lu 1.3
Th 1.3
Pa 1.5
U 1.7
Np 1.3
Pu 1.3
Am 1.3
Cm 1.3
Bk 1.3
Cf 1.3
Es 1.3
Fm 1.3
Md 1.3
No 1.5
0.7–1.1
1.2–1.6
1.7–2.1
2.2–2.6
2.7–4.0


Atomic Size Increases
Electronegativity Increases
Ionization Energy Increases
Atomic Size Increases
Electronegativity Increases
Ionization Energy Increases
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La-Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac-Lr Rf Db Sg Bh Hs Mt Ds Rg Cn Uut Uuq Uup Uuh Uus Uuo
LANTHANIDES
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
ACTINIDES
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

- *To calculate Pauling electronegativity for an element, it is necessary to have data on the dissociation energies of at least two types of covalent bond formed by that element.*
- *The difference in electronegativity between atoms A and B is given by:*

$$\chi_A - \chi_B = eV^{-1/2}\sqrt{E_d(AB) - \frac{[E_d(AA) + E_d(BB)]}{2}}$$

where:

The dissociation energies, E_d, of the A-B, A-A and B-B bonds are expressed in electron volts, the factor $(eV)^{-1/2}$ being included to ensure a dimensionless result.

Example:

Calculate the difference in Pauling electronegativity between hydrogen and bromine if the dissociation energies: H–Br, 3.79 eV; H–H, 4.52 eV; Br–Br 2.00 eV.

Solution:

Note that 1 kcal/mol = 4.3363 ×10⁻² eV

$$\chi_A - \chi_B = \left(1.602 \times 10^{-19}\right)^{-1/2} \sqrt{\left(3.79 - \left[\frac{4.52 + 2.00}{2}\right]\right) \times 1.602 \times 10^{-19}}$$

$\chi_A - \chi_B = 0.728$

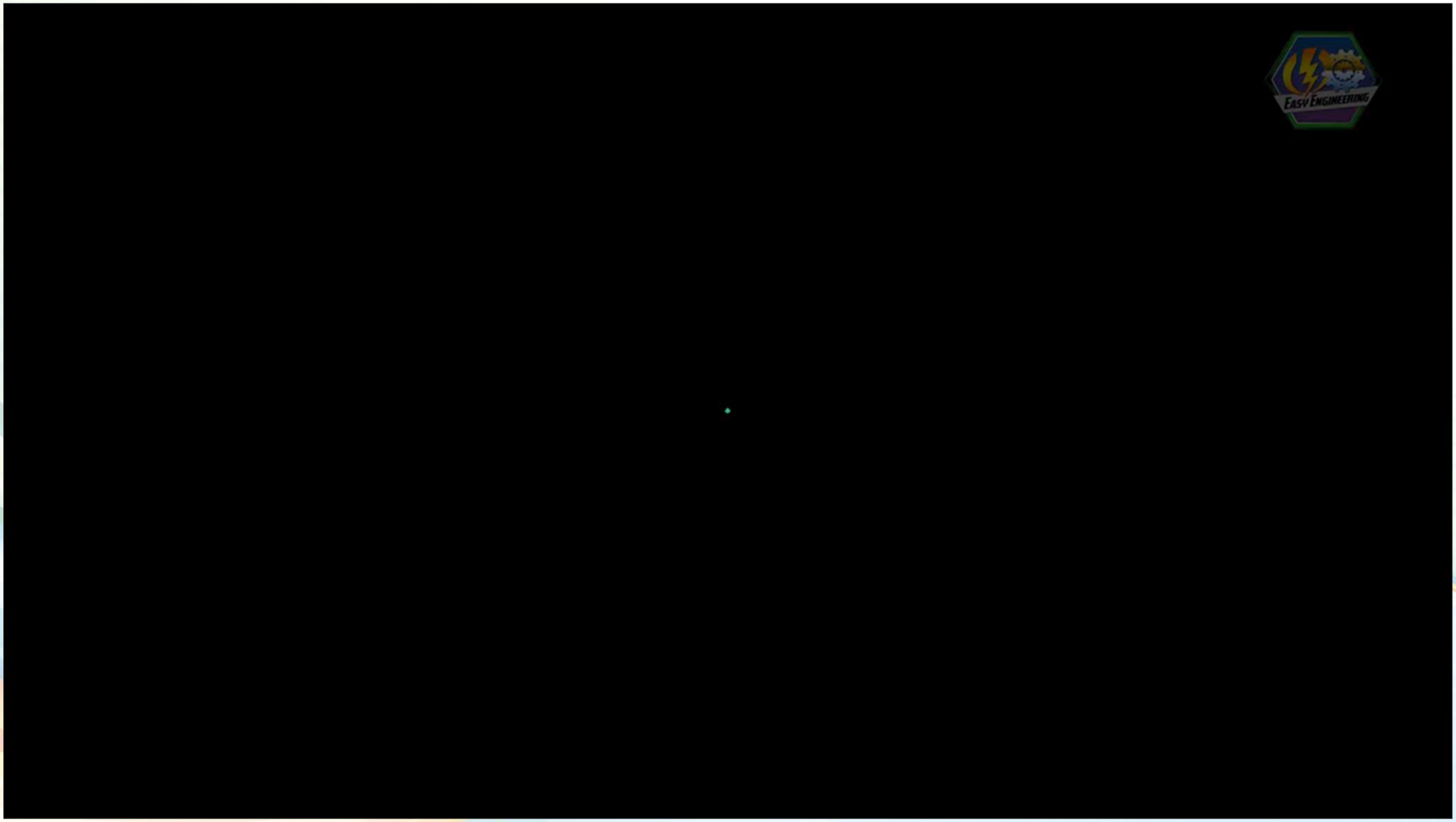
Standard Bond Energies

Single Bonds	ΔH°*	Single Bonds	ΔH°*	Multiple Bonds	ΔH°*
H–H	104.2	B–F	150	C=C	146
C–C	83	B–O	125	N=N	109
N–N	38.4	C–N	73	O=O	119
O–O	35	N–CO	86	C=N	147
F–F	36.6	C–O	85.5	C=O (CO_2)	192
Si–Si	52	O–CO	110	C=O (aldehyde)	177
P–P	50	C–S	65	C=O (ketone)	178
S–S	54	C–F	116	C=O (ester)	179
Cl–Cl	58	C–Cl	81	C=O (amide)	179
Br–Br	46	C–Br	68	C=O (halide)	177
I–I	36.	C–I	51	C=S (CS_2)	138
H–C	99	C–B	90	N=O (HONO)	143
H–N	93	C–Si	76	P=O ($POCl_3$)	110
H–O	111	C–P	70	P=S ($PSCl_3$)	70
H–F	135	N–O	55	S=O (SO_2)	128
H–Cl	103	S–O	87	S=O (DMSO)	93
H–Br	87.5	Si–F	135	P=P	84
H–I	71	Si–Cl	90	P≡P	117
H–B	90	Si–O	110	C≡O	258
H–S	81	P–Cl	79	C≡C	200
H–Si	75	P–Br	65	N≡N	226
H–P	77	P–O	90	C≡N	213

* Average Bond Dissociation Enthalpies in kcal per mole
(There can be considerable variability in some of these values.)

Types of Bonding

- Primary
  - Ionic
  - Covalent
  - Metallic
- Secondary
  - Fluctuating induced dipole
  - Permanent dipole bond
  - Polar molecule-induced dipole



Ionic Bonding

Formation of ionic bond:

1- Mutual ionization occurs by electron transfer (remember electronegativity table)

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

2- Ions are attracted by strong columbic interaction

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

Ionic Bonding

Metal

Nonmetal

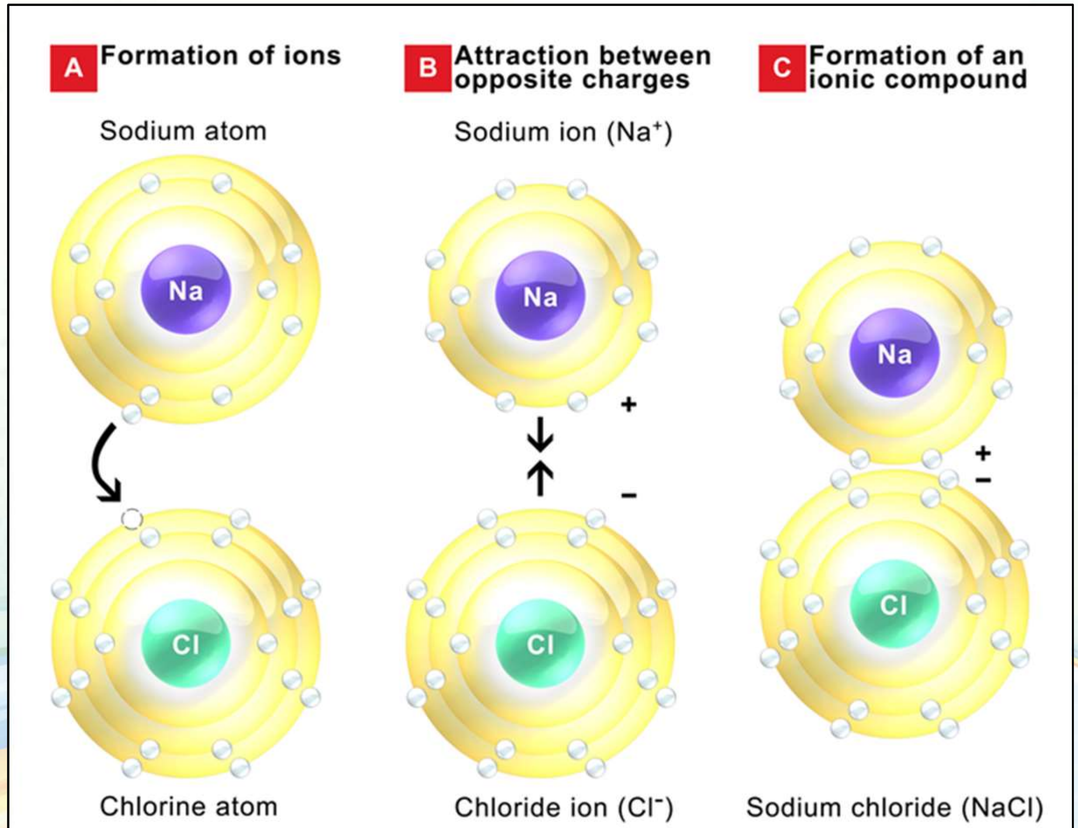
Donates electrons — Accepts electrons

Dissimilar electronegativities

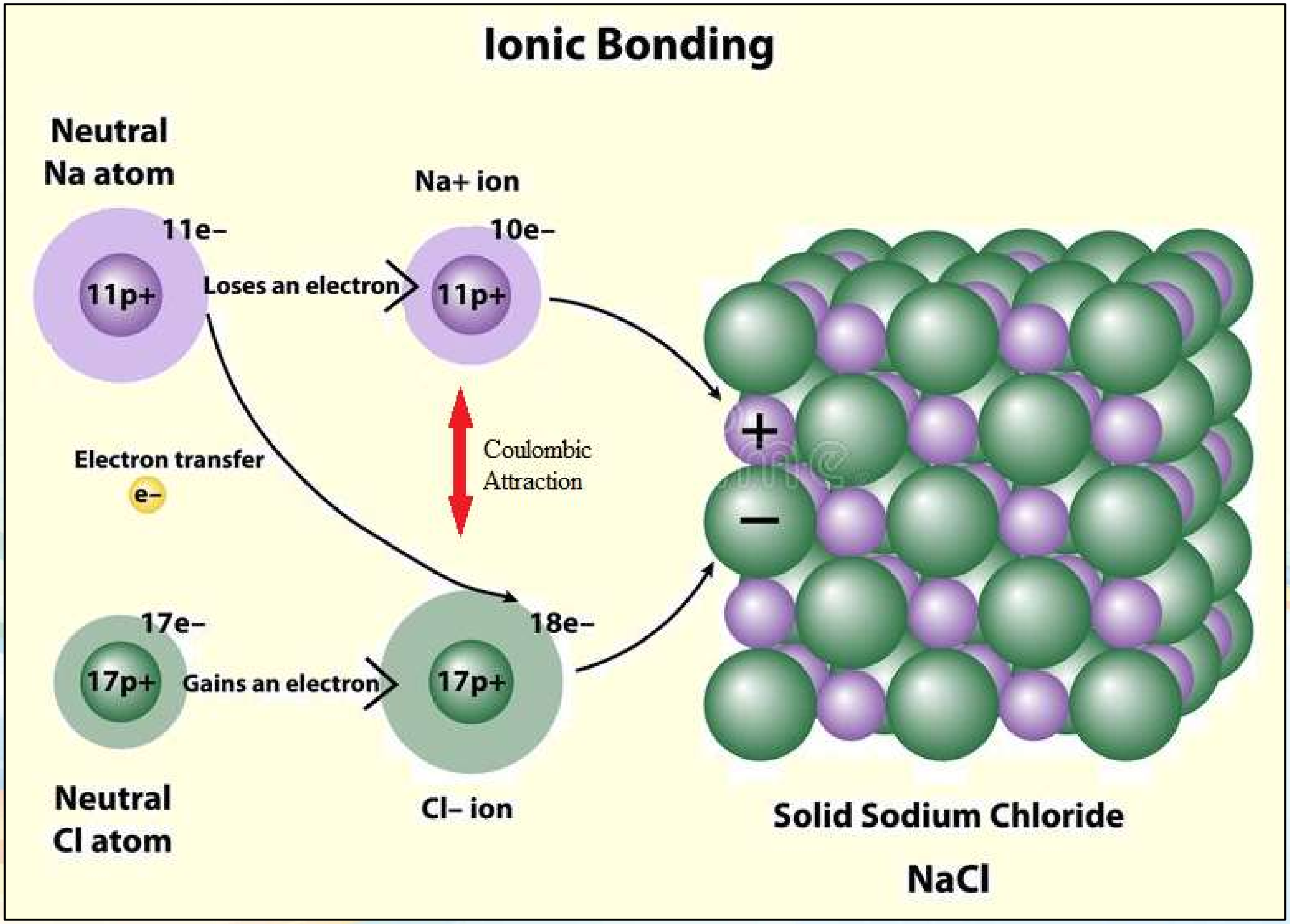
Example: NaCl

Na $1s^2\ 2s^2\ 2p^6\ 3s^1$ Cl $1s^2\ 2s^2\ 2p^6\ 3s^2 3p^5$

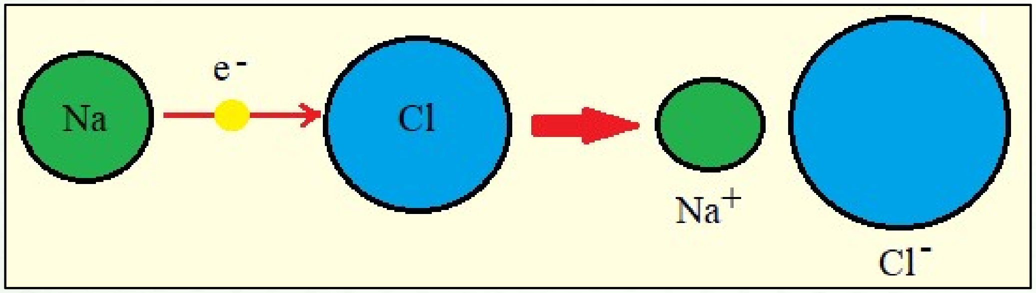
Na^{1+} $1s^2\ 2s^2\ 2p^6$ Cl^{1-} $1s^2\ 2s^2\ 2p^6\ 3s^2 3p^6$

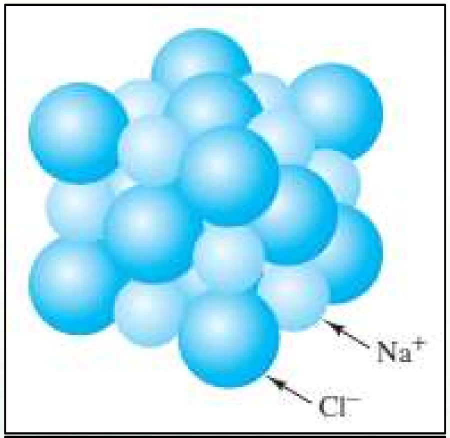


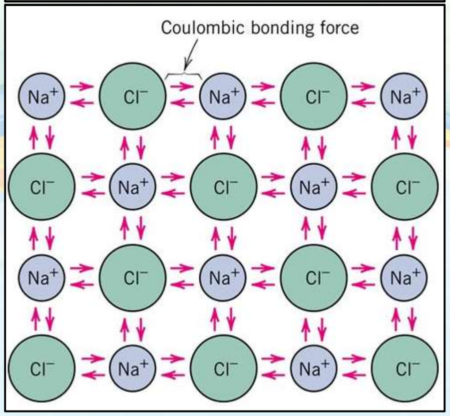
Formation of an Ionic Bond


Ionic Bonding
Neutral
Na atom
Na+ ion
11e–
10e–
11p+
Loses an electron
11p+
Electron transfer
e–
Coulombic
Attraction
+
–
17e–
18e–
17p+
Gains an electron
17p+
Neutral
Cl atom
Cl– ion
Solid Sodium Chloride
NaCl

Ionic Bonding

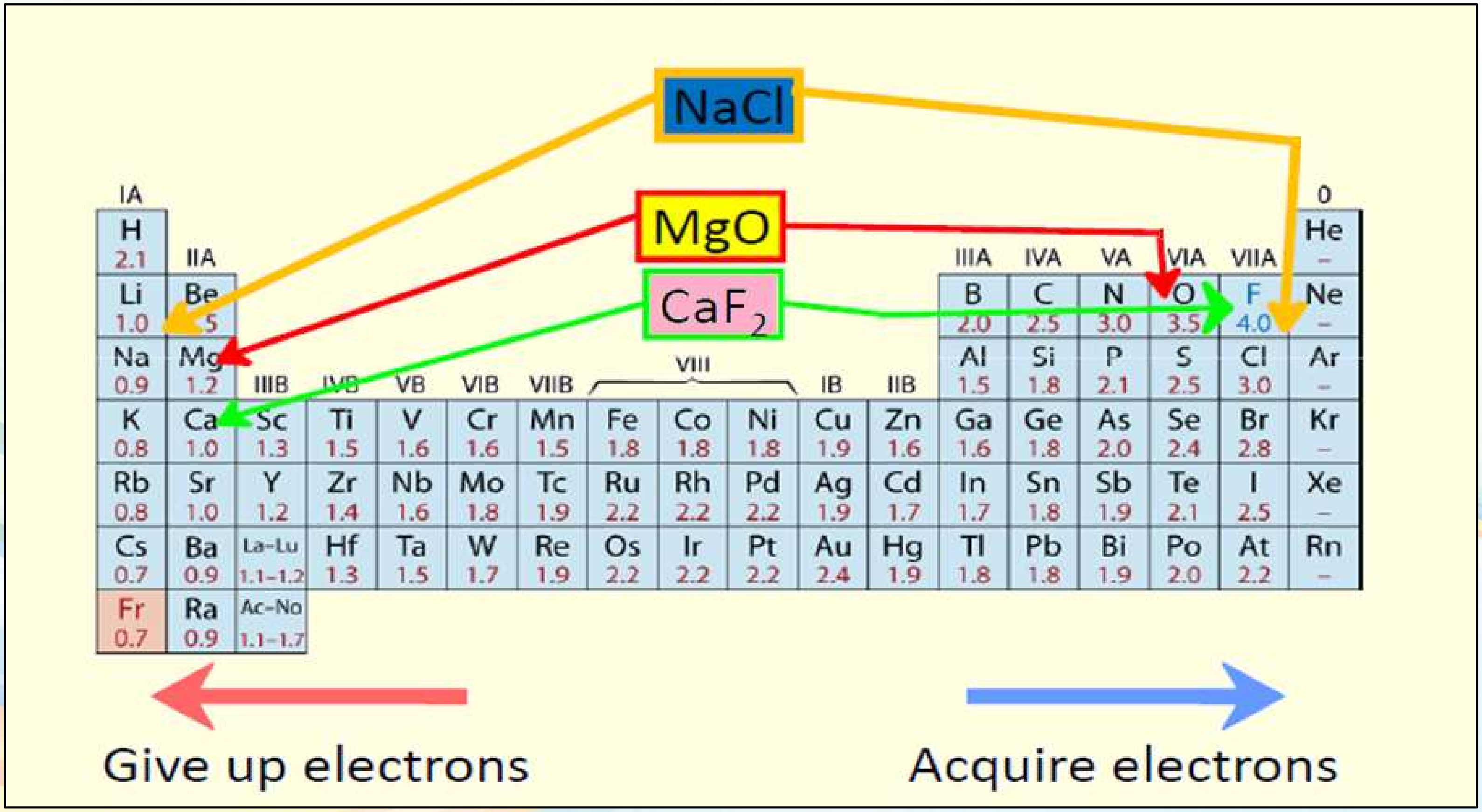






- ✓ *Electron transfer reduces the energy of the system of atoms, that is, electron transfer is energetically favorable.*
- ✓ *Note relative sizes of ions: Na shrinks and Cl expands*

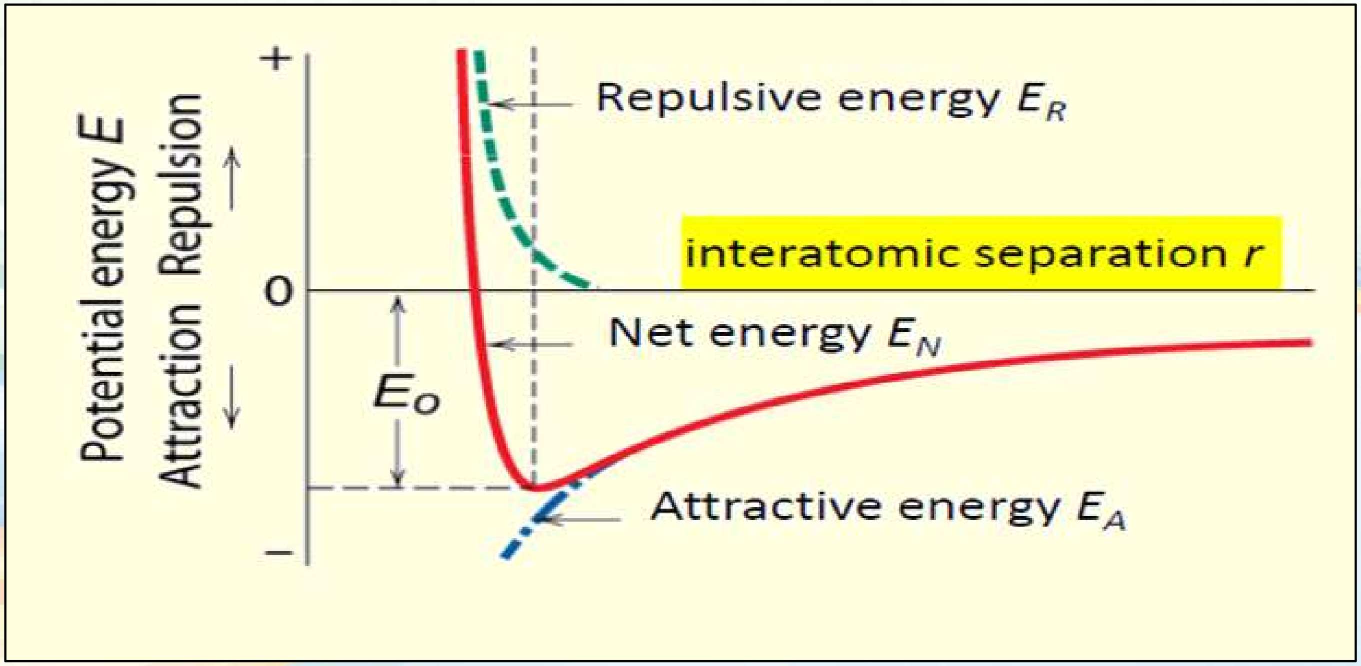
Ionic Bonding



Potential Energy

- In order for molecules to exist in aggregates in gases, liquids, or solids, there must be forces that attract the molecules together.

$E_N = E_A + E_R$



Potential Energy

- When the repulsive and attractive forces are equal the potential net energy is at a minimum and the system is stable.

Repulsive Forces

- The force is repulsive when the molecules are brought close enough together that the outer charge clouds of the molecules touch, and this causes the molecules to repel each other.
- The repulsive forces are necessary so that the molecules do not destroy each other

Attractive Forces

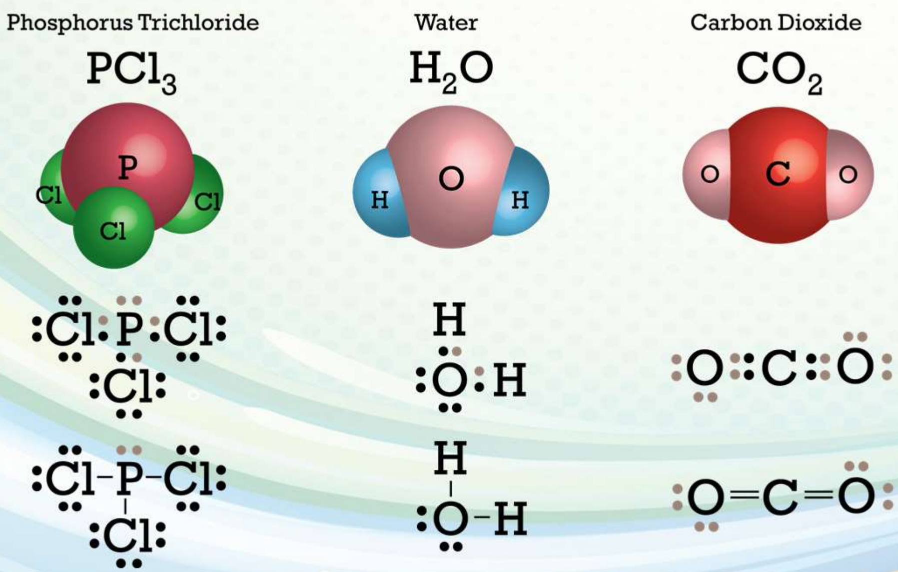
- The forces that bring molecules together are called forces of attraction.

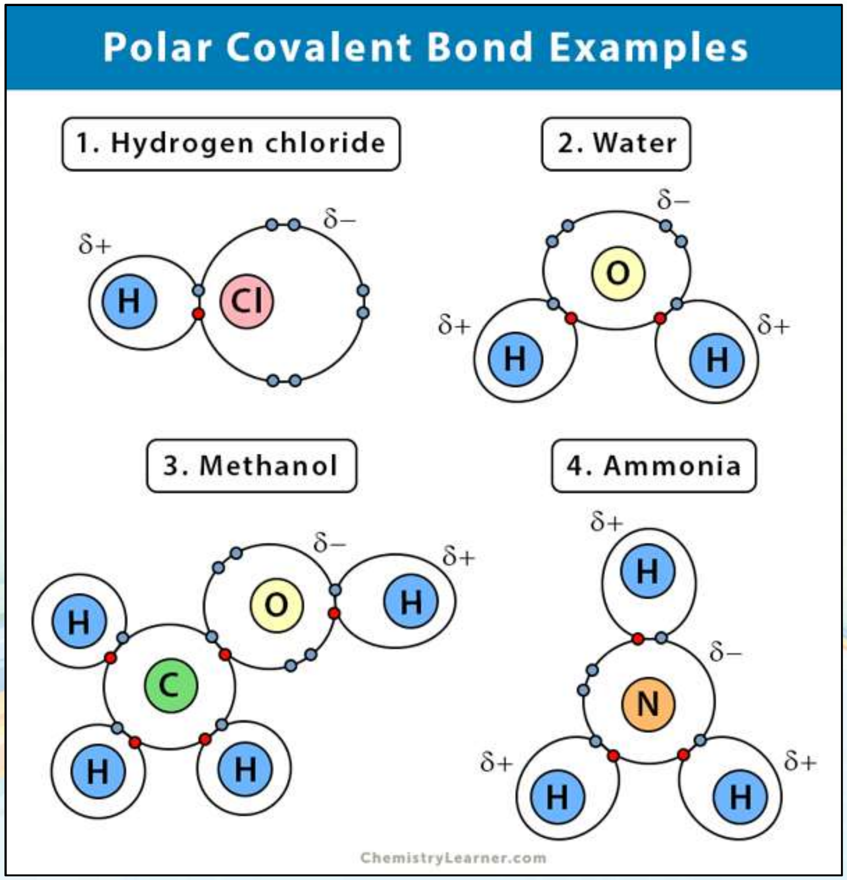
Covalent Bonding

- A covalent bond is formed when electrons are shared between atoms.
- Covalent bonds are between non-metals and non-metals or hydrogen and non-metals.
- They share electrons so that both of them can have a stable octet.
- Covalent bonds are HIGHLY directional bonds.
- There are two types of covalent bonds:

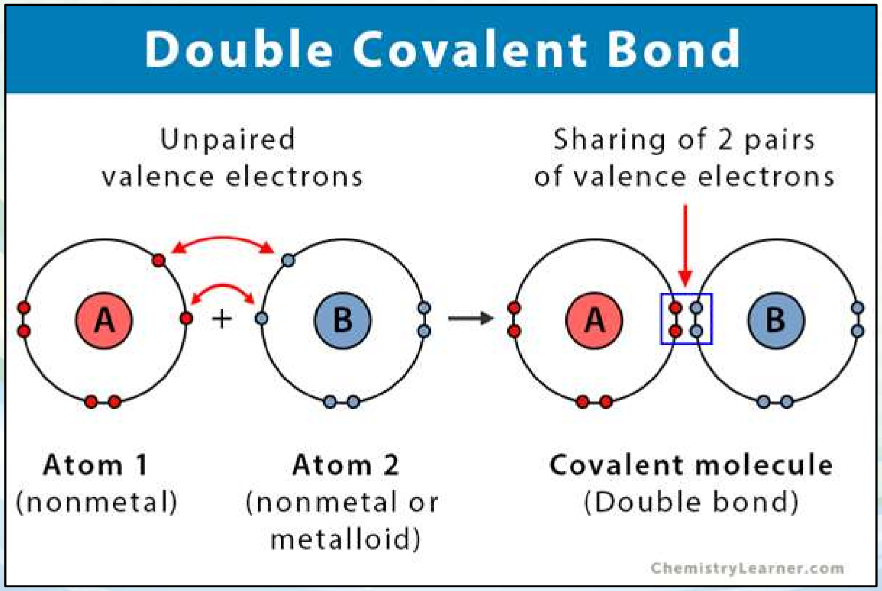
1. Non-polar: result when two exact non-metals equally share electrons.
2. Polar: result when two different non-metals share electrons.

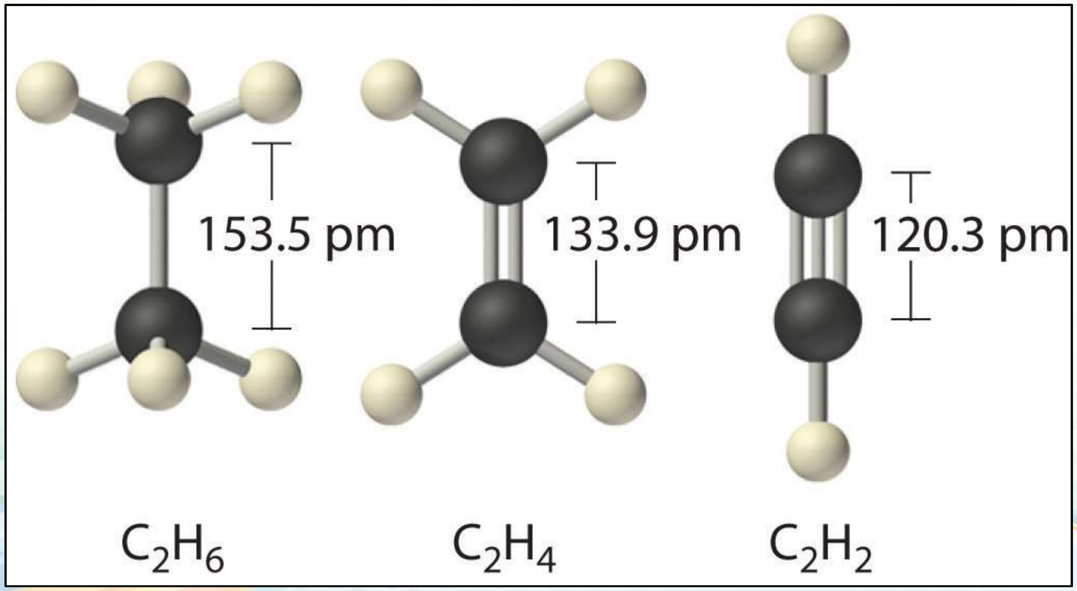
Covalent Bonding



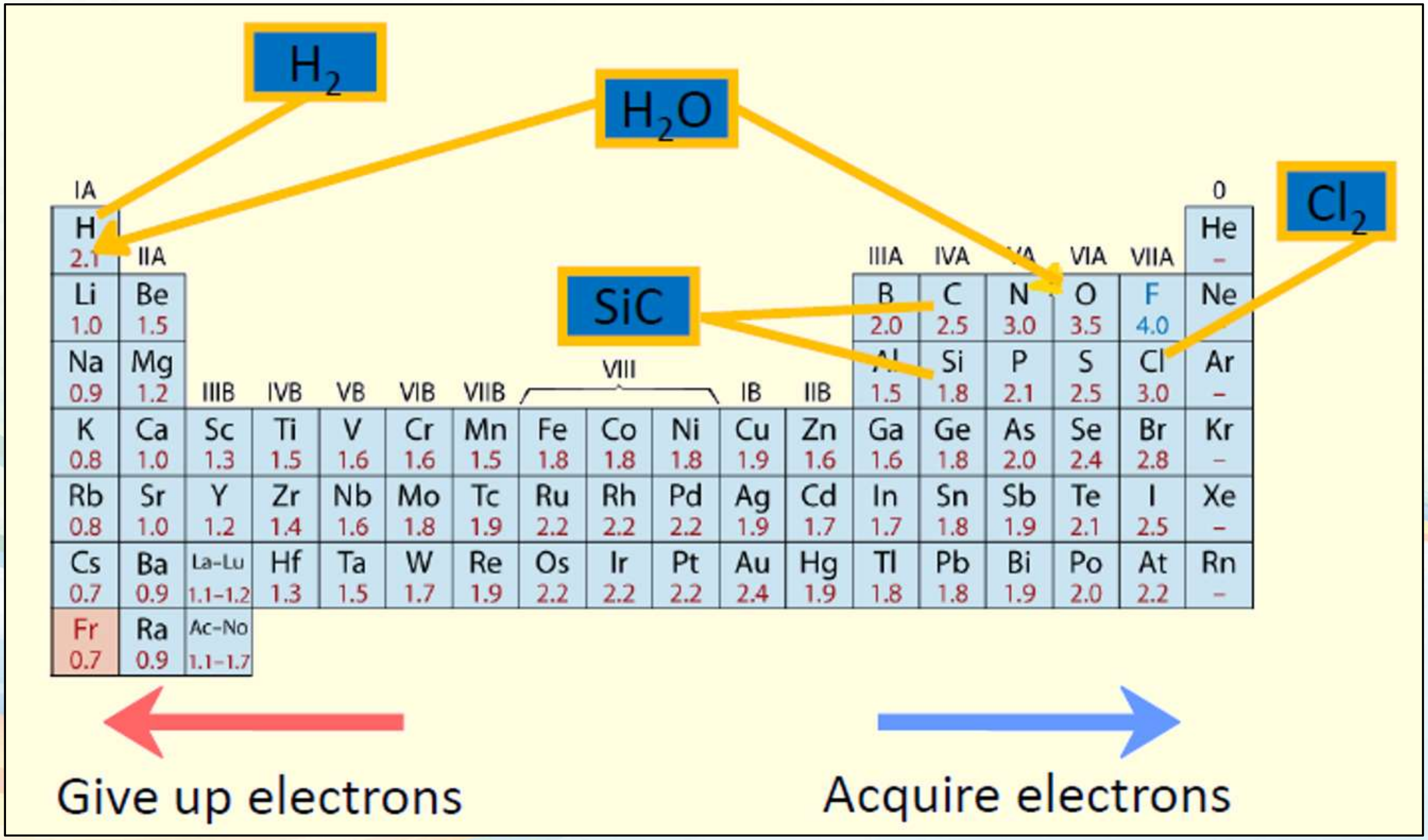


Covalent Bonding





Examples of Covalent Bonding



Naming Covalent Compounds

- Covalent compounds are much easier to name than ionic compounds; Examples:
  - ✓ P_2O_5 - diphosphorus pentoxide
  - ✓ CO - carbon monoxide
  - ✓ CF_4 - carbon tetrafluoride
- Some important exceptions to this naming scheme occur, examples:
  - ✓ H_2O is "water"
  - ✓ NH_3 is "ammonia"
  - ✓ CH_4 is "methane"

No of atoms	Prefix
1	Mono-
2	Di-
3	Tri-
4	Tetra-
5	Penta-
6	Hexa-
7	Hepta-

What are the properties of covalent compounds

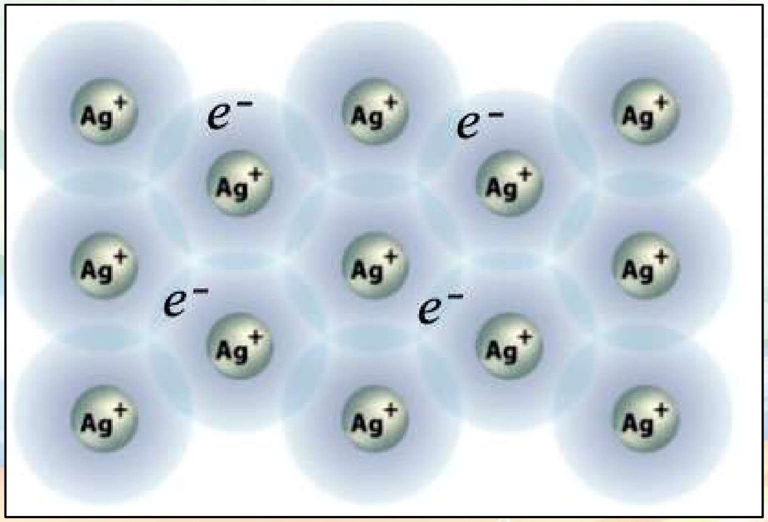
- Covalent compounds generally have much lower melting and boiling points than ionic compounds.
- Covalent compounds are soft and squishy (compared to ionic compounds).
- Covalent compounds tend to be more flammable than ionic compounds.
- Covalent compounds don't conduct electricity in water.
- Like dissolves like. This means that compounds tend to dissolve in other compounds that have similar properties (particularly polarity).
- Since water is a polar solvent and most covalent compounds are fairly nonpolar.

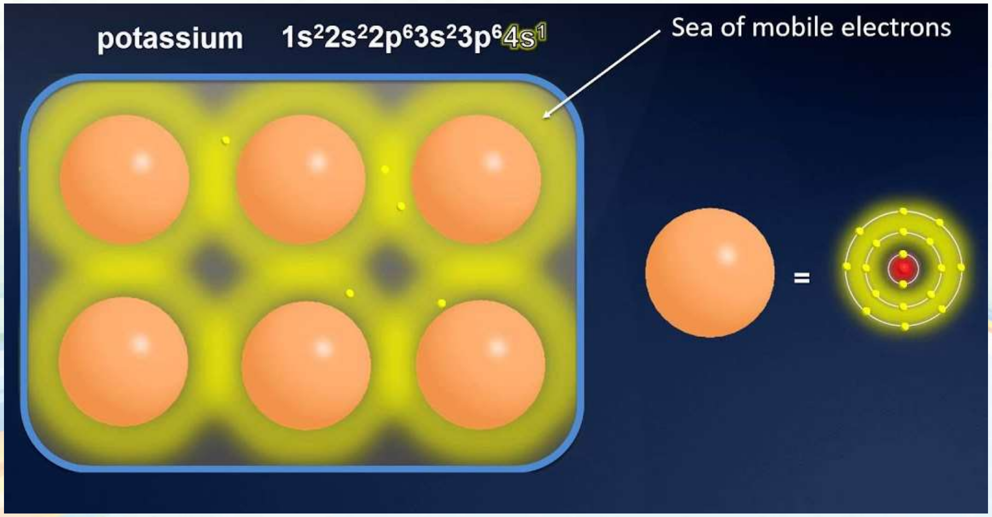
Metallic Bonds

- Metallic bonding occurs in metallic substances.
- Atoms of metals are held together in this structure by the sharing effect of the electrons amongst all of the atoms.
- This forms a "sea" or a "cloud" of free electrons that floats around the surface of metals.
- The crystal lattice of metals consists of ions NOT atoms surrounded by a 'sea of electrons' forming another type of giant lattice.

Metallic Bonds

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





Properties of Metallic Bonds

- The strong bonding generally results in dense, strong materials with high melting and boiling points.
- Metals are good conductors of electricity because these 'free' electrons carry the charge of an electric current when a potential difference (voltage) is applied across a piece of metal.
- Metals are also good conductors of heat. This is also due to the free moving electrons.
- Typical metals also have a silvery surface, but remember this may be easily tarnished by corrosive oxidation in air and water.
- Unlike ionic solids, metals are very malleable, they can be readily bent, pressed or hammered into shape. The layers of atoms can slide over each other without fracturing the structure . The reason for this is the mobility of the electrons

Secondary bonding - Intermolecular Forces

- Secondary, Van der Waals, or physical bonds are weak in comparison to the primary bonds.
- Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present.
- 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
- Dipole interactions occur between:

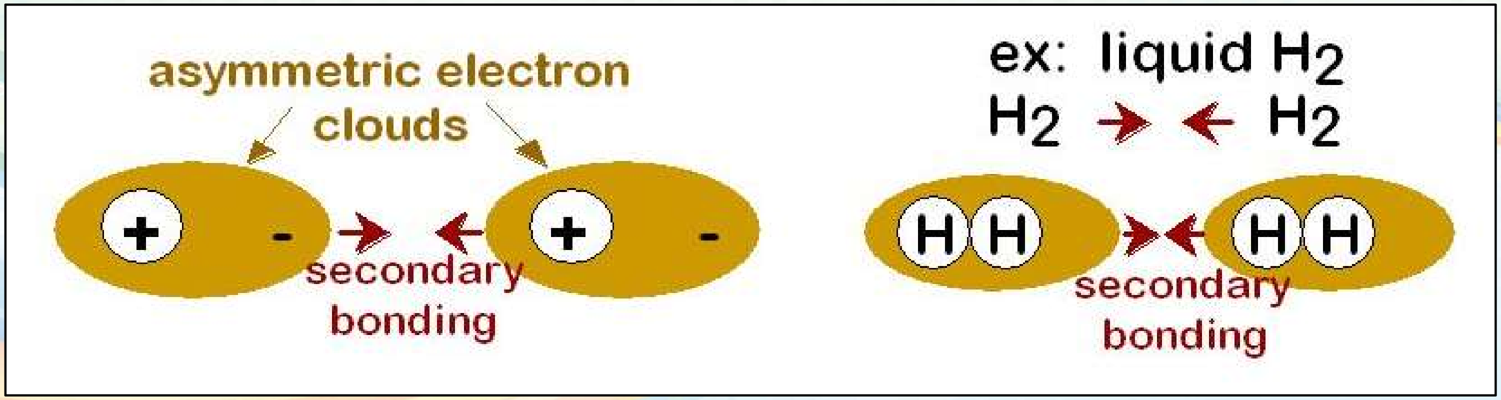
  1- Fluctuated induced dipoles.

  2- Permanent dipole bond.

  3- Polar molecule-induced dipole

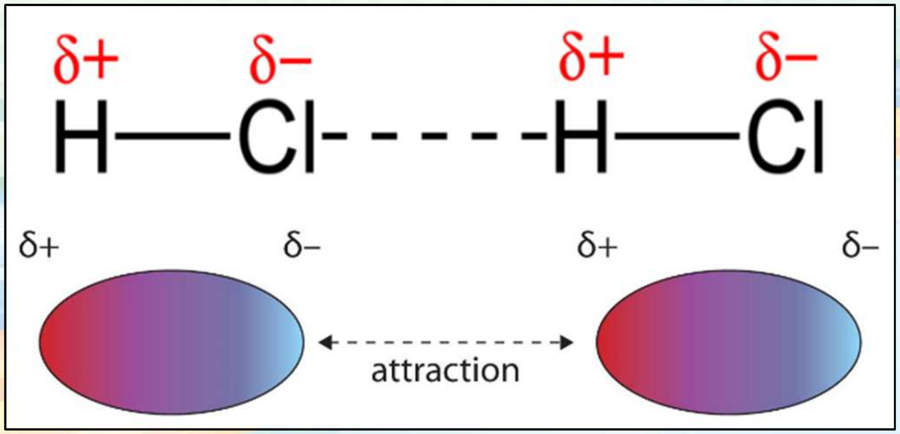
Fluctuating induced dipoles

- Very weak electric dipole bonding can take place among atoms due to an instantaneous asymmetrical distribution of electron densities around their nuclei.
- This type of bonding is termed fluctuation since the electron density is continuously changing.



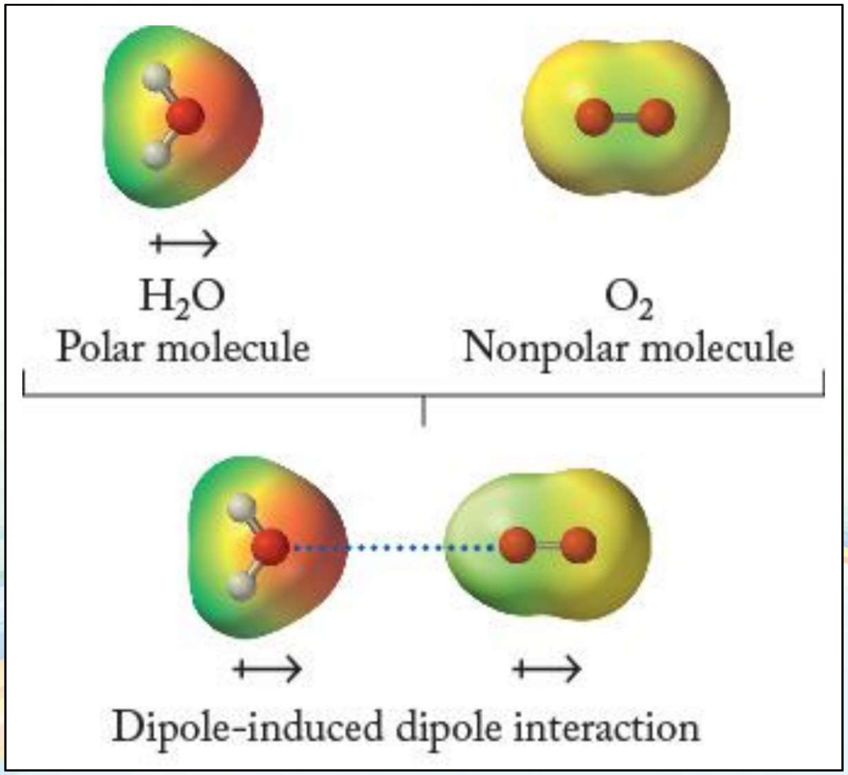
Permanent dipoles

- *Coulombic forces also exist between adjacent polar molecules.*
- *Weak intermolecular bonds are formed between molecules which possess permanent dipoles.*
- *A dipole exists in a molecule if there is asymmetry in its electron density distribution.*



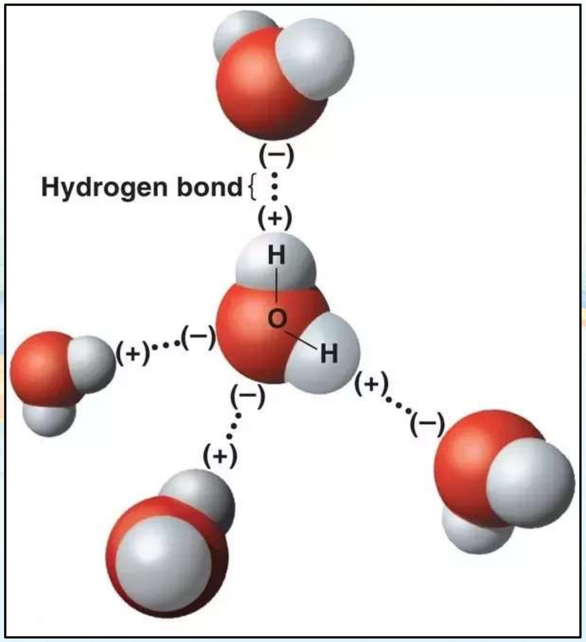
Polar molecules - induced dipole

- Polar molecules (with asymmetric arrangement of positively and negatively charged regions) can induce dipoles in adjacent nonpolar molecules



Hydrogen bonding

- Hydrogen bonding, a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents.
- An intermolecular attraction between a partially positively charged hydrogen in one molecule and a partially negatively charged oxygen, nitrogen, or fluorine in a nearby molecule



Example:

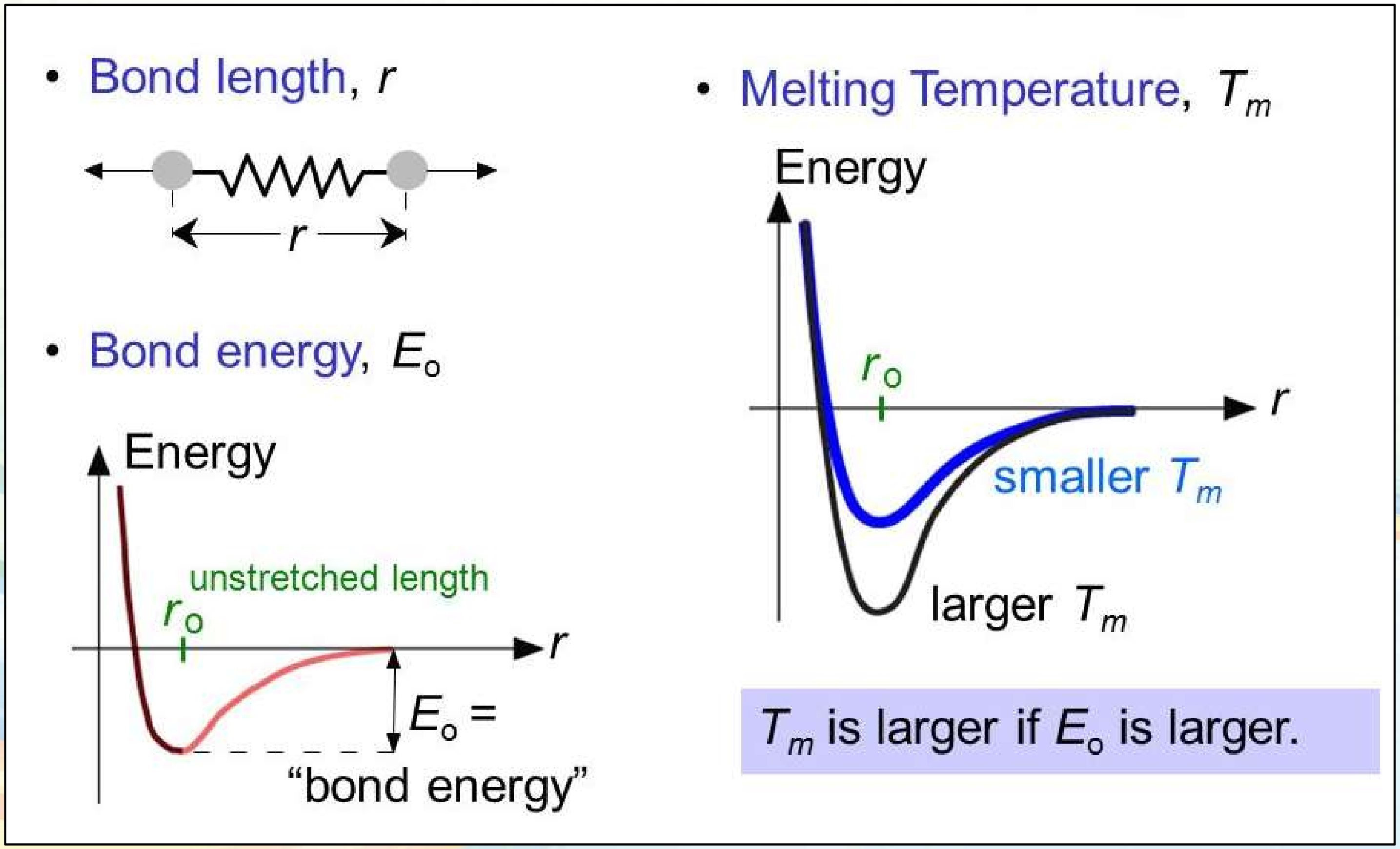
Hydrogen bond in water. The H end of the molecule is positively charged and can bond to the negative side of another H2O molecule (the O side of the H2O dipole)

Type	Bond Energy	Comments
Ionic	Large	Nondirectional (ceramics)
Covalent	Variable Large-Diamond Small-Bismuth	Directional (semiconductors, ceramics, polymer chains)
Metallic	Variable Large-Tungsten Small-Mercury	Nondirectional (metals)
Secondary	Smallest	Directional Inter-chain (polymer) Inter-molecular

Bonding and materials properties

- Materials with large bonding energies usually have high melting temperatures.
- There is a correlation between the magnitude of the bonding energy and the state of materials
  - ✓ Solids have large bonding energies
  - ✓ Liquids tend to have relatively lower energies
- The expansion/contraction during heating/cooling of materials is related to the shape of its E(r) curve.
- A deep and narrow 'trough,' which typically occurs for materials having large bonding energies, usually imply a low coefficient of thermal expansion.

Properties From Bonding: T_m



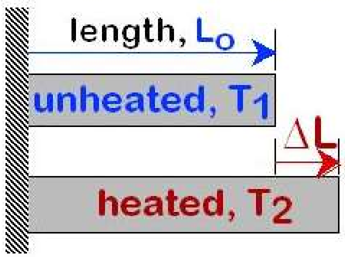
Properties From Bonding: Tm

Bonding Energies and Melting Temperatures for Various Substances

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

Properties From Bonding: α

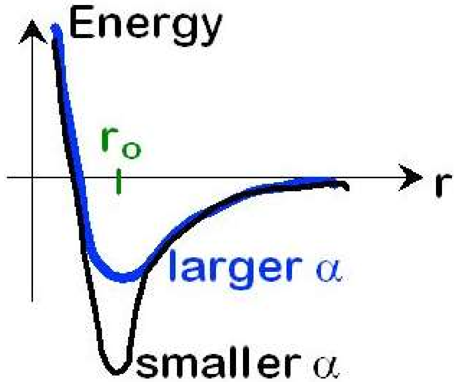
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ symmetry at r_o



α is larger if E_o is smaller.

Example

For a K^+ - Cl^- ion pair, attractive and repulsive energies EA and ER, respectively, depend on the distance between the ions r, according to

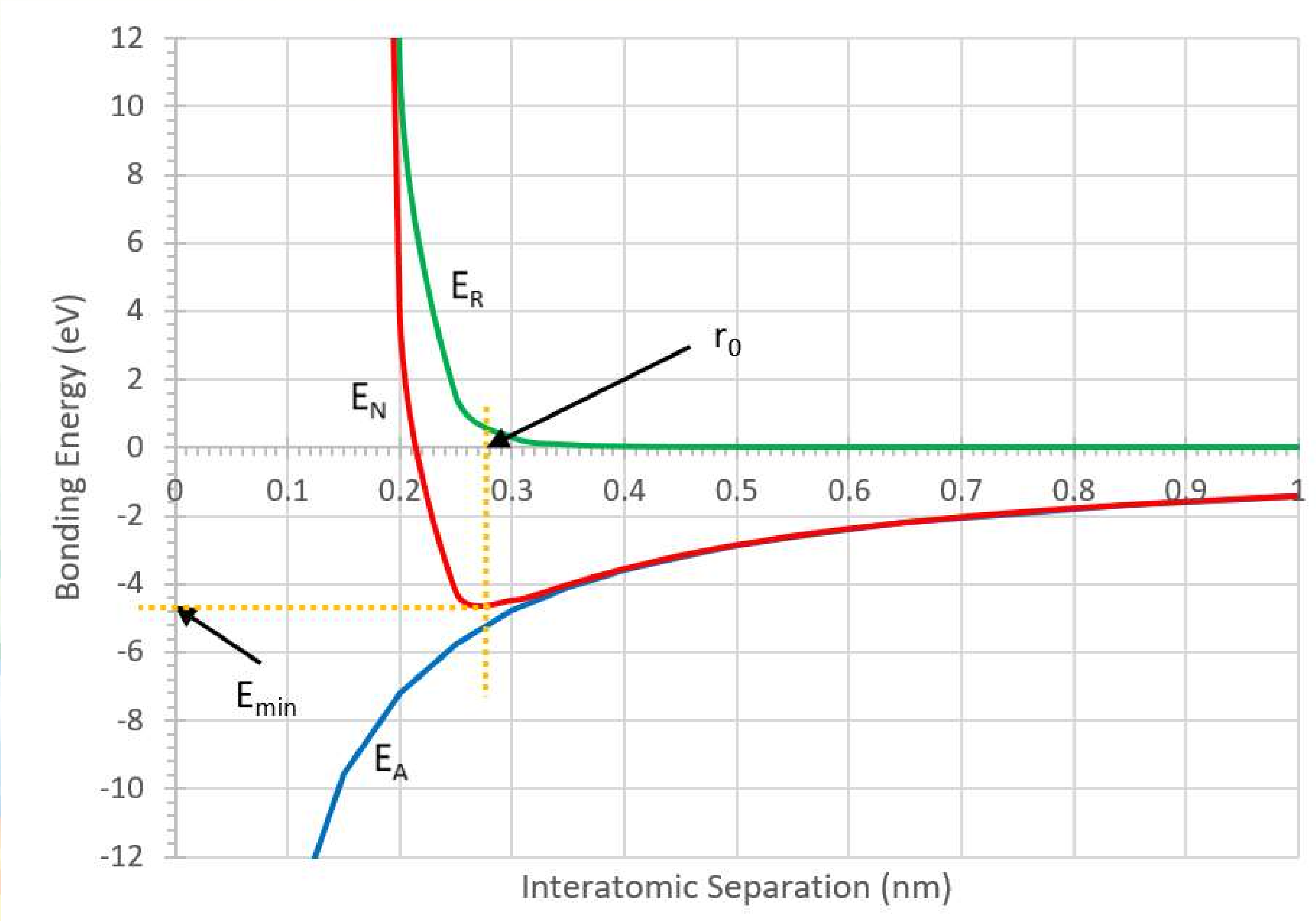
$$E_A = -\frac{1.436}{r} \text{ and } E_R = \frac{5.8 \times 10^{-6}}{r^9}$$

For these expressions, energies are expressed in electron volts per K+ - Cl- pair, and r is the distance in nanometers. The net energy EN is just the sum of the two expressions above. Determine:

(i) The equilibrium spacing ro between the K+ and Cl- ions.

(ii) The magnitude of the bonding energy Eo between the two ions.

r nm	EA	ER	EN
0.1	-14.36	5800	5785.64
0.15	-9.57333333	150.8713103	141.298
0.2	-7.18	11.328125	4.148125
0.25	-5.744	1.5204352	-4.22356
0.3	-4.78666667	0.294670528	-4.492
0.35	-4.10285714	0.073589456	-4.02927
0.4	-3.59	0.022125244	-3.56787
0.45	-3.19111111	0.007665057	-3.18345
0.5	-2.872	0.0029696	-2.86903
0.55	-2.61090909	0.0012594	-2.60965
0.6	-2.39333333	0.000575528	-2.39276
0.65	-2.20923077	0.000280032	-2.20895
0.7	-2.05142857	0.000143729	-2.05128
0.75	-1.91466667	7.72461E-05	-1.91459
0.8	-1.795	4.32134E-05	-1.79496
0.85	-1.68941176	2.50413E-05	-1.68939
0.9	-1.59555556	1.49708E-05	-1.59554
0.95	-1.51157895	9.20271E-06	-1.51157
1	-1.436	5.8E-06	-1.43599


12
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Bonding Energy (eV)
Interatomic Separation (nm)
E_R
E_N
E_A
r₀
E_{min}