Chapter 2

ATOMIC STRUCTURE

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Outline

1- Review of Atomic Structure

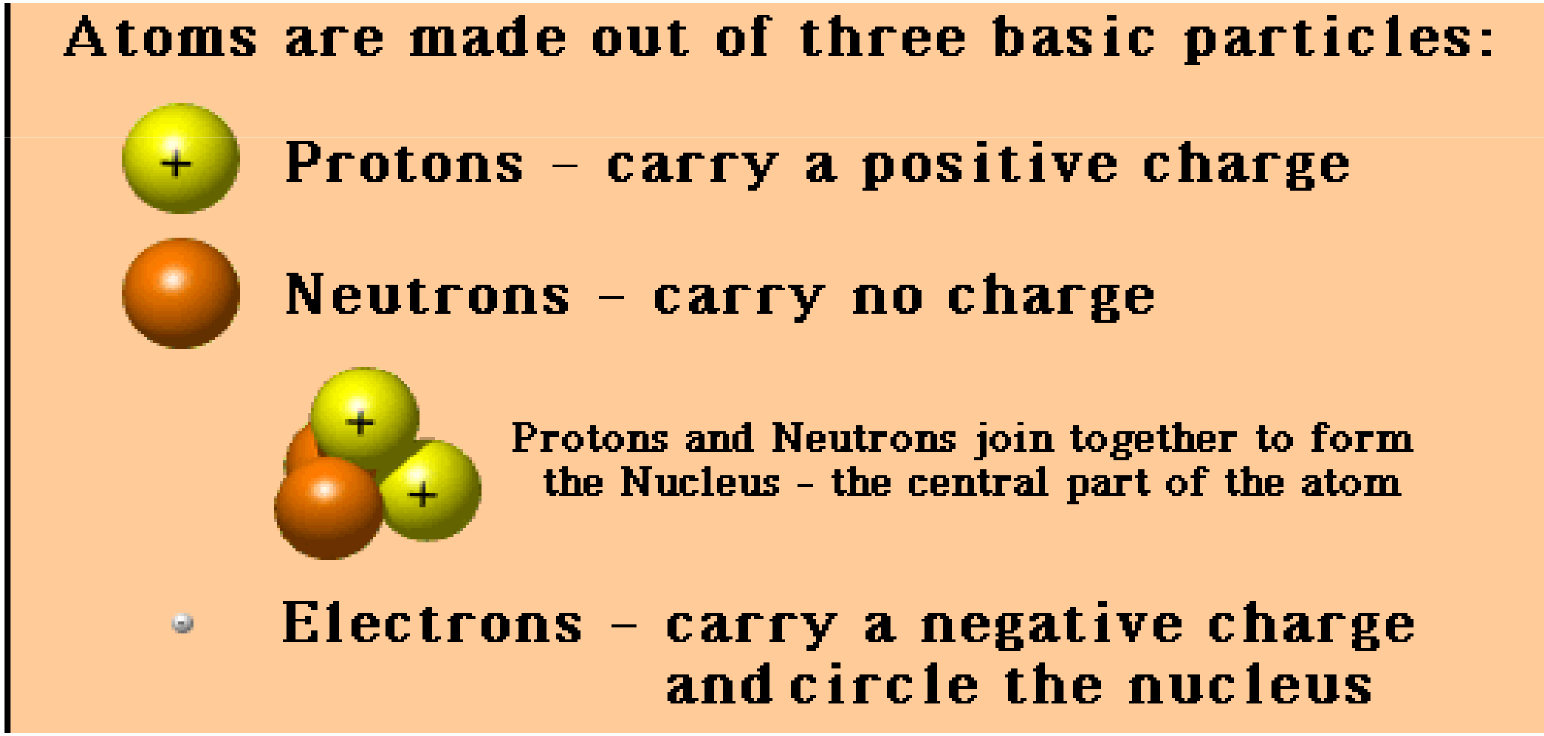
- Electrons, Protons, Neutrons
- Atomic Bonding in Solids
- Periodic Table
- Primary Interatomic Bonds
- Secondary Bonding (Van der Waals)

2- Molecules and Molecular Solids

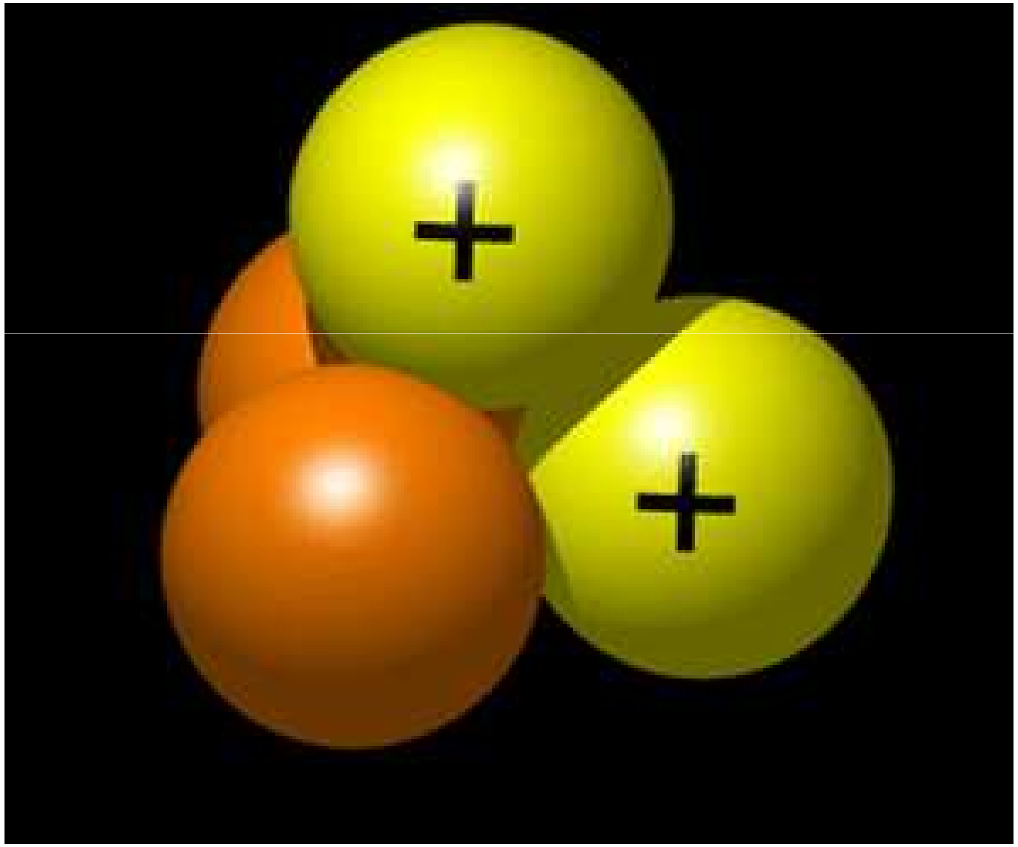
Review of Atomic Structure

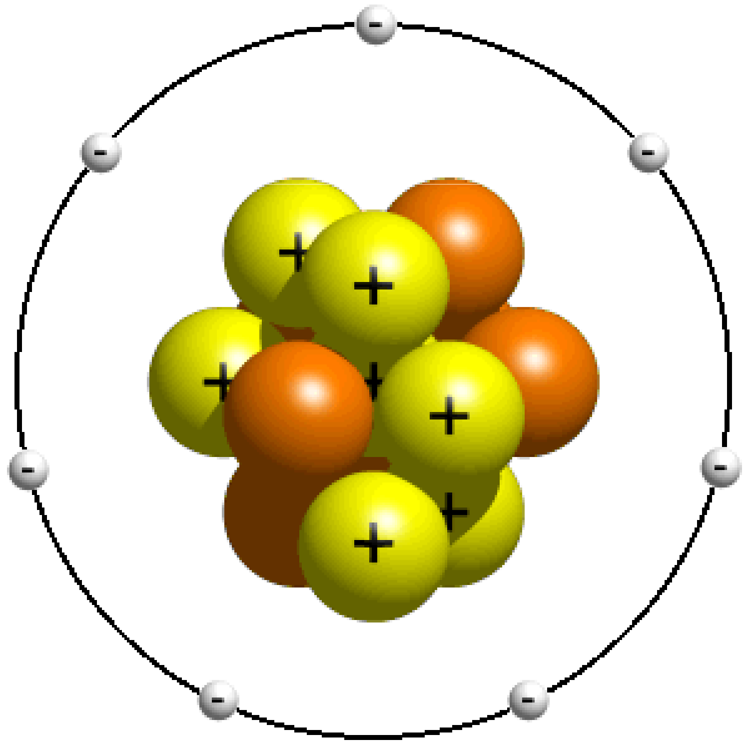
What are atoms?

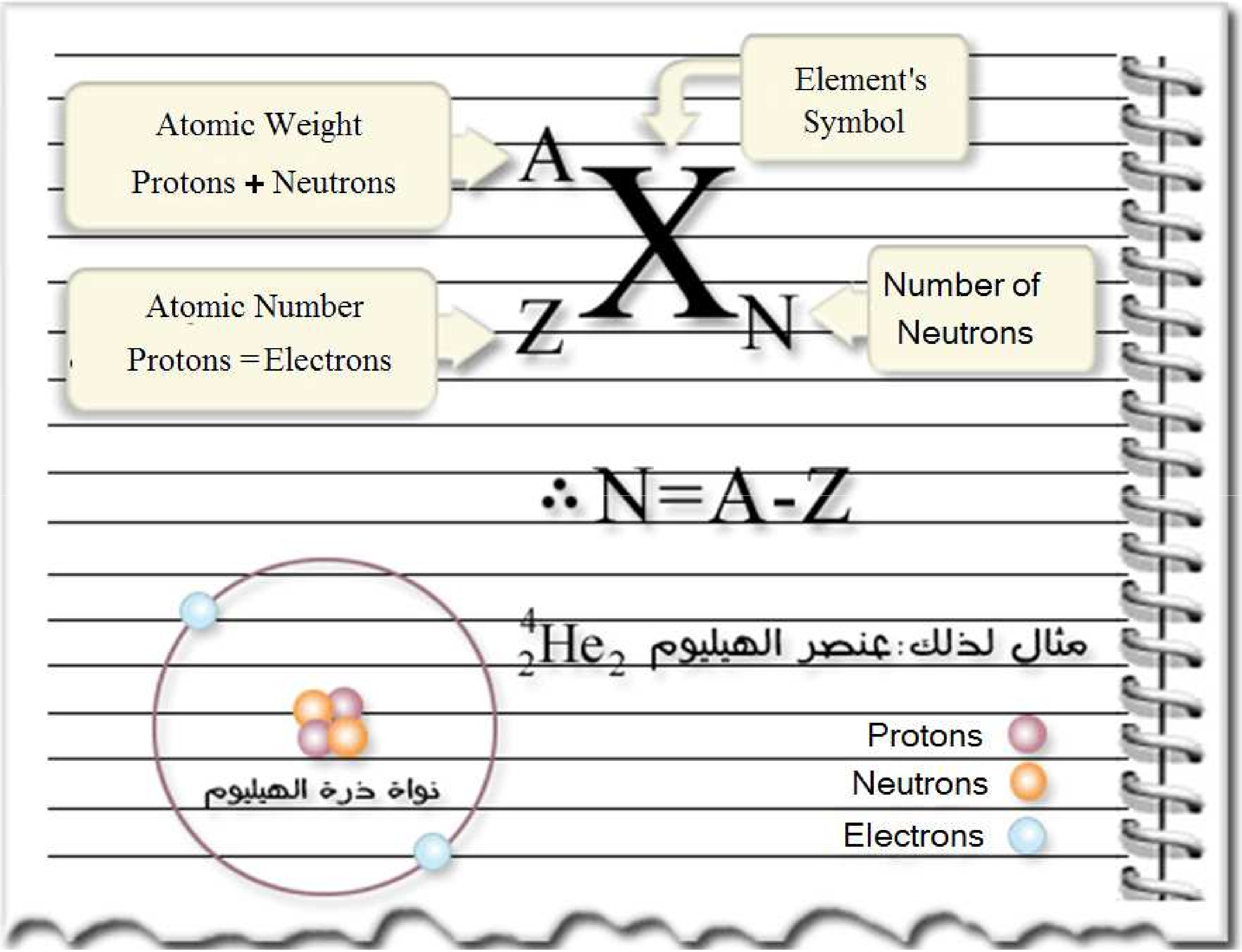
Atoms are the basic building blocks of matter that make up everyday objects.



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.





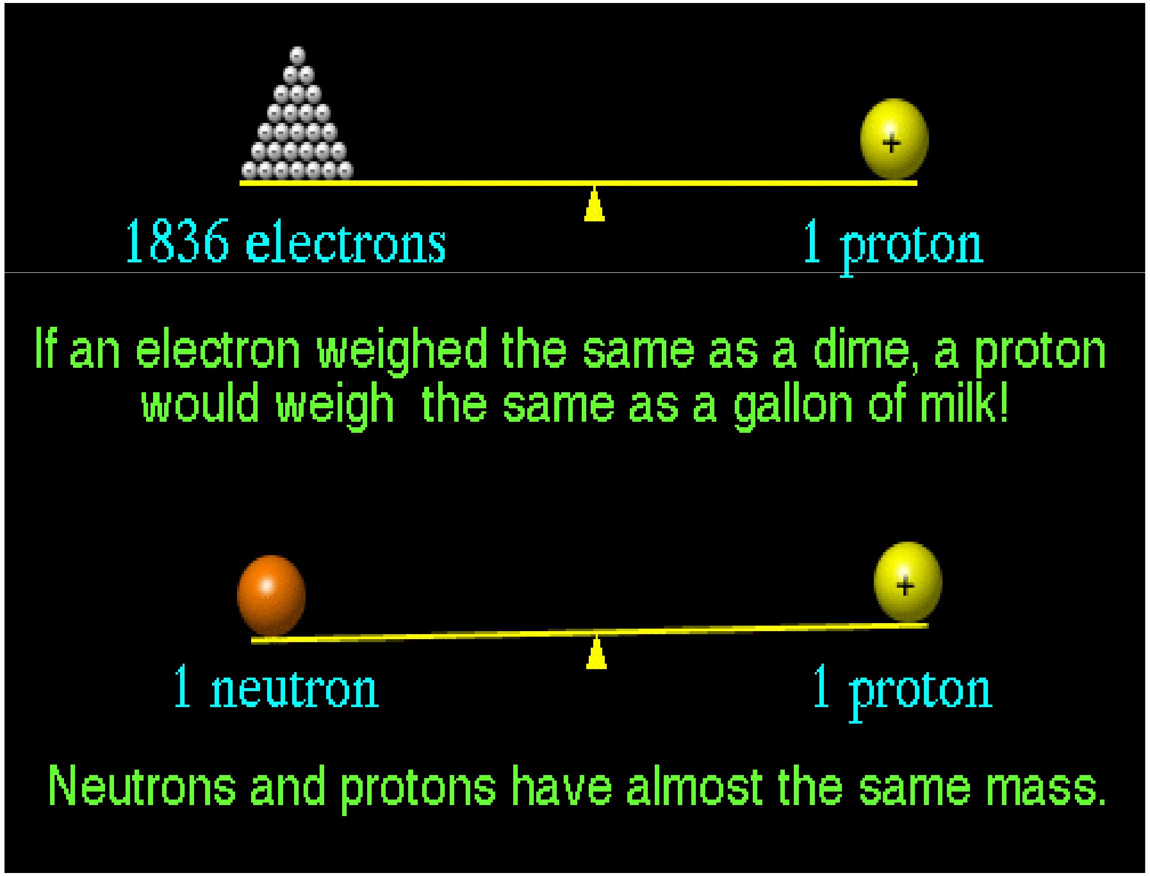


Atomic Weight
Protons + Neutrons
Element's Symbol
A
X
Z
N
Atomic Number
Protons =Electrons
Number of Neutrons
∴ N=A-Z
مثال لذلك: عنصر الهيليوم $^{4}_{2}He_{2}$
نواة ذرة الهيليوم
Protons
Neutrons
Electrons

Charges:

Electron's and Proton's charges are of the same magnitude, 1.6×10^{-19} Coulombs.

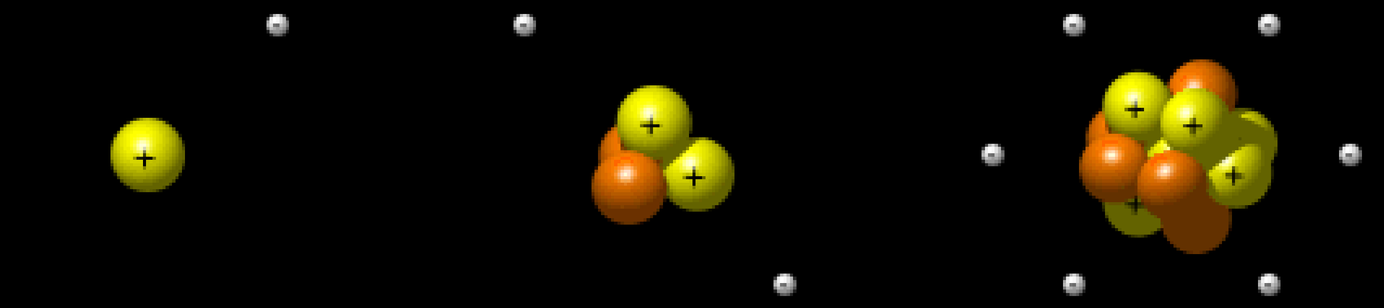
Masses:



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.

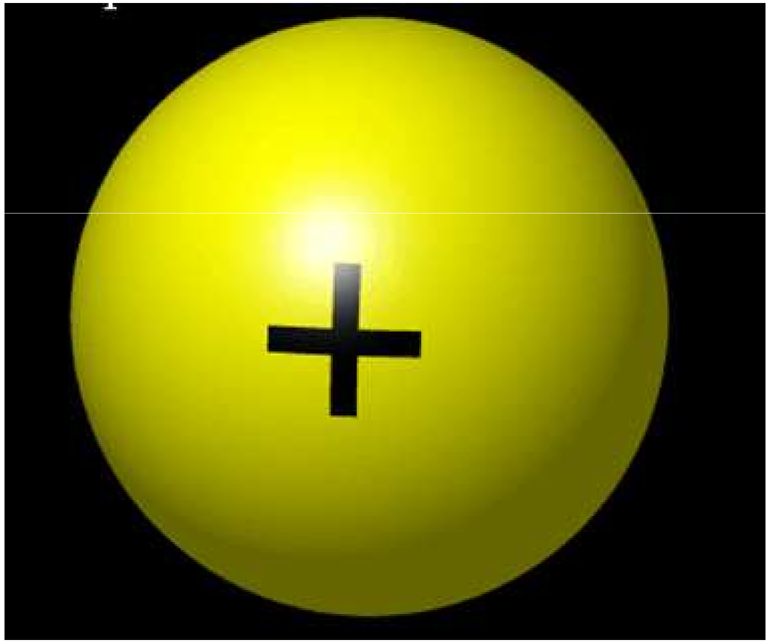
Atoms always have as many electrons as protons.
Atoms usually have about as many neutrons as protons.



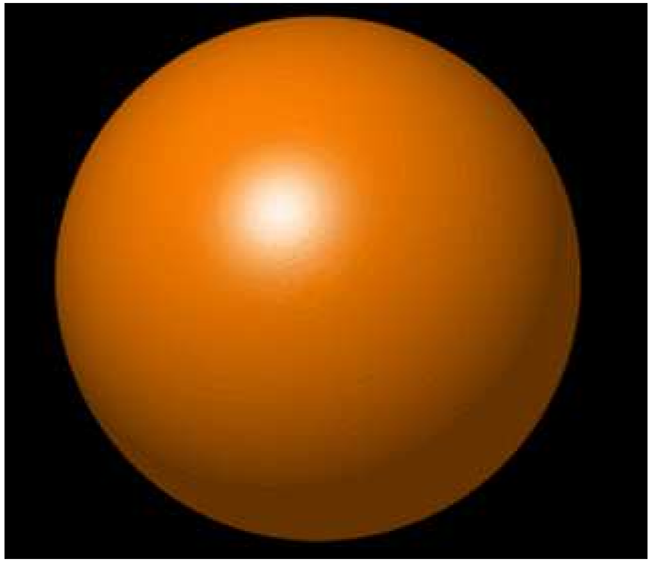
Hydrogen	Helium	Carbon
1 proton	2 protons	6 protons
1 electron	2 electrons	6 electrons
0 neutrons	2 neutrons	6 neutrons

Adding a proton makes a new kind of atom!
Adding a neutron makes an isotope of that atom,
a heavier version of that atom!

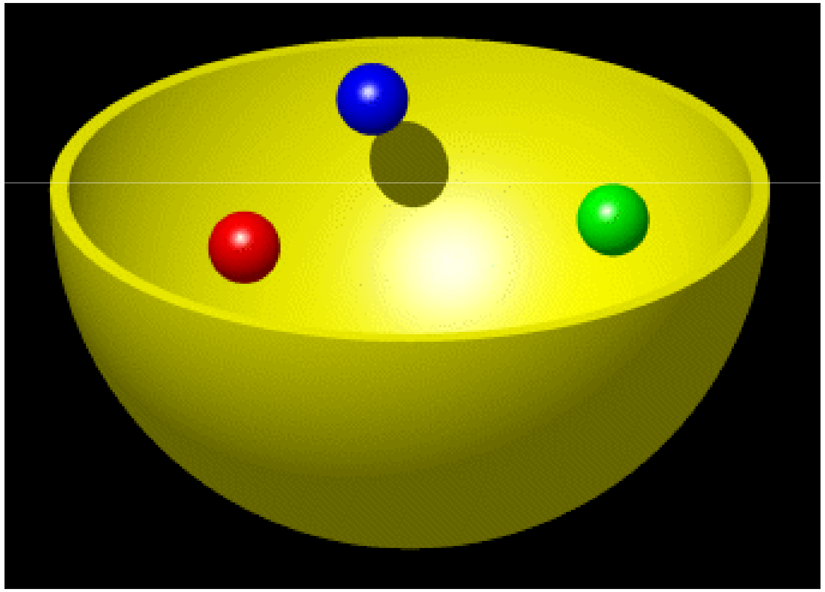
Scientists thought there was nothing smaller than the proton in the nucleus of the atom



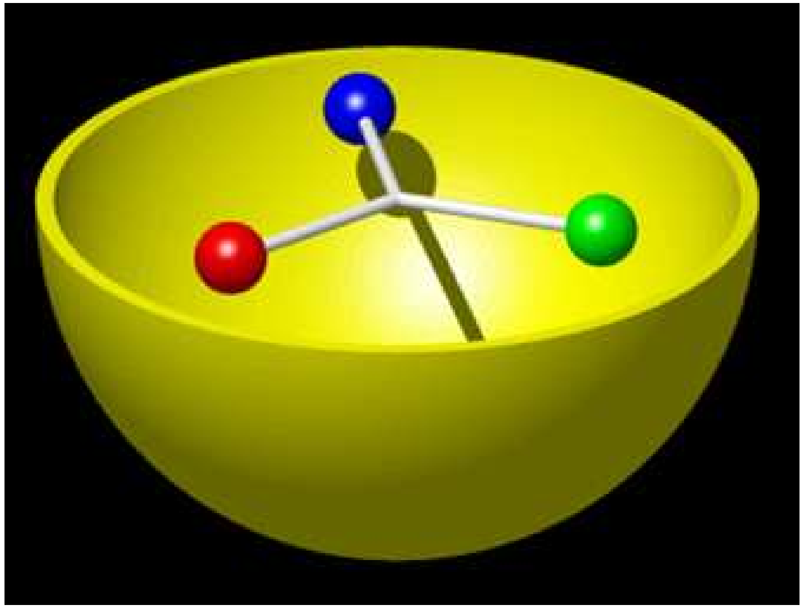
Scientists discovered the neutron in 1932. They thought that there was nothing smaller in the atom's nucleus?



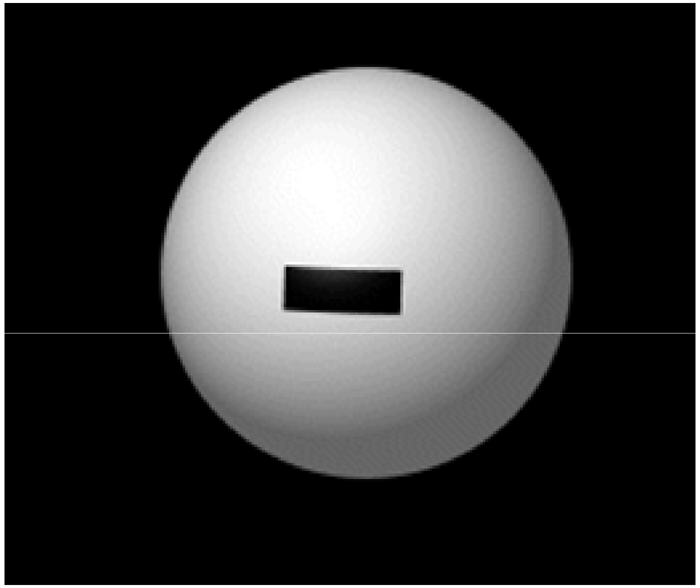
In 1968, scientists discovered new particles inside the proton. They called these particles quarks.



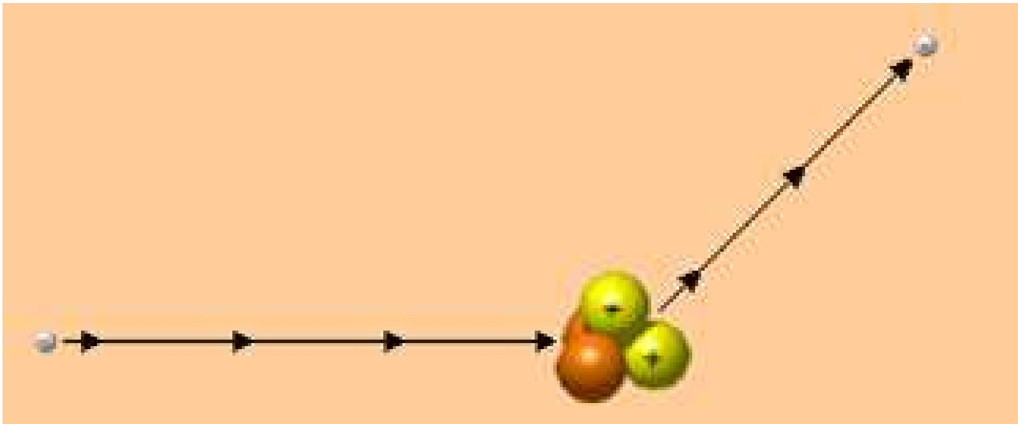
There are three quarks in each proton. The quarks are held to each other by other particles called gluons.



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 cm^3, n, for material of density d (g/cm3) and atomic mass M (g/mol) is:

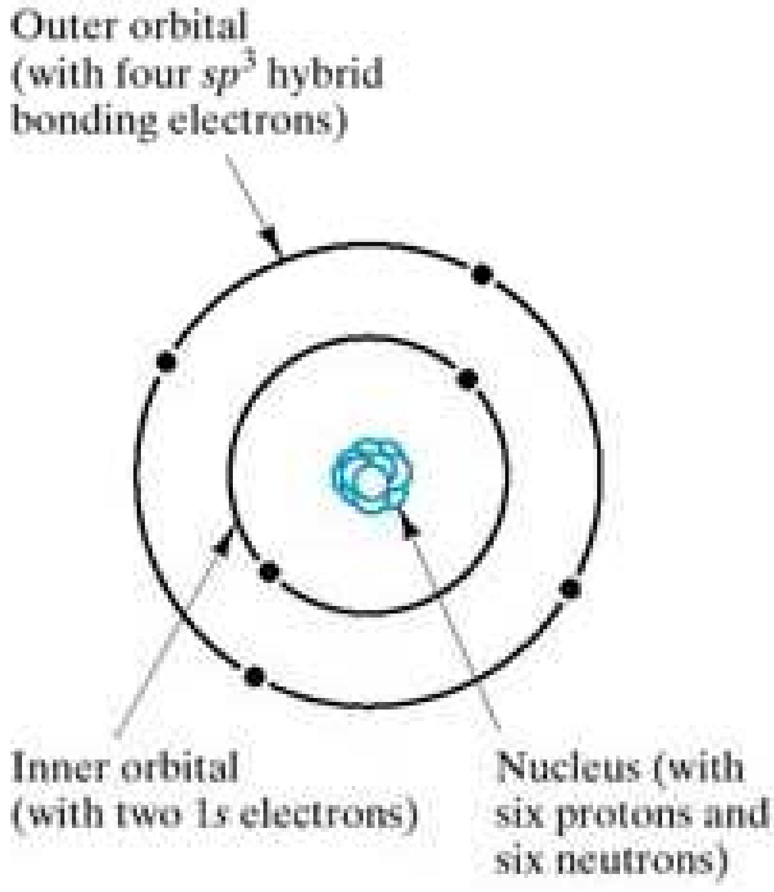
$$n = N_{av} \times d / M$$

- Mean distance between atoms $L = (1/n)^{1/3}$
- Example:
- Diamond (carbon): $d = 3.5\ g/cm^3$, $M = 12\ g/mol$

$$n = 6\times10^{23}\ atoms/mol \times 3.5\ g/cm^3/12\ g/mol$$
$$= 17.5 \times 10^{22}\ atoms/cm^3$$
$$L = (1/17.5 \times 10^{22})^{1/3}$$
$$= 0.179\ nm$$

Electrons in Atoms

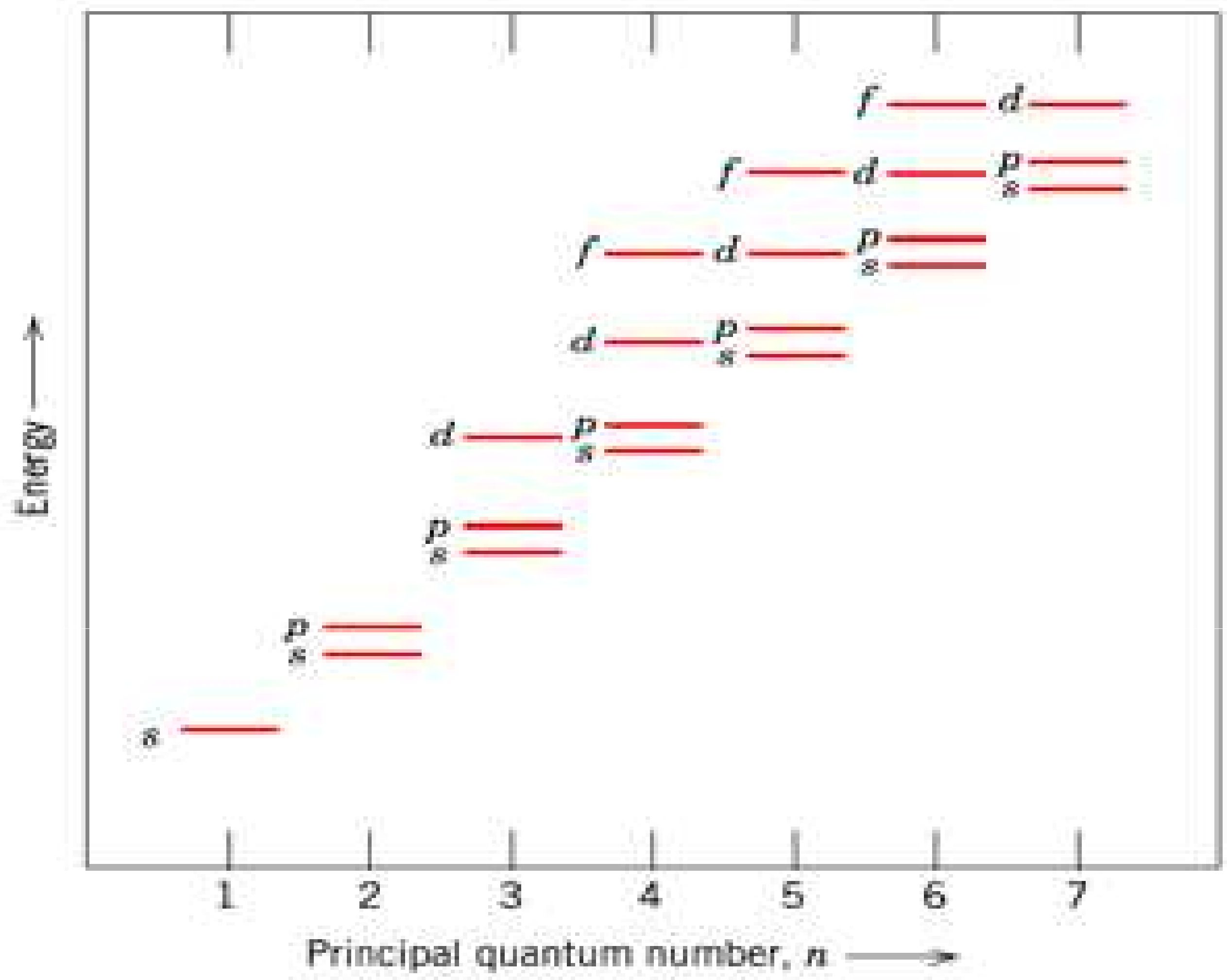
- The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.
- This "Bohr" picture looks like a mini planetary system. But quantum mechanics tells us that this analogy is not Correct.
- Electrons move not in circular orbits, as in popular drawings, but in 'fuzzy' orbits.



- 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
    1) Chemical
    2) Electrical
    3) Thermal
    4) 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,…

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)

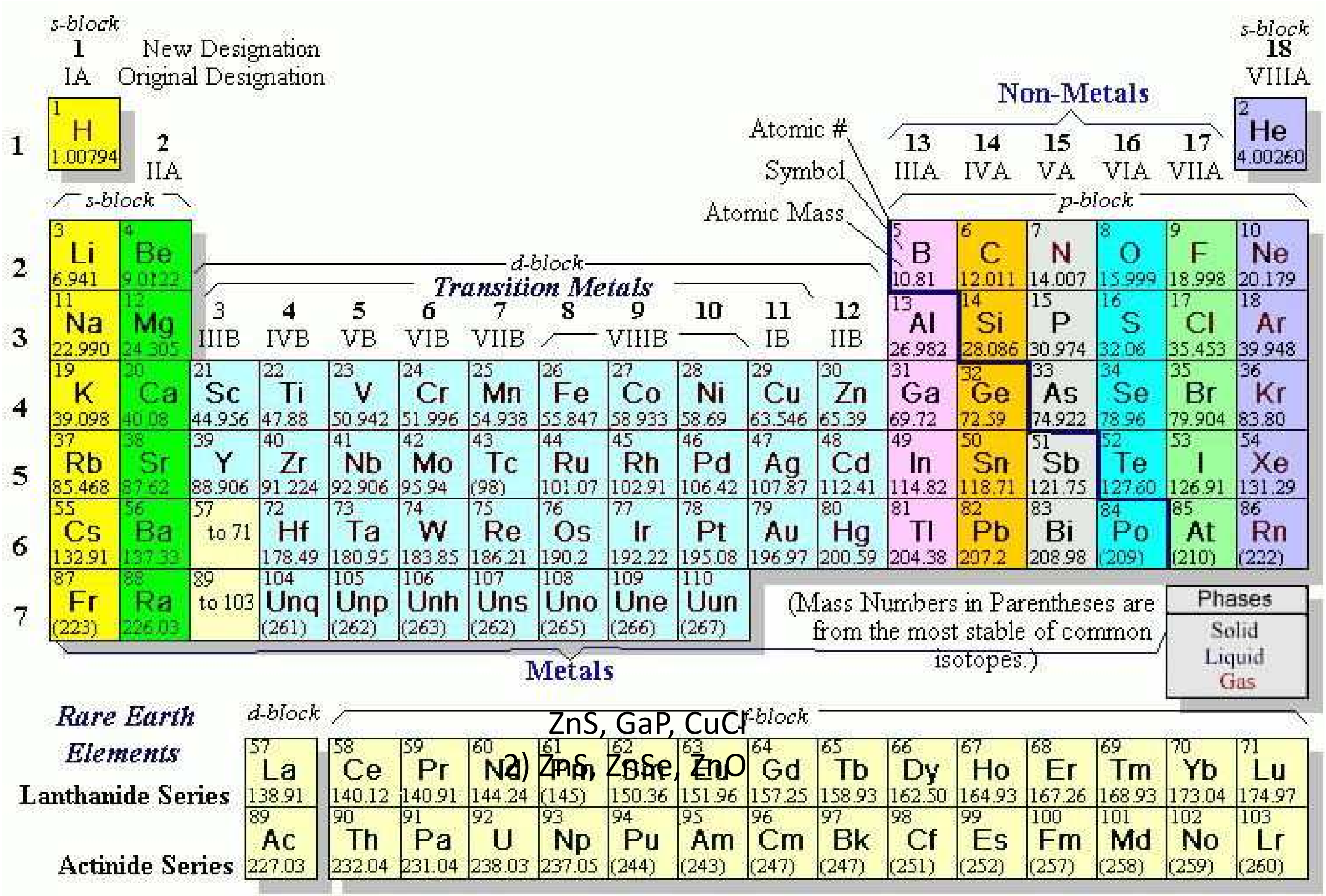
- Most elements: Electron configuration not stable.

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: C (atomic number = 6)

$1s^2$ $2s^2\ 2p^2$ → Valence electron



ZnS, GaP, CuCl

2) ZnS, ZnSe, ZnO

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.

The Periodic Table

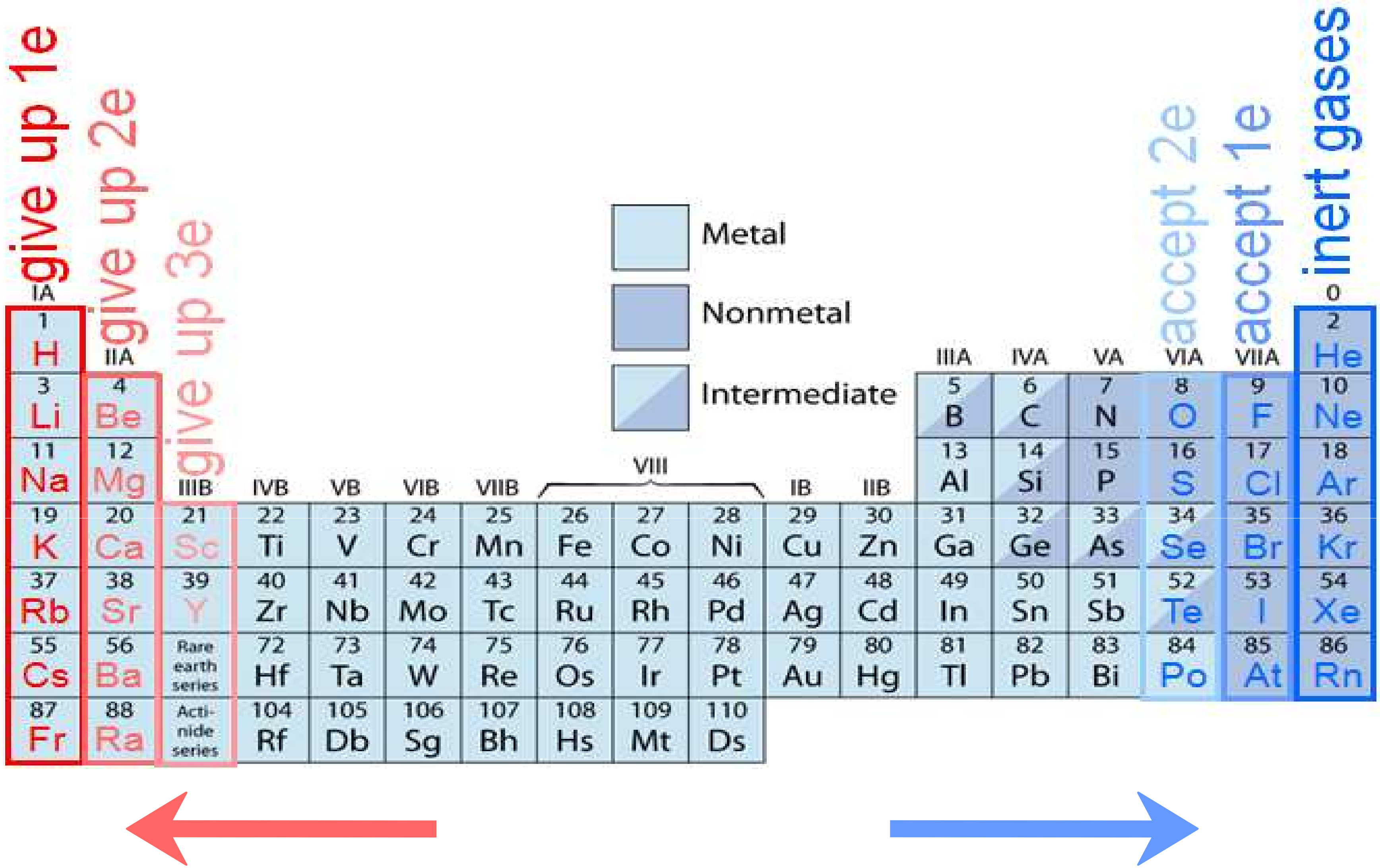
0: Inert gases (He, Ne, Ar...) have filled subshells: chemically inactive

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

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



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

Electronegative elements:
Readily acquire electrons
to become - ions.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
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	Kr –
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	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	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 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Smaller electronegativity

Larger electronegativity

- Ranges from 0.7 to 4.0
- 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 electronvolts, 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.

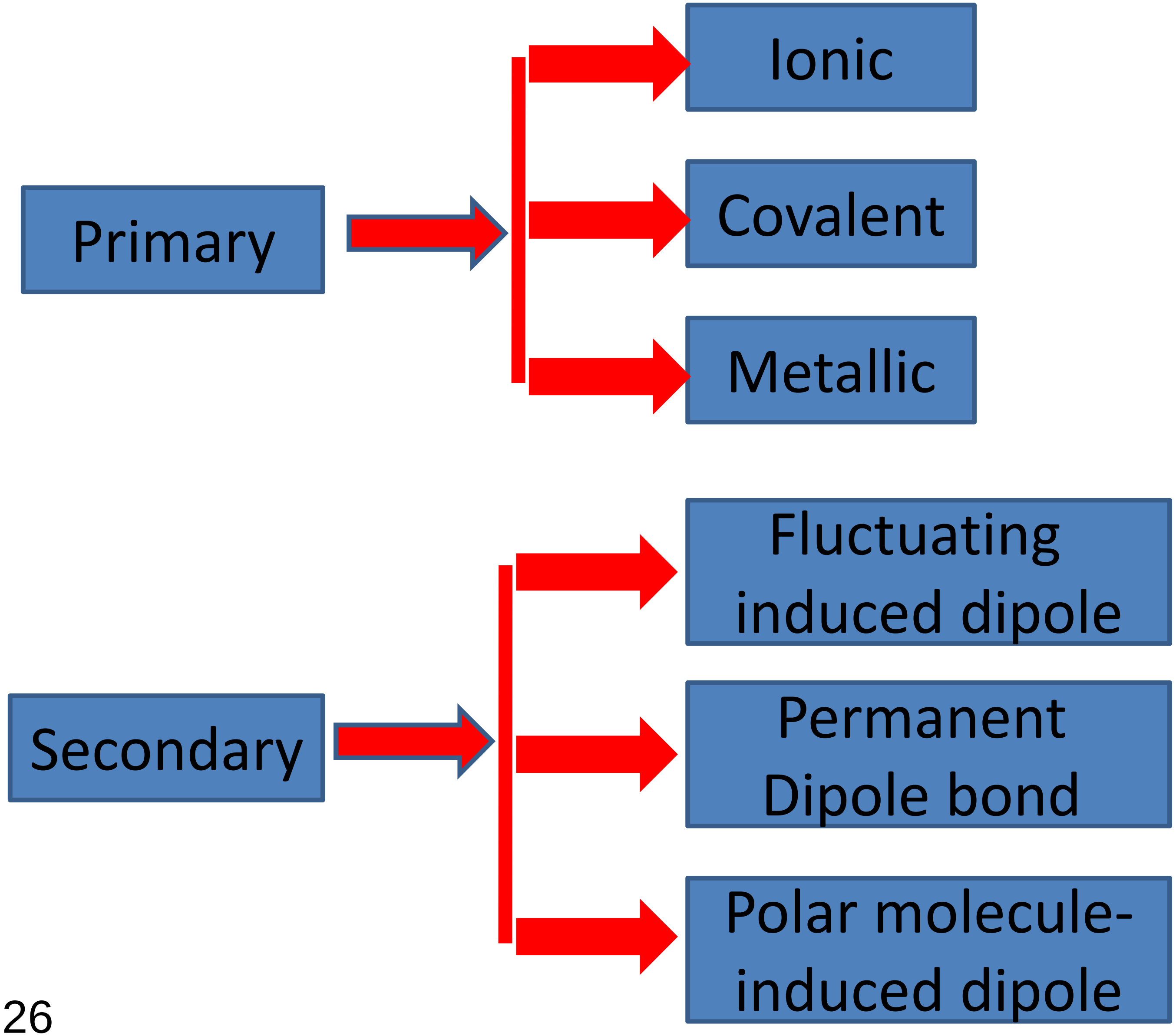
Solution:

$$\chi_H - \chi_{Br} =$$

$$= \left(1.602 \times 10^{-19}\right)^{-0.5} * \sqrt{(3.79 - (4.52 + 2.00)/2) * 1.602 \times 10^{-19}}$$

$$= 0.728$$

Types of Bonding



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 — Donates electrons

Nonmetal — Accepts electrons

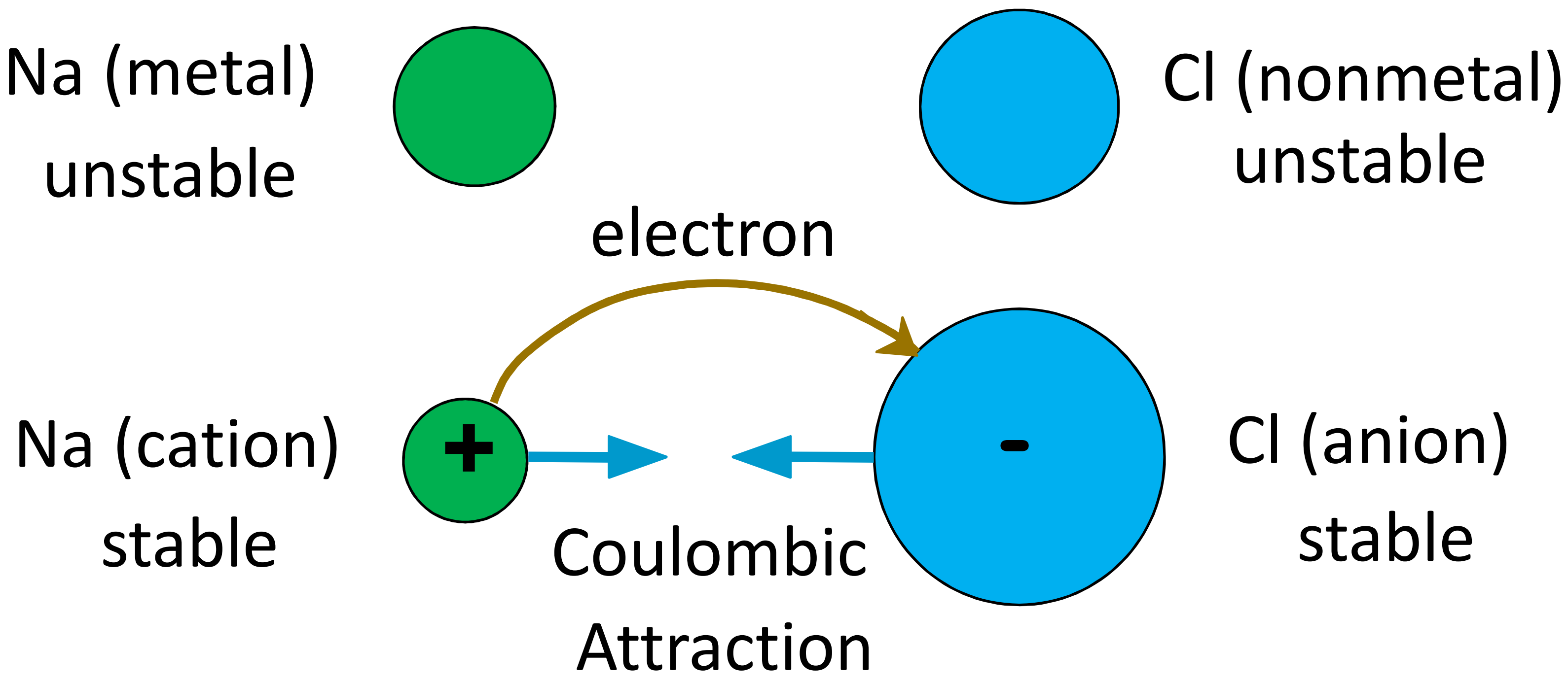
Dissimilar electronegativities

Example: NaCl

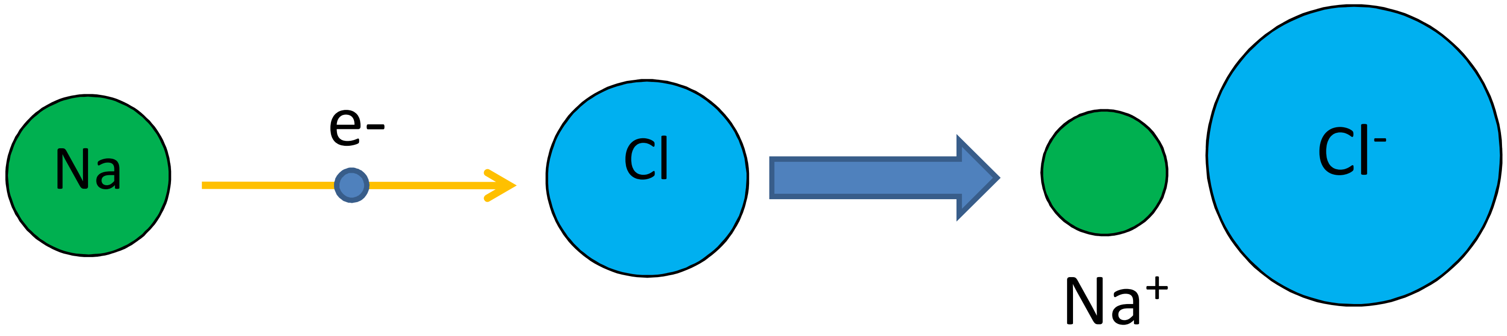
Na $1s^2\ 2s^2\ 2p^6\ 3s^1$ Cl $1s^2\ 2s^2\ 2p^6\ 3s^2 3p^5$

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

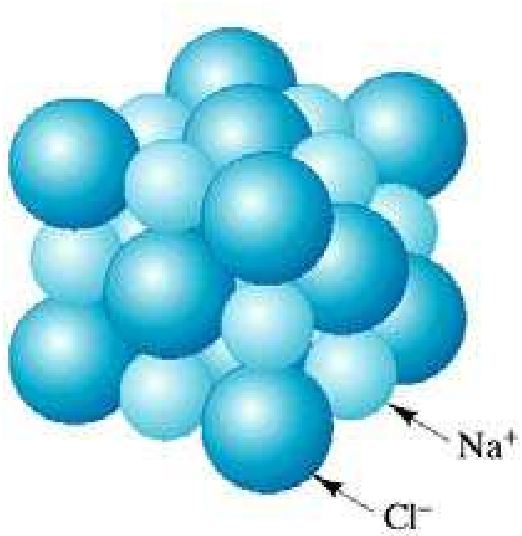
Ionic Bonding

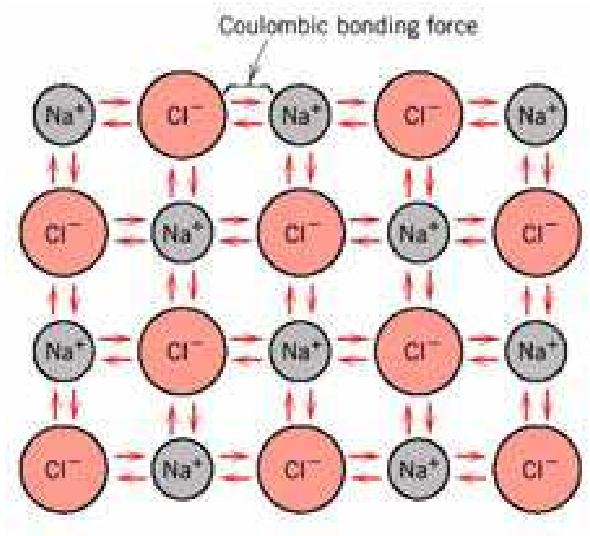


Ionic Bonding

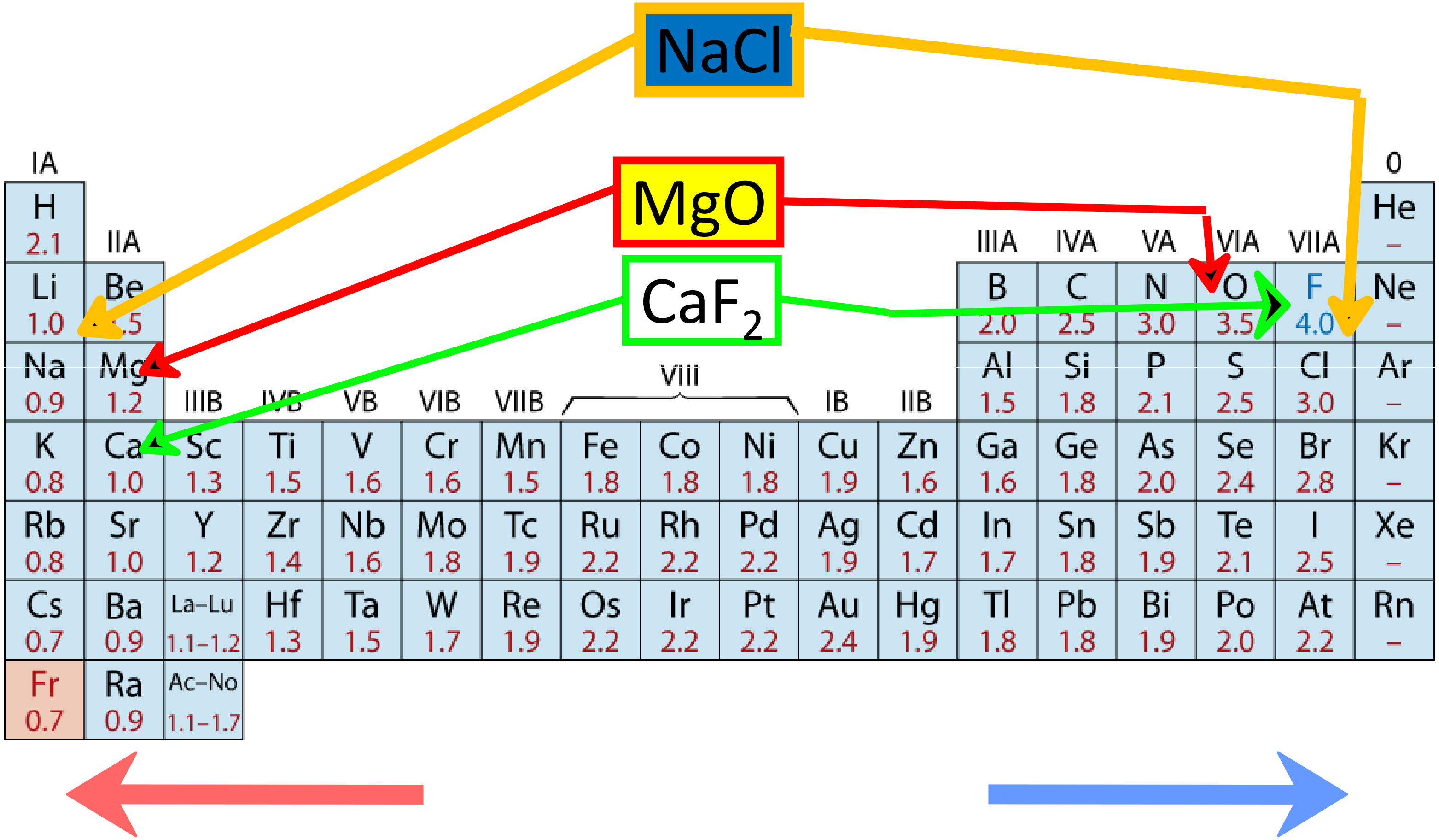


- Electron transfer reduces the energy of the system of atoms, that is, electron transfer is energetically favorable
- Note relative sizes of ions: Na shrinks and Cl expands





Ionic Bonding



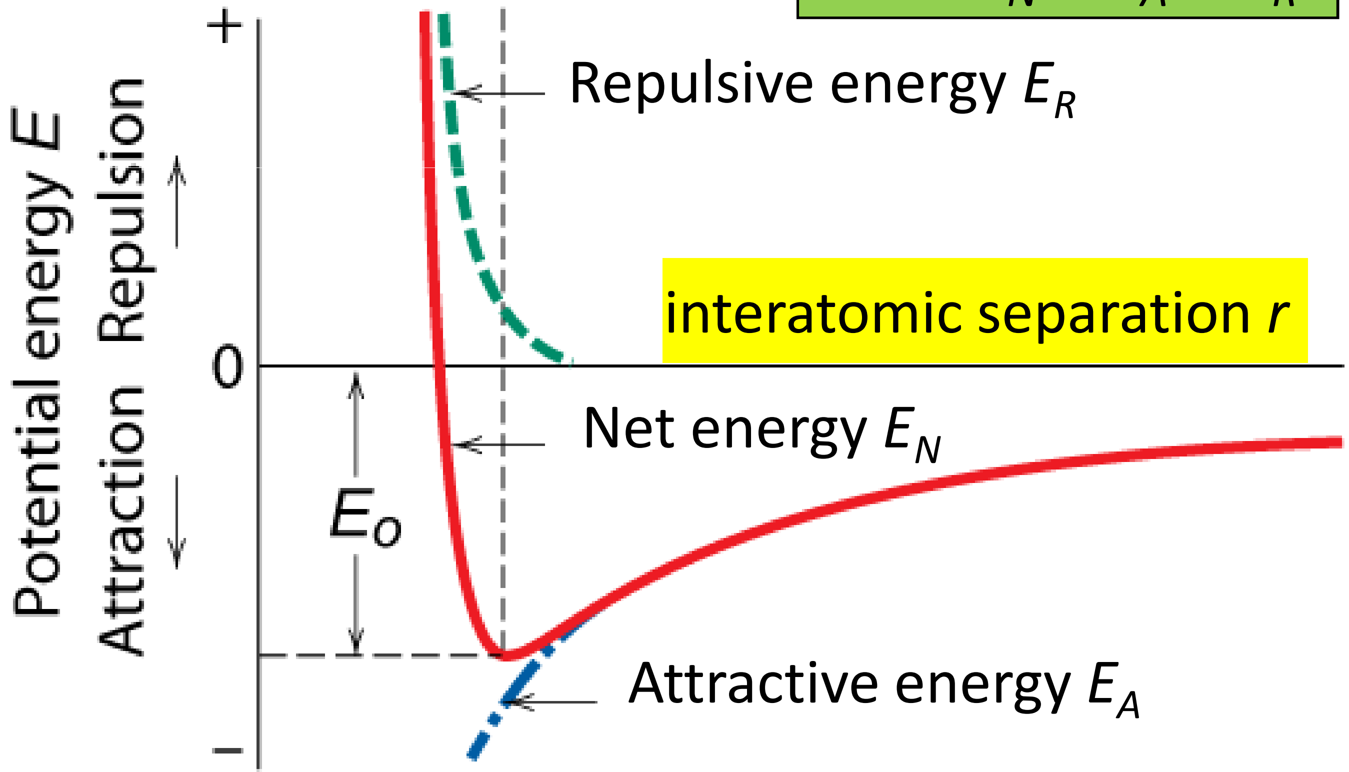
Give up electrons

Acquire electrons

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.

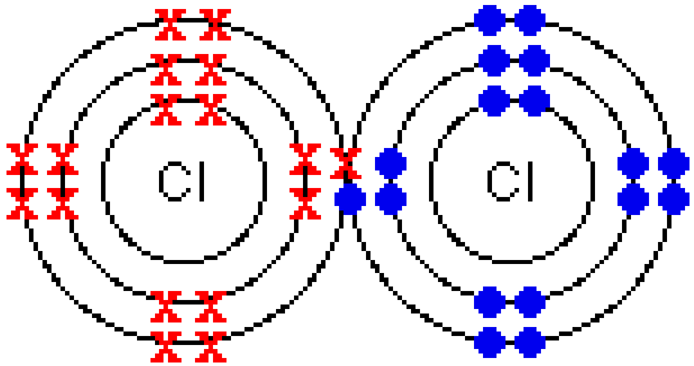
Covalent Bonding

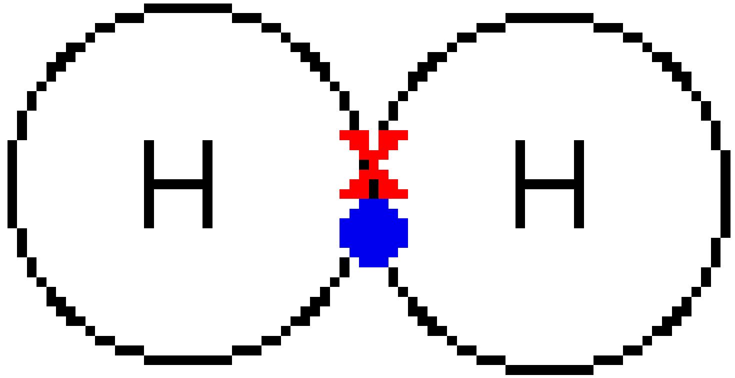
- A covalent bond is formed when electrons are shared between atoms.
- Covalent bonds are between non-metals and non-metals or hydrogen and non-metals.
- They share electrons so that both of them can have a stable octet.
- Covalent bonds are HIGHLY directional bonds.
- There are two types of covalent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

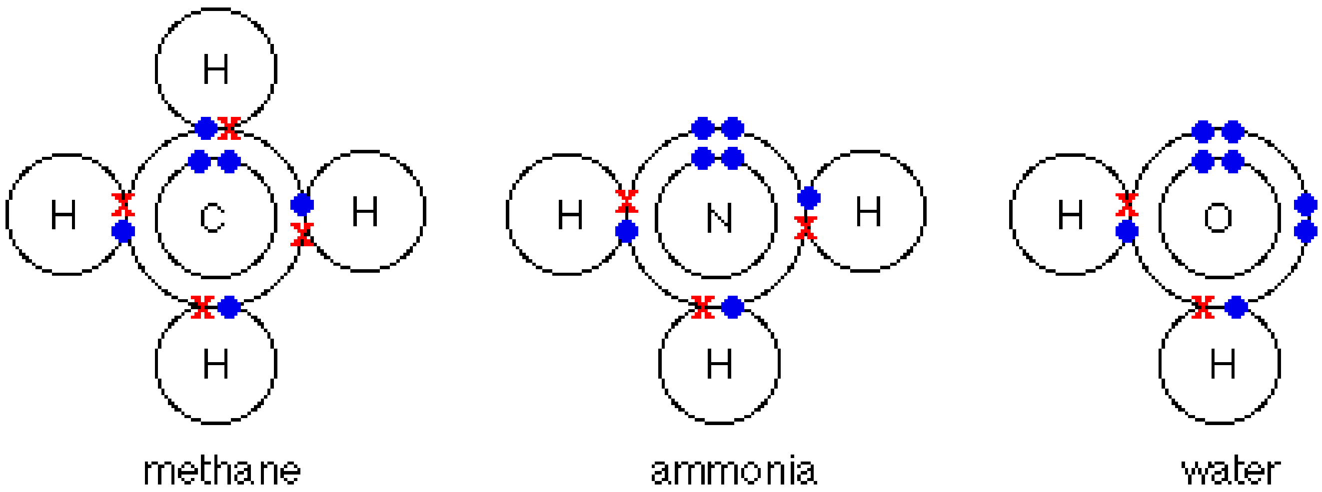
– Non-polar: result when two exact non-metals equally share electrons.

– Polar: result when two different non-metals share electrons.

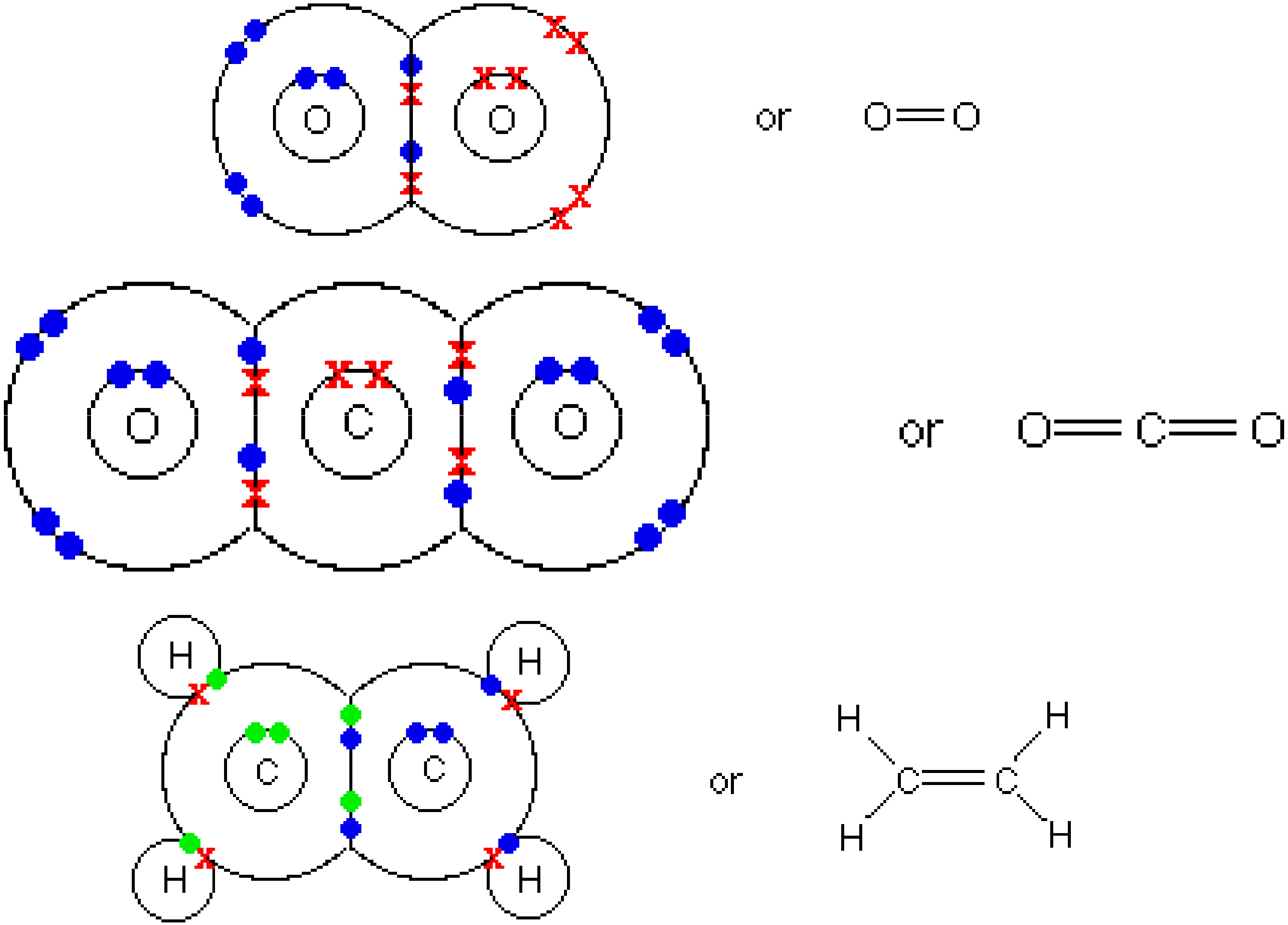
Covalent Bonding



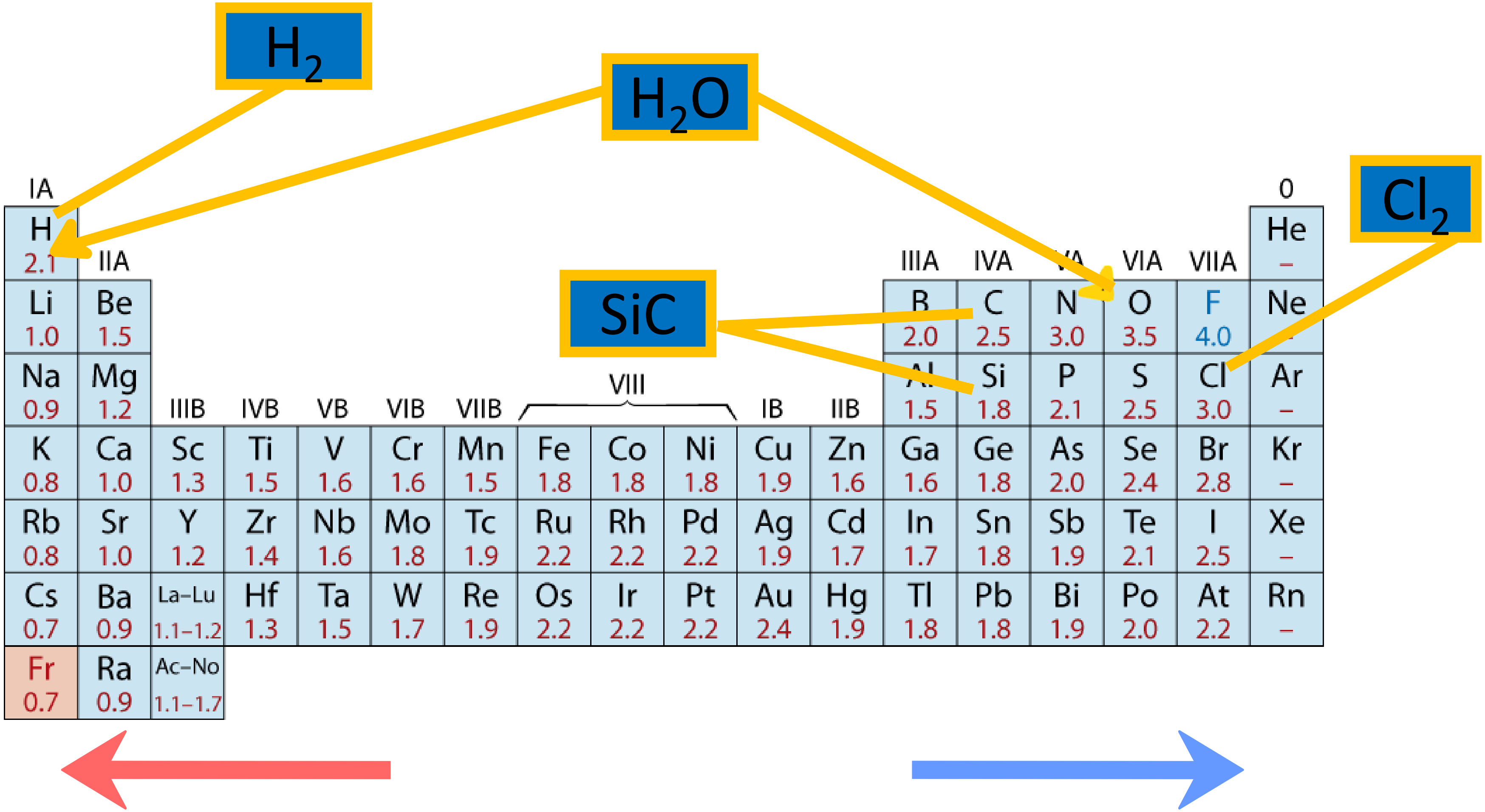




Covalent Bonding



Examples of Covalent Bonding



Give up electrons

Acquire electrons

Naming Covalent Compounds

Covalent compounds are much easier to name than ionic compounds.

Examples:

P_2O_5 - this is named diphosphorus pentoxide.

CO - this is carbon monoxide.

CF_4 - this is 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

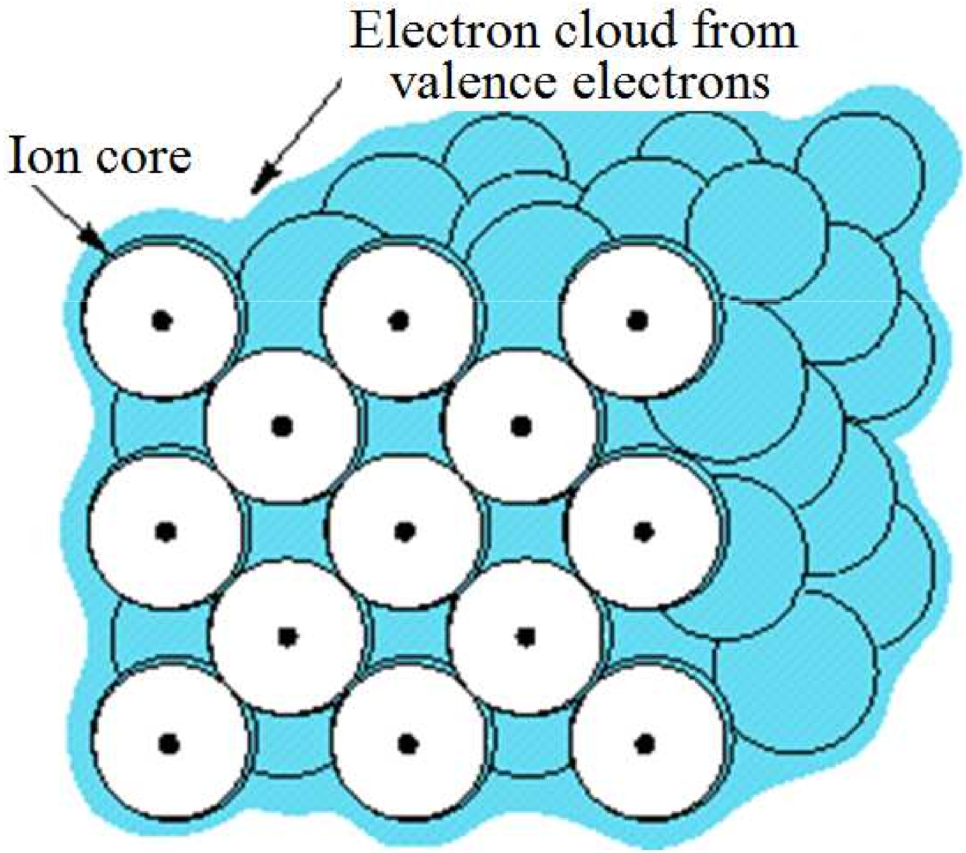
1) Covalent compounds generally have much **lower melting and boiling points** than ionic compounds.
2) Covalent compounds are **soft** and squishy (compared to ionic compounds, anyway).
3) Covalent compounds tend to be **more flammable** than ionic compounds.
4) Covalent compounds **don't conduct electricity** in water.
5) Covalent compounds **aren't usually very soluble 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**.

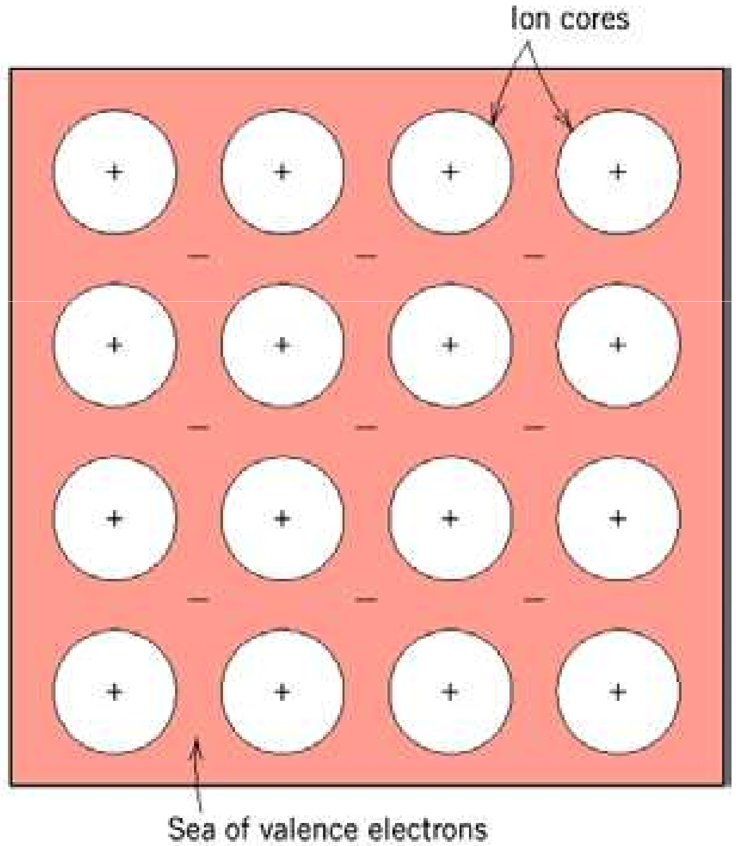
Metallic Bonds

- 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.
- Dipole interactions occur between:

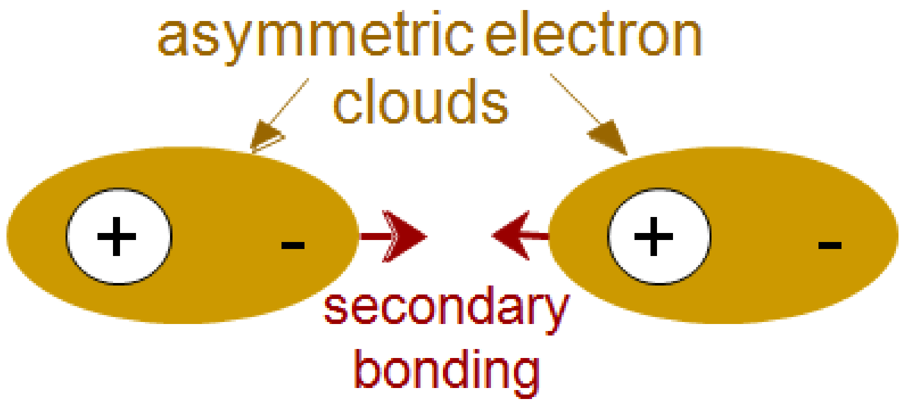
  1- Fluctuated induced dipoles.

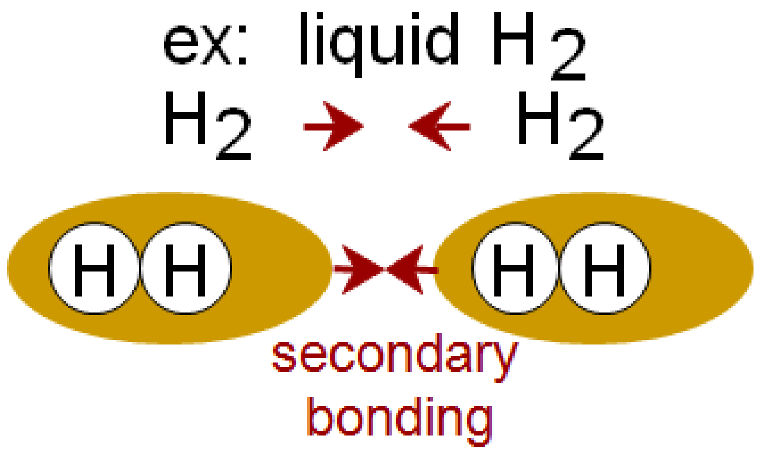
  2- Permanent dipole bond.

  3- Polar molecule-induced dipole

Fluctuating induced dipoles

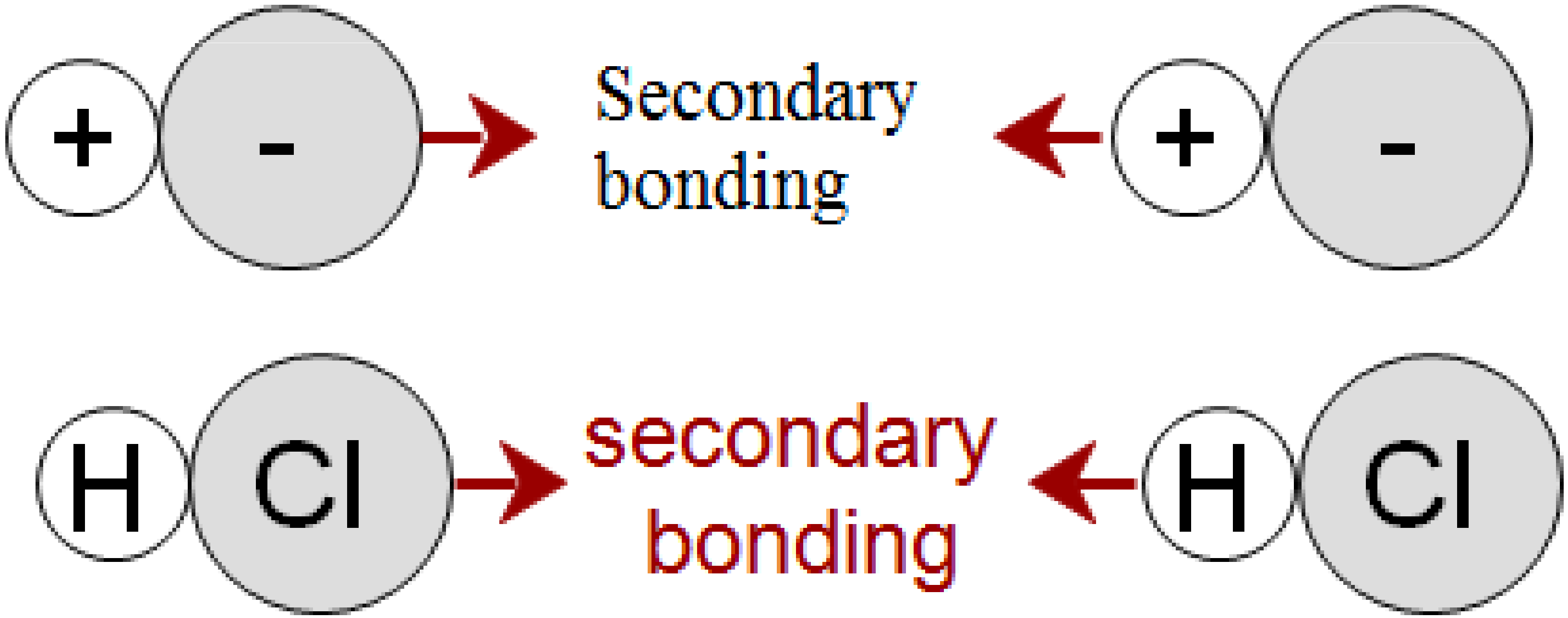
- Weak electric dipole bonding can take place among atoms due to an instantaneous asymmetrical distribution of electron densities around their nuclei.
- This type of bonding is termed fluctuation since the electron density is continuously changing.





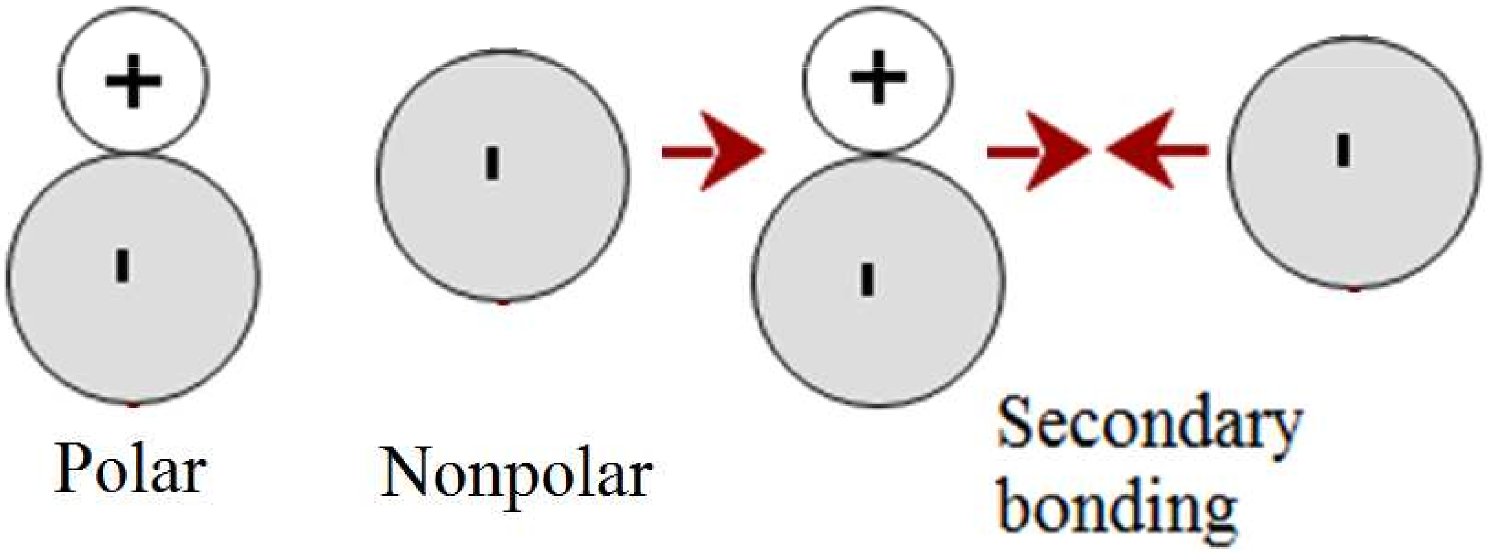
Permanent dipoles

- 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

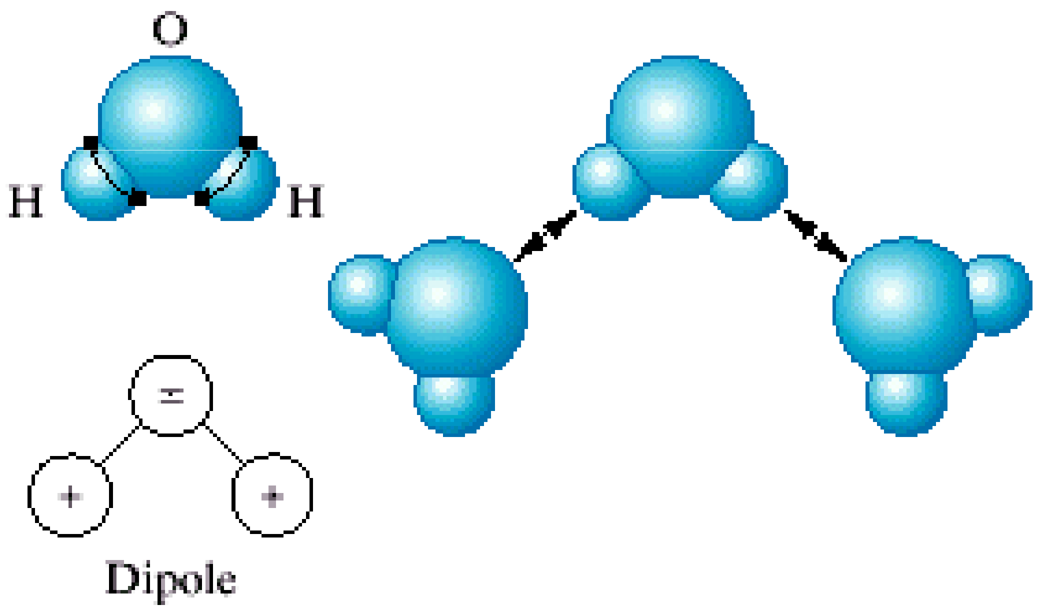
Polar molecules (with asymmetric arrangement of positively and negatively charged regions) can induce dipoles in adjacent nonpolar molecules



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.

Example: hydrogen bond in water. The H end of the molecule is positively charged and can bond to the negative side of another H_2O molecule (the O side of the H_2O 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

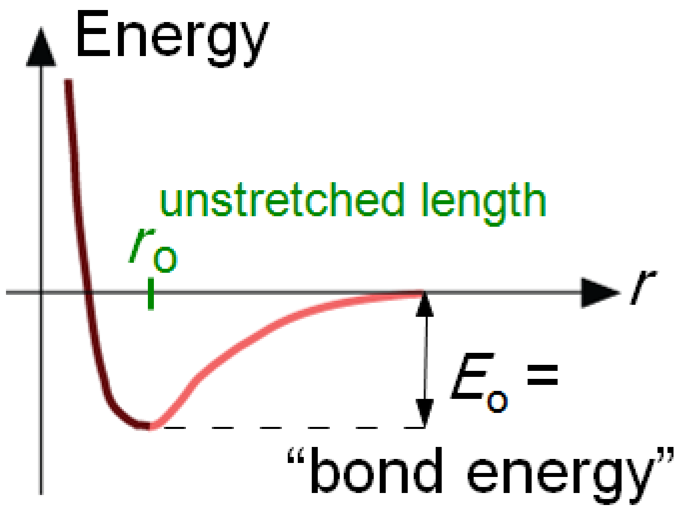
Bonding and materials properties

- 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.

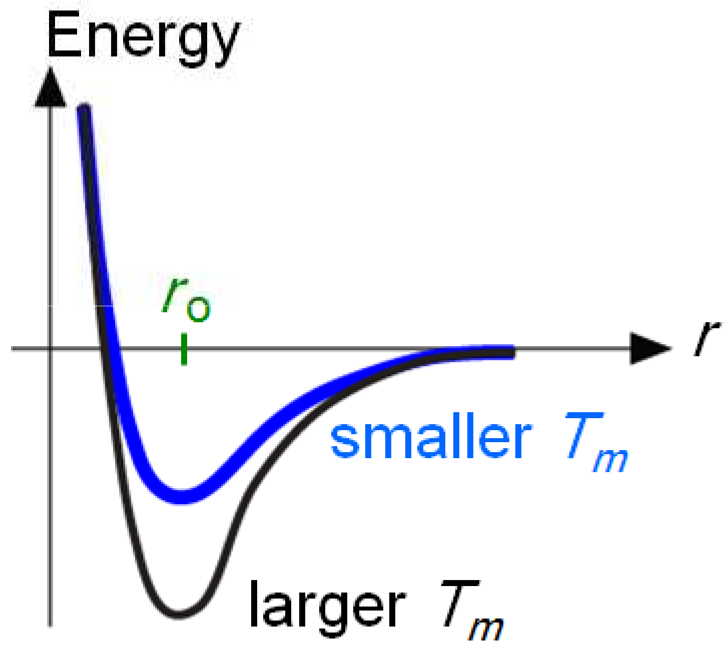
Properties From Bonding: T_m

- Bond length, r

- Bond energy, E_o



- Melting Temperature, T_m

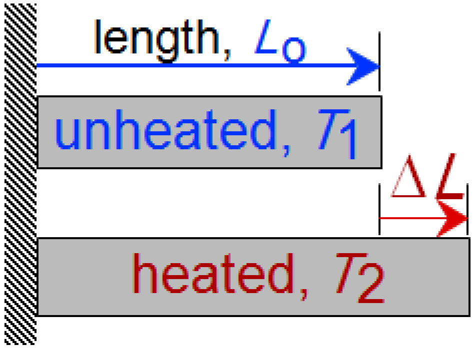


T_m is larger if E_o is larger.

Properties From Bonding: T_m

Bonding Type	Substance	Bonding Energy kJ/mol (kcal/mol)	Bonding Energy eV/Atom, Ion, Molecule	Melting Temperature (°C)
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

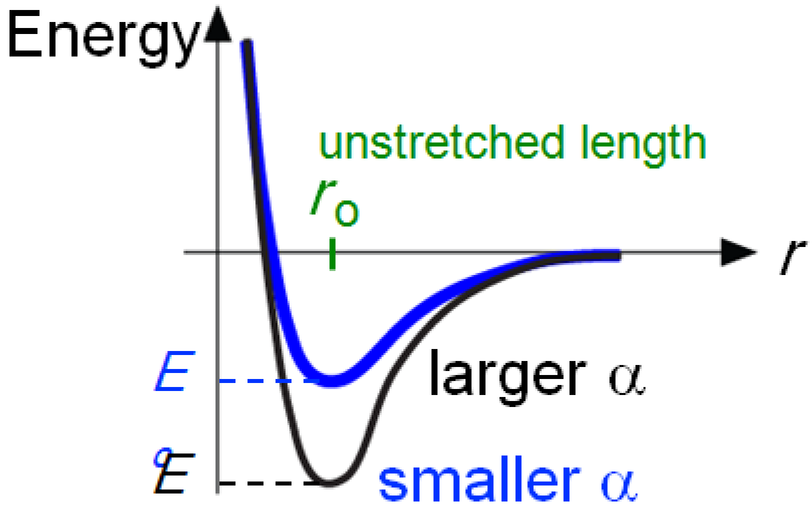
Properties From Bonding: α



coeff. thermal expansion

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

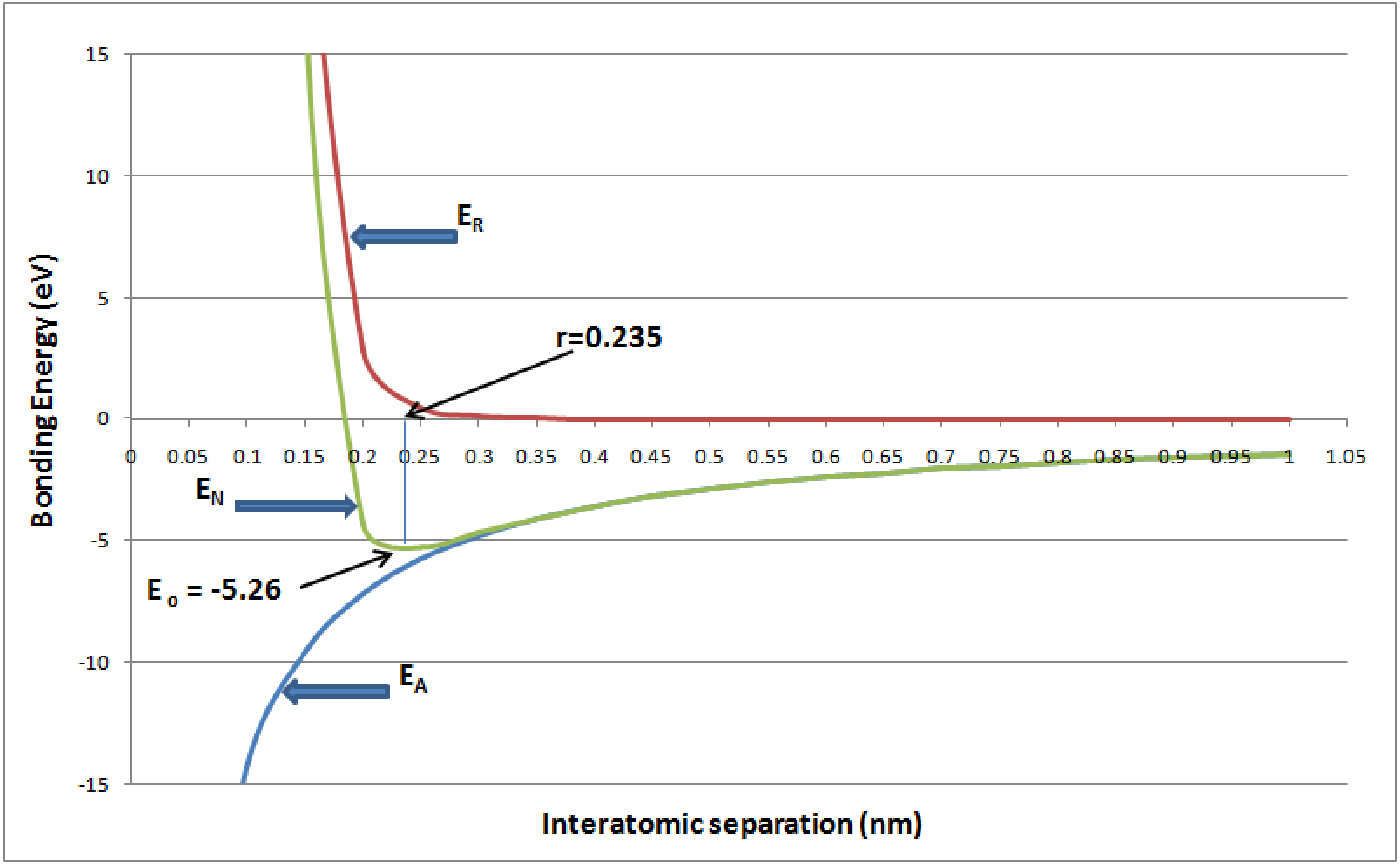
- α ~ symmetry at r_o



α is larger if E_o is smaller.

T_m is larger if E_o is larger.

r	E_A	E_R	E_N
0.05	-28.72	187392.00	187363.28
0.1	-14.36	732.00	717.64
0.15	-9.57	28.56	18.99
0.2	-7.18	2.86	-4.32
0.25	-5.74	0.48	-5.26
0.3	-4.79	0.11	-4.68
0.35	-4.10	3.25E-02	-4.07
0.4	-3.59	1.12E-02	-3.58
0.45	-3.19	4.35E-03	-3.19
0.5	-2.87	1.87E-03	-2.87
0.55	-2.61	8.74E-04	-2.61
0.6	-2.39	4.36E-04	-2.39
0.65	-2.21	2.30E-04	-2.21
0.7	-2.05	1.27E-04	-2.05
0.75	-1.91	7.31E-05	-1.91
0.8	-1.80	4.36E-05	-1.79
0.85	-1.69	2.69E-05	-1.69
0.9	-1.60	1.70E-05	-1.60
0.95	-1.51	1.10E-05	-1.51
1	-1.44	7.32E-06	-1.44



15
10
5
0
-5
-10
-15
0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45 0.5 0.55 0.6 0.65 0.7 0.75 0.8 0.85 0.9 0.95 1 1.05
Bonding Energy (eV)
Interatomic separation (nm)
E_R
r=0.235
E_N
E_o = -5.26
E_A