

Chapter 2

Atomic Structure

The University of Jordan
Chemical Engineering Department
First Semester 2022
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Outline

1- Review of Atomic Structure

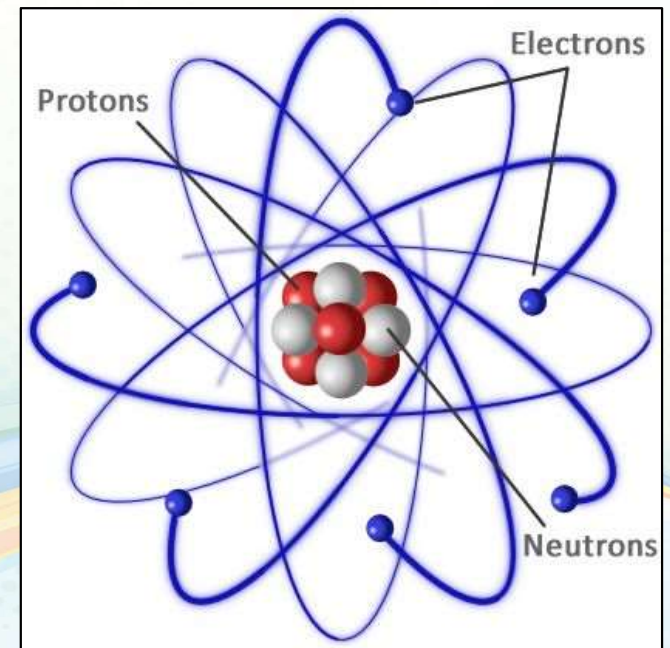
- *Electrons, Protons, Neutrons.*
- *Atomic Bonding in Solids.*
- *Periodic Table.*
- *Primary Interatomic Bonds .*
- *Secondary Bonding (Van der Waals).*

2- Molecules and Molecular Solids

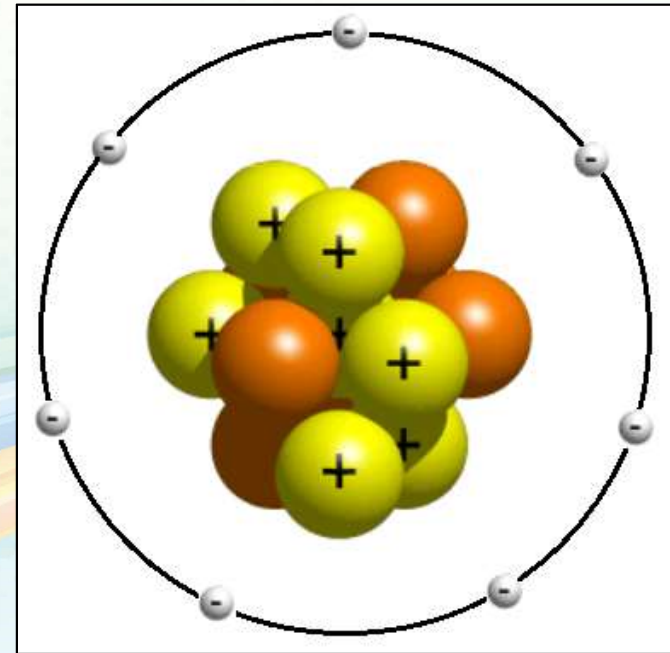
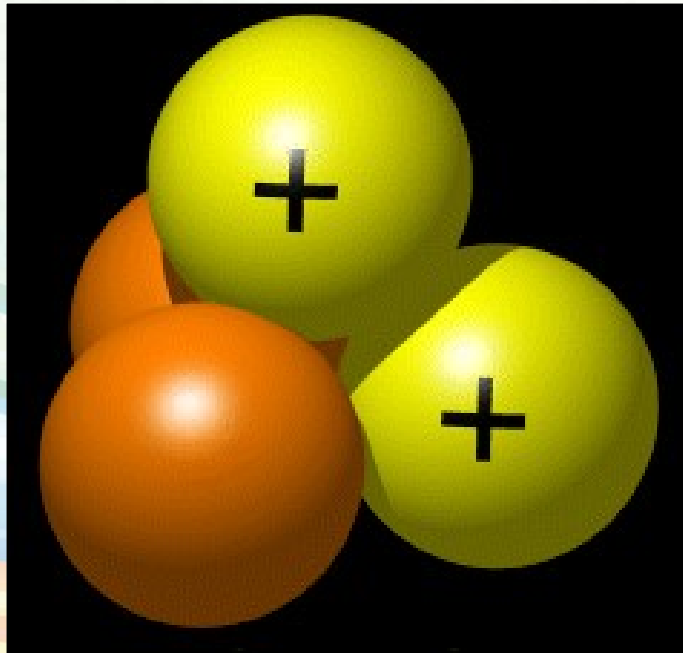
Review of Atomic Structure

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

A

Element's
Symbol

Atomic Number
Protons = Electrons

Z

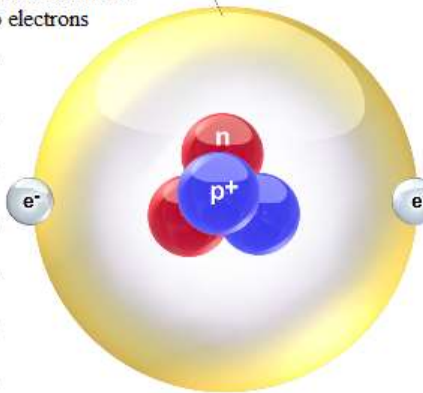
X

N

Number of
Neutrons

$$\therefore N = A - Z$$

The first energy level
can hold a maximum
of two electrons



Helium, He

Atomic number: 2 Mass number: 4
(2 protons + 2 neutrons) 2 electrons

As an example: Helium atom ${}^4_2\text{He}_2$

● Protons

● Neutrons

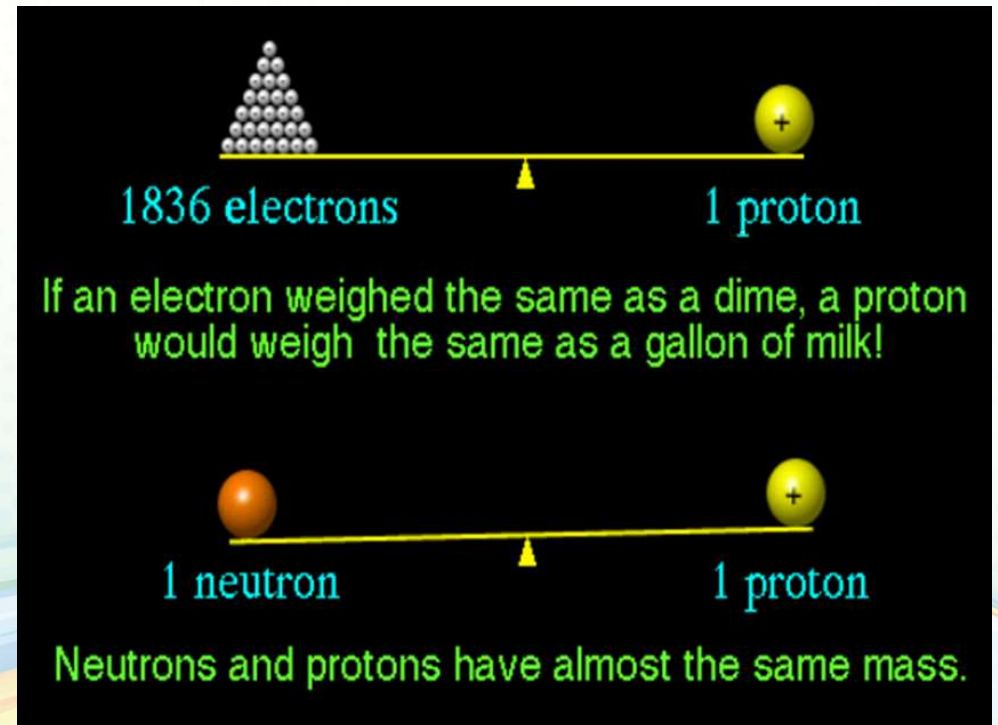
● Electrons

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



1 proton
1 electron
0 neutrons

Helium



2 protons
2 electrons
2 neutrons

Carbon

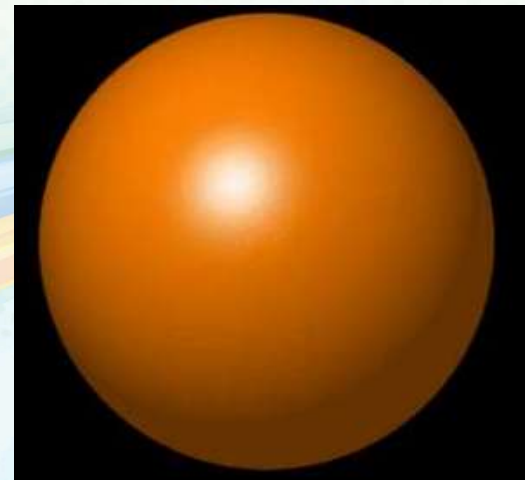
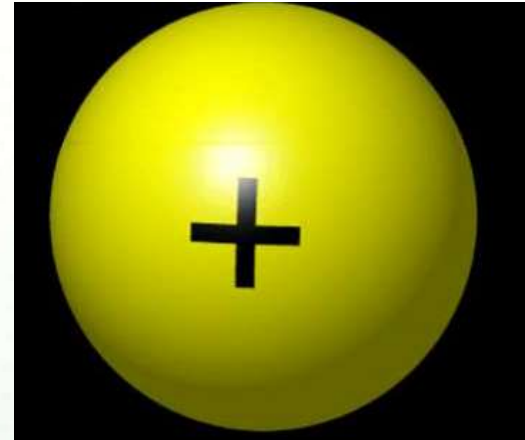


6 protons
6 electrons
6 neutrons

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

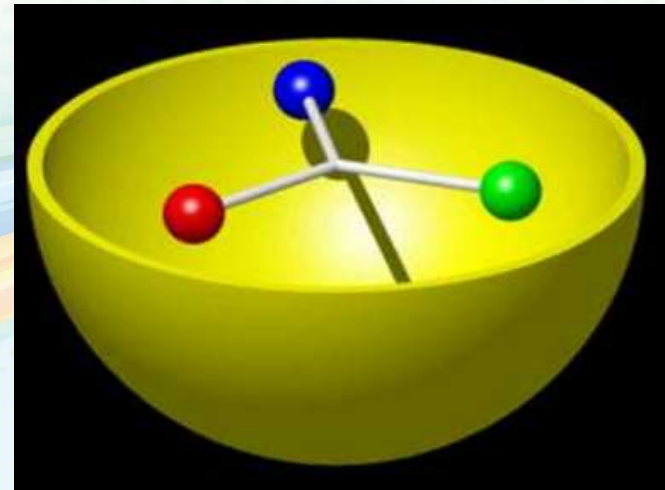
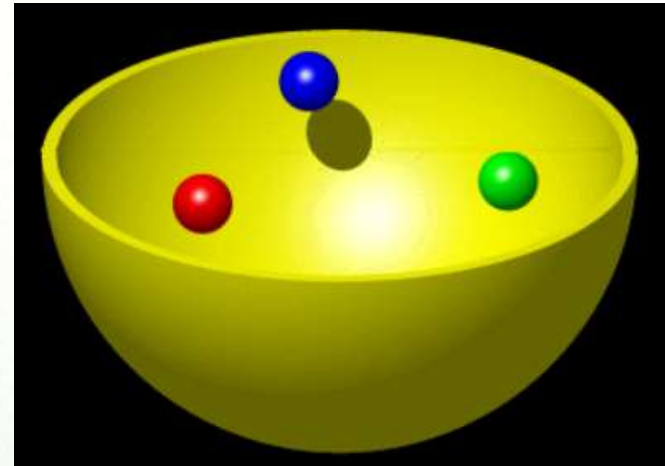
➤ *Scientists thought there was nothing smaller than the proton in the nucleus of the atom.*

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

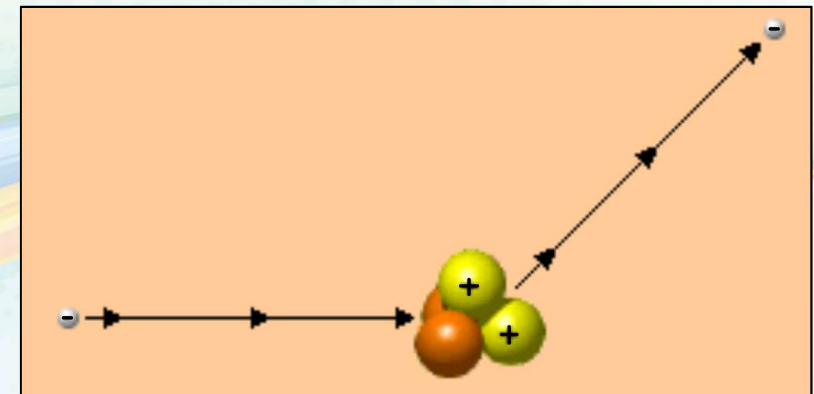
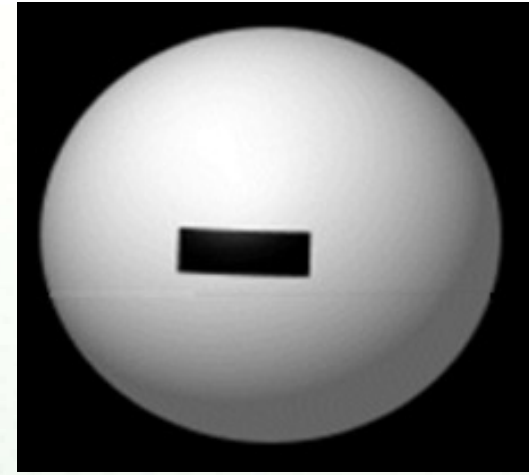


➤ In 1968, scientists discovered new particles inside the proton. They called these particles quarks.

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

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

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

- Mean distance between atoms

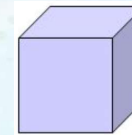
$$L = \left(\frac{1}{n}\right)^{1/3}$$

Example:

Diamond (carbon): $d = 3.5 \text{ g}/\text{cm}^3$, $M = 12 \text{ g}/\text{mol}$

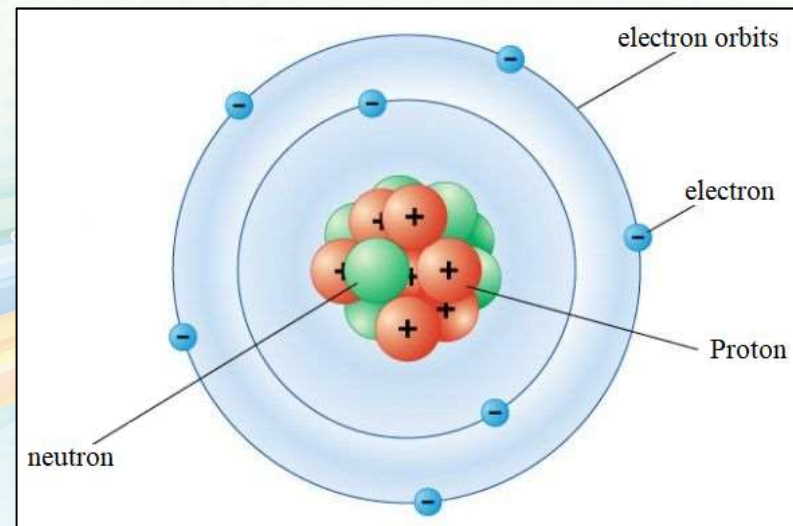
$$\begin{aligned} n &= (6 \times 10^{23} \text{ atoms/mol} \times 3.5 \text{ g}/\text{cm}^3) / (12 \text{ g/mol}) \\ &= 17.5 \times 10^{22} \text{ atoms}/\text{cm}^3 \end{aligned}$$

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



Electrons in Atoms

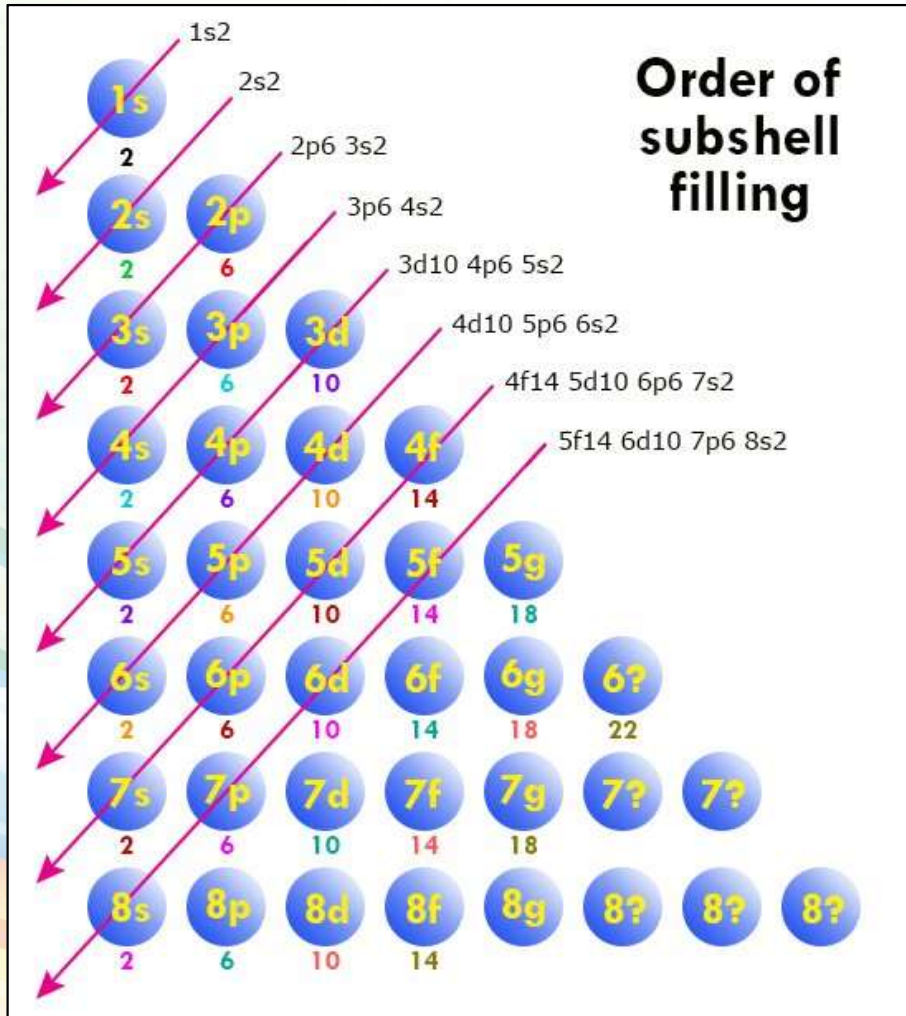
- *The electrons form a cloud around the nucleus, of radius of 0.05 – 2 nm.*
- *This “Bohr” picture looks like a mini planetary system. But quantum mechanics tells us that this analogy is not Correct.*
- *Electrons move not in circular orbits, as in popular drawings, but in 'fuzzy' orbits.*



- *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	$\mathcal{K}$	S	1	2	2
2	$\mathcal{L}$	S	1	2	8
		P	3	6	
3	$\mathcal{M}$	S	1	2	18
		P	3	6	
		D	5	10	
4	$\mathcal{N}$	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, ...

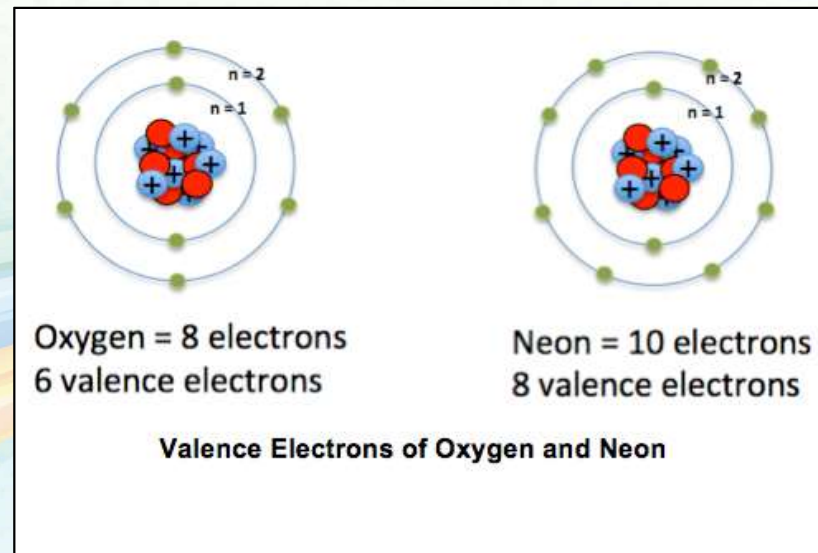
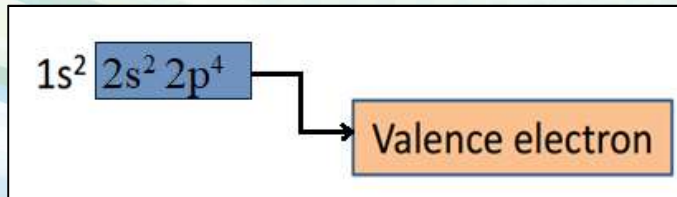
➤ *Most elements: Electron configuration not stable.*

<u>Element</u>	<u>Atomic #</u>	<u>Electron configuration</u>
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)



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, $\text{Fe} = 26: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. 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.*

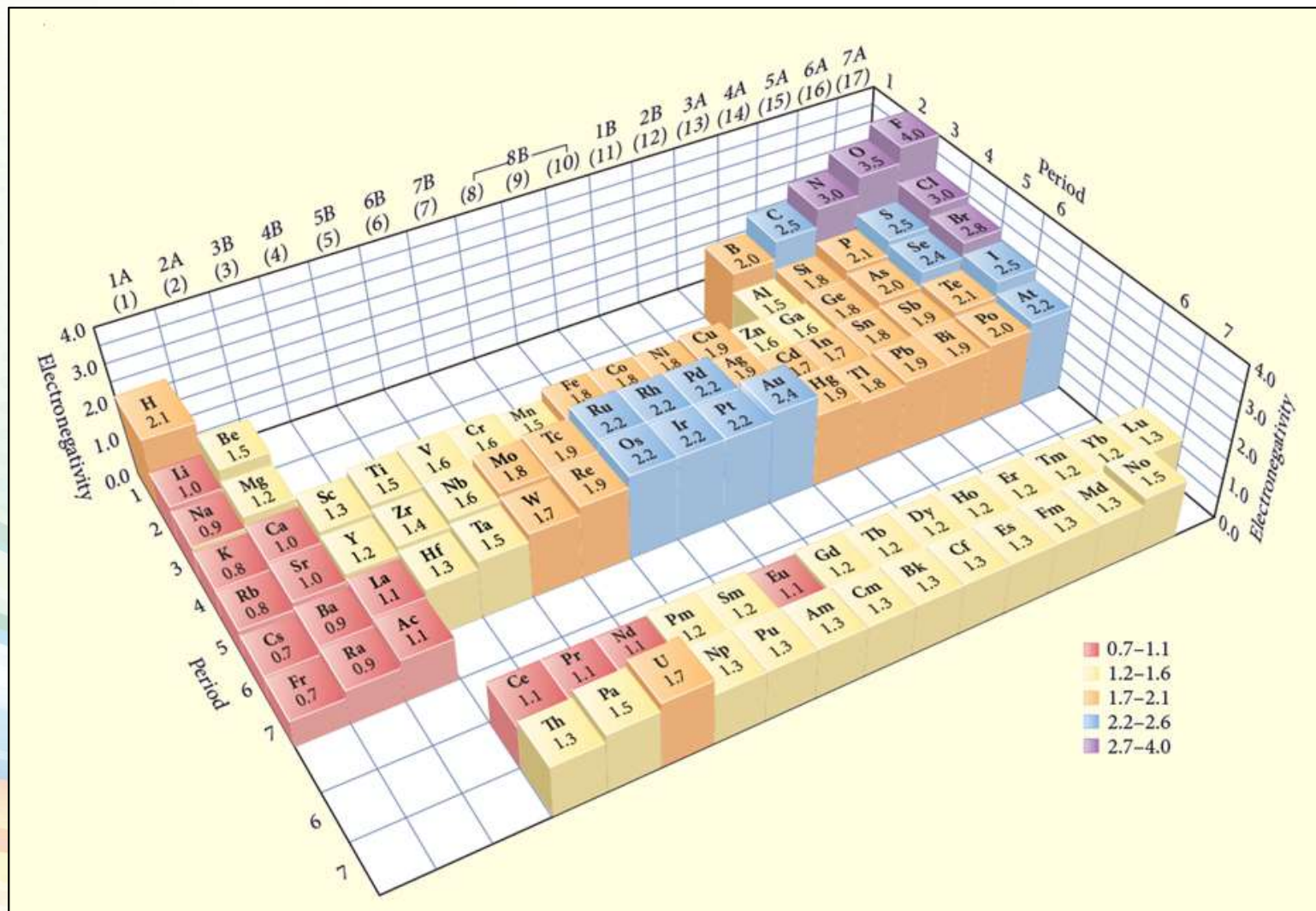
Periodic Table of the Elements

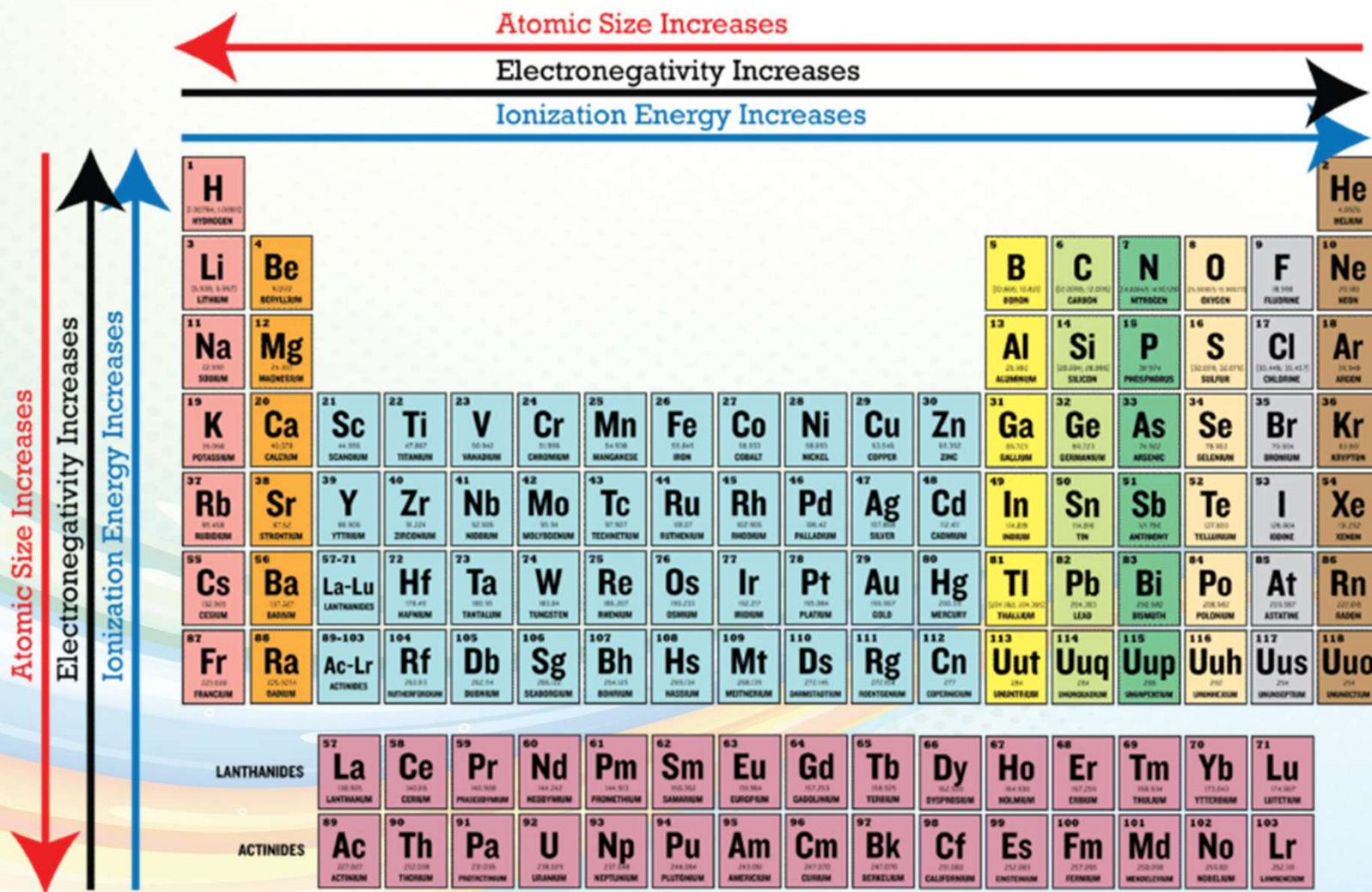
Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen 1.01	2 He Helium 4.00																
2	3 Li Lithium 6.94	4 Be Beryllium 9.01																
3	11 Na Sodium 22.99	12 Mg Magnesium 24.31																
4	19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80
5	37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
6	55 Cs Cesium 132.91	56 Ba Barium 137.33	♦	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 (209) Po Polonium [209]	85 (210) At Astatine [210]	86 (222) Rn Radon [222]
7	87 Fr Francium [223]	88 Ra Radium [226]	★	104 Rf Rutherfordium [261]	105 Db Dubnium [268]	106 Sg Seaborgium [271]	107 Bh Bohrium [270]	108 Hs Hassium [277]	109 Mt Meitnerium [276]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [284]	114 Fl Flerovium [289]	115 Mc Moscovium [288]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]
				57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
				89 Ac Actinium [227]	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium [237]	94 Pu Plutonium [244]	95 Am Americium [243]	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium [251]	99 Es Einsteinium [252]	100 Fm Fermium [257]	101 Md Mendelevium [258]	102 No Nobelium [259]	103 Lr Lawrencium [262]

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





- 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: $\text{H}-\text{Br}$, 3.79 eV ; $\text{H}-\text{H}$, 4.52 eV ; $\text{Br}-\text{Br}$ 2.00 eV .

Solution:

Note that $1 \text{ kcal/mol} = 4.3363 \times 10^{-2} \text{ eV}$

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

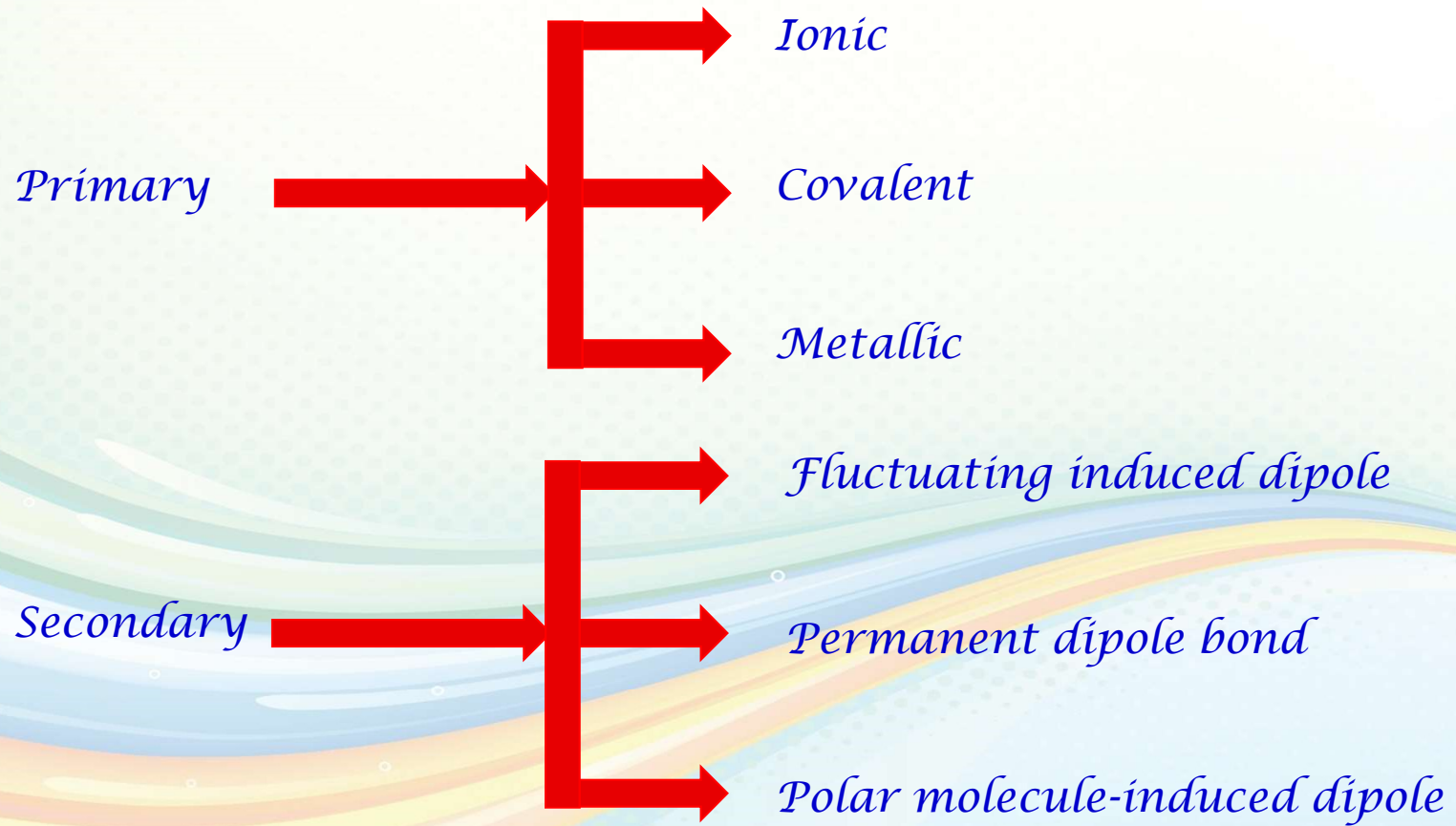
$$\chi_A - \chi_B = 0.728$$

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



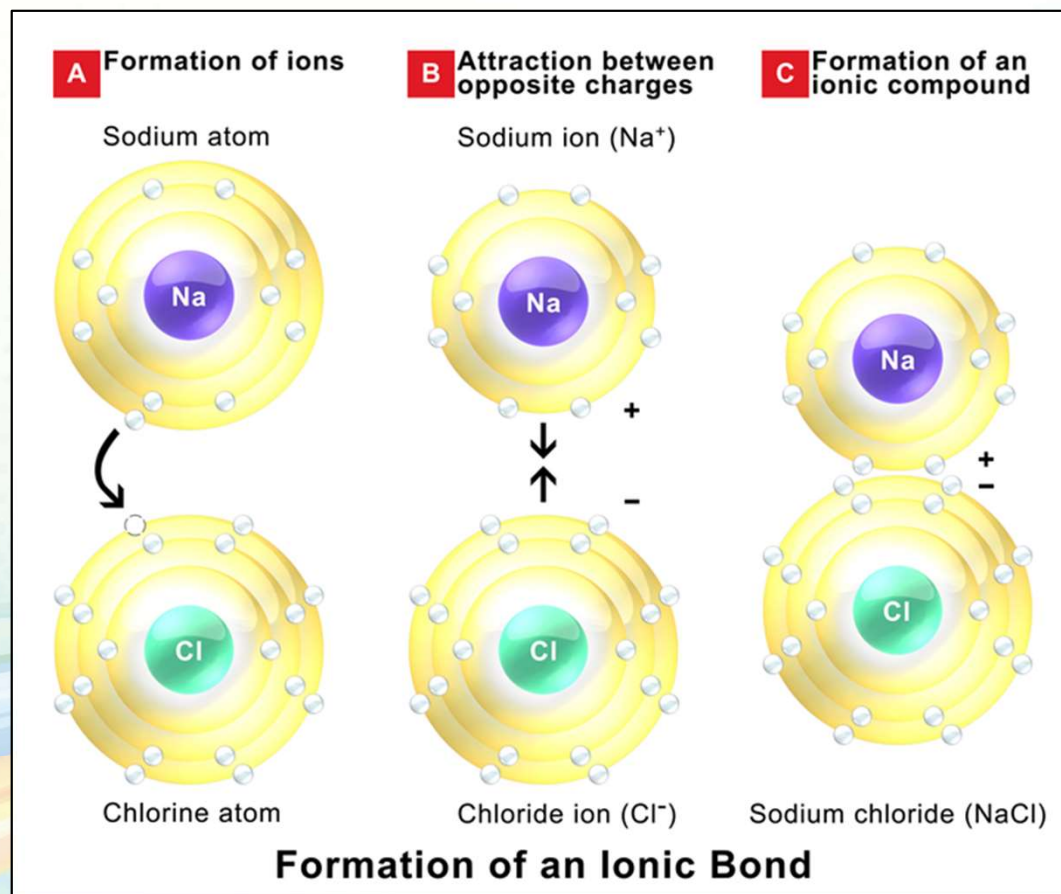
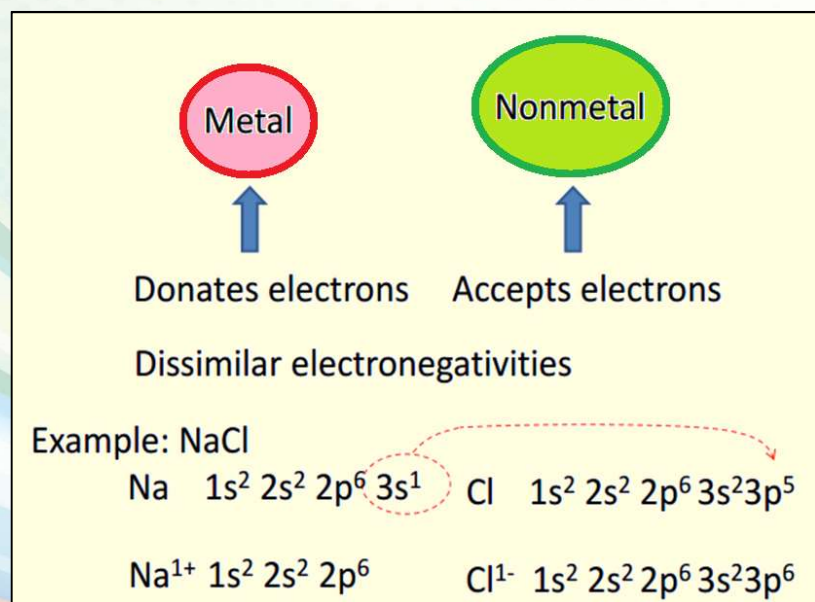


Ionic Bonding

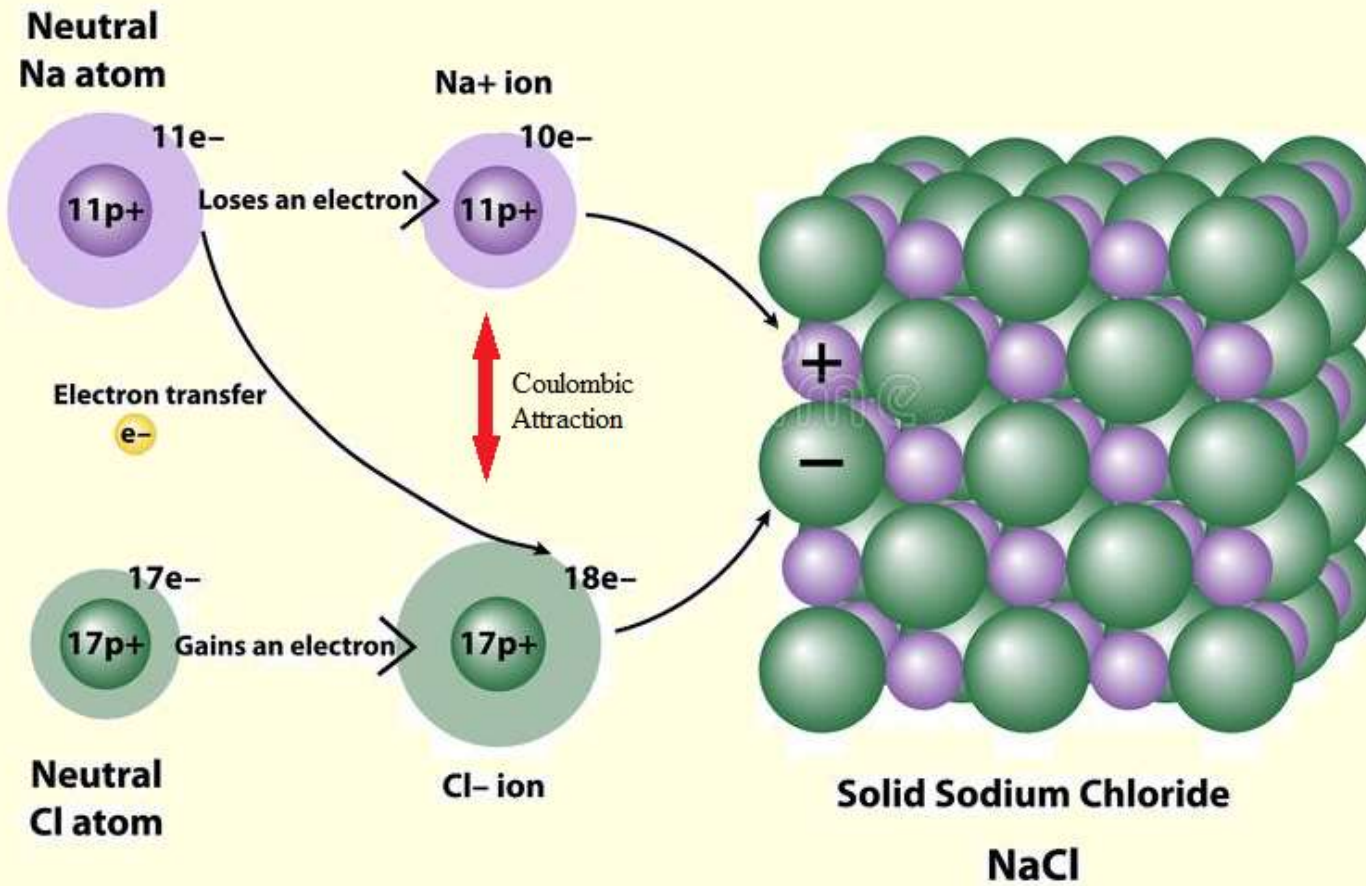
Formation of ionic bond:

- 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)

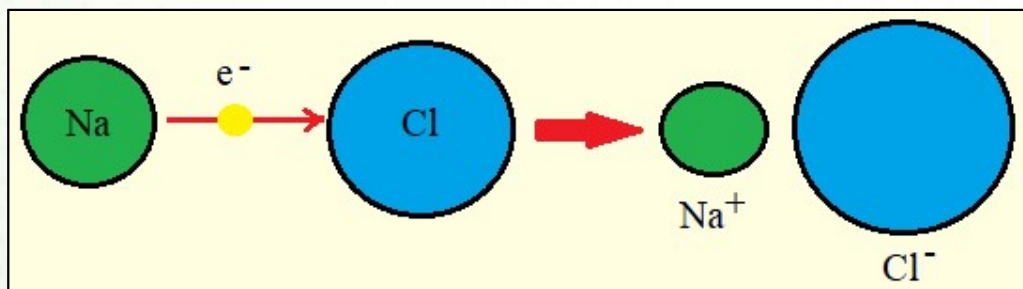
Ionic Bonding



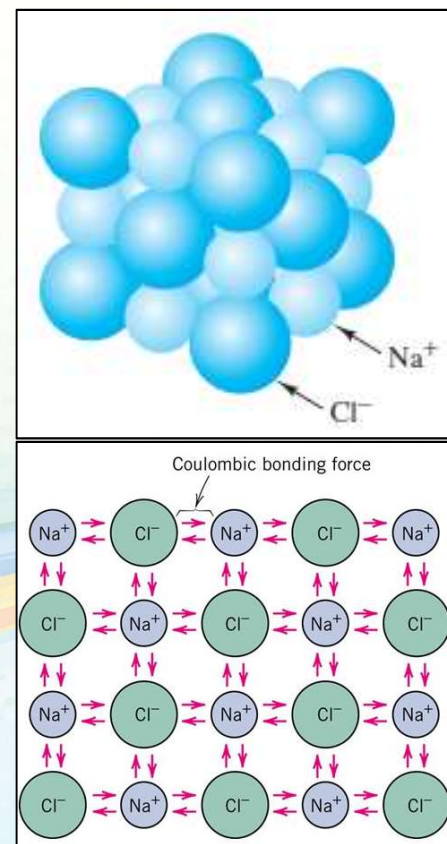
Ionic Bonding



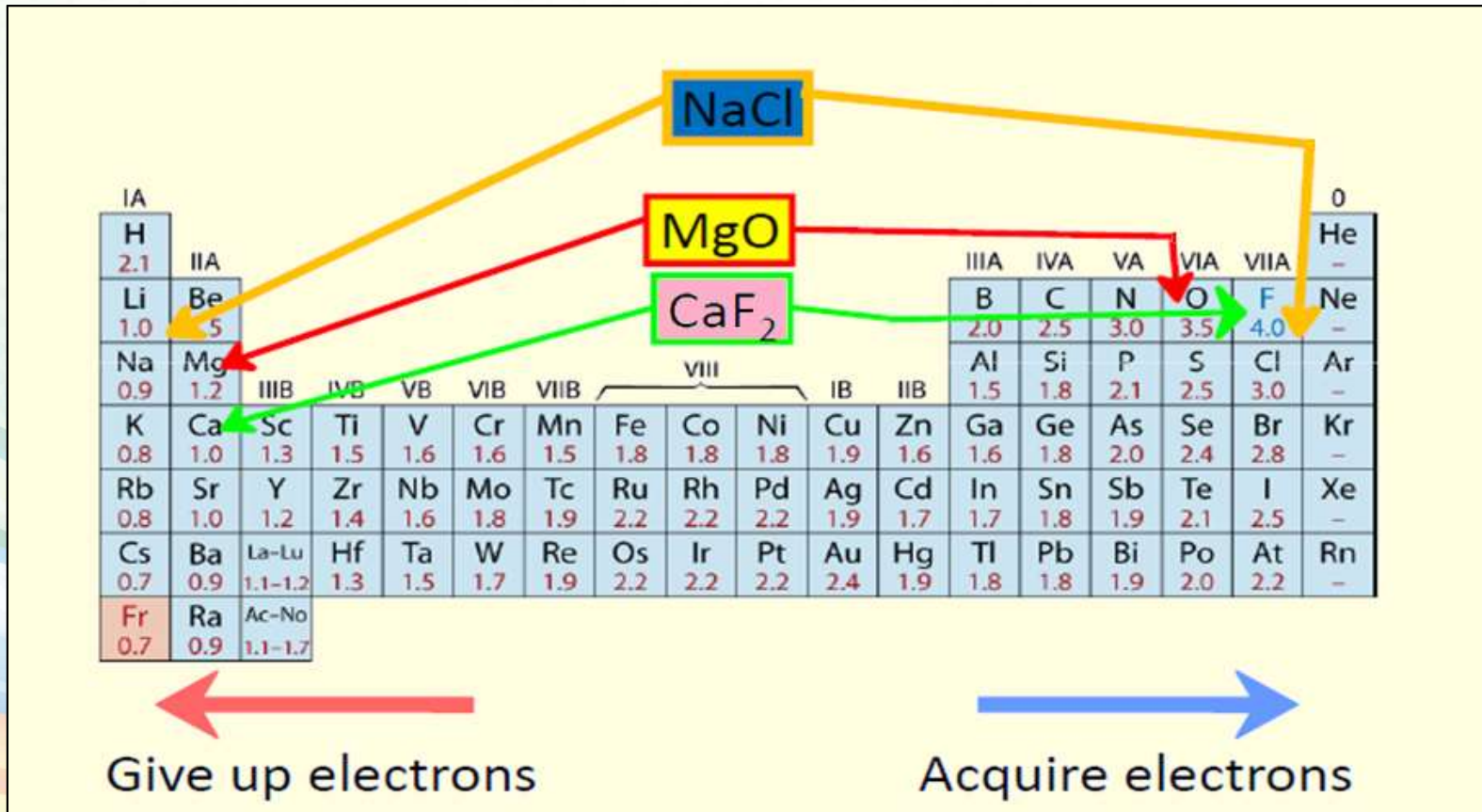
Ionic Bonding



- ✓ 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



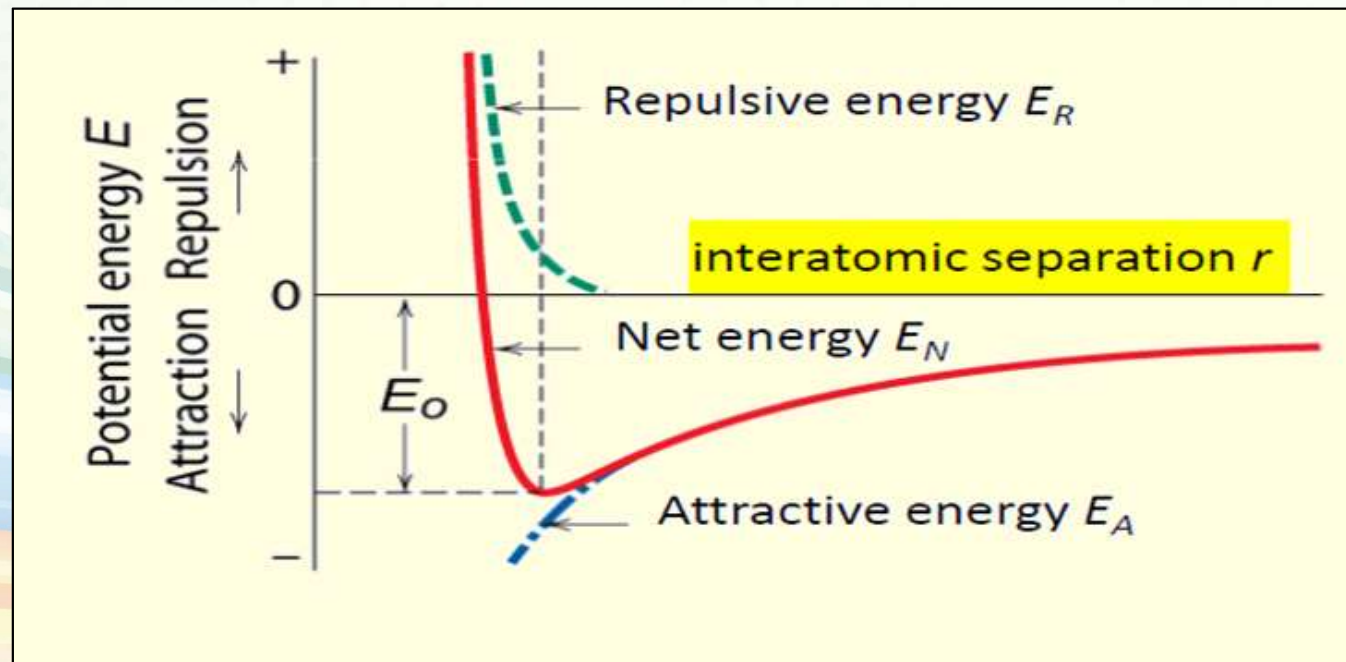
Ionic Bonding



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

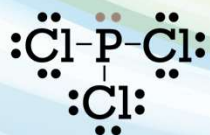
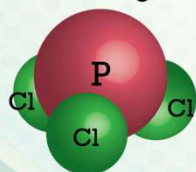
- The forces that bring molecules together are called forces of attraction.

Covalent Bonding

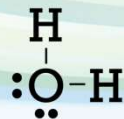
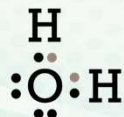
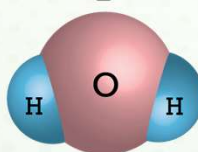
- *A covalent bond is formed when electrons are shared between atoms.*
- *Covalent bonds are between non-metals and non-metals or hydrogen and non-metals.*
- *They share electrons so that both of them can have a stable octet.*
- *Covalent bonds are HIGHLY directional bonds.*
- *There are two types of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

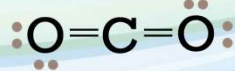
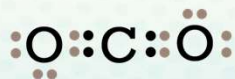
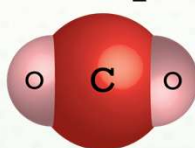
Phosphorus Trichloride



Water

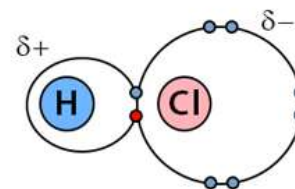


Carbon Dioxide

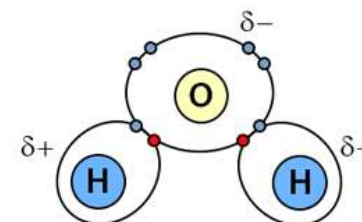


Polar Covalent Bond Examples

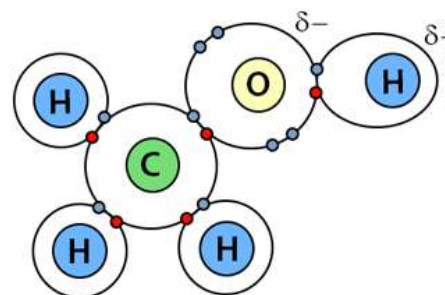
1. Hydrogen chloride



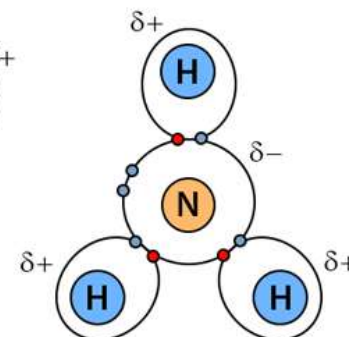
2. Water



3. Methanol

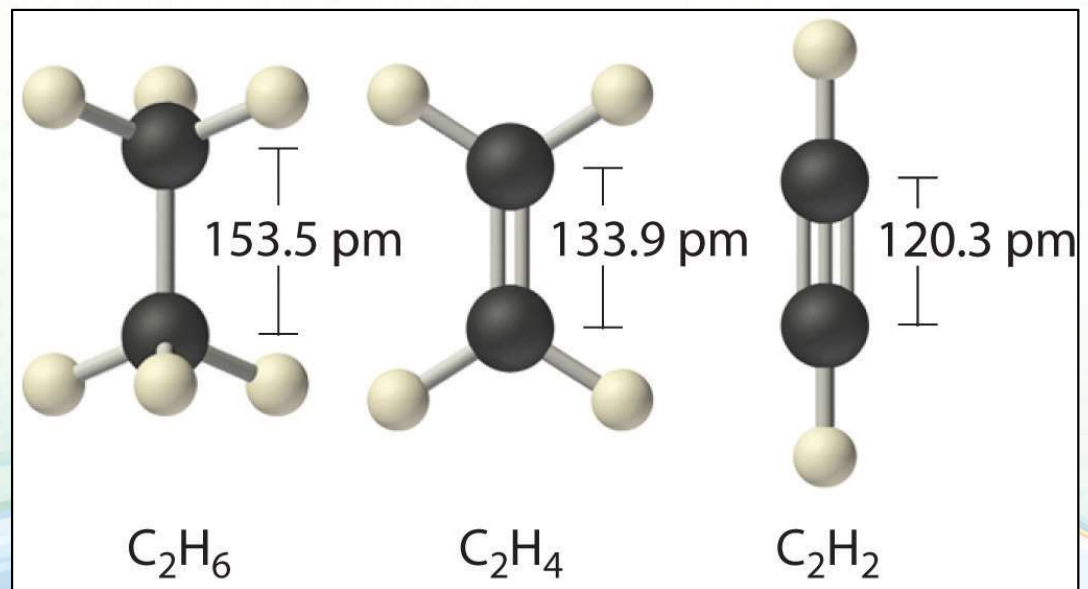
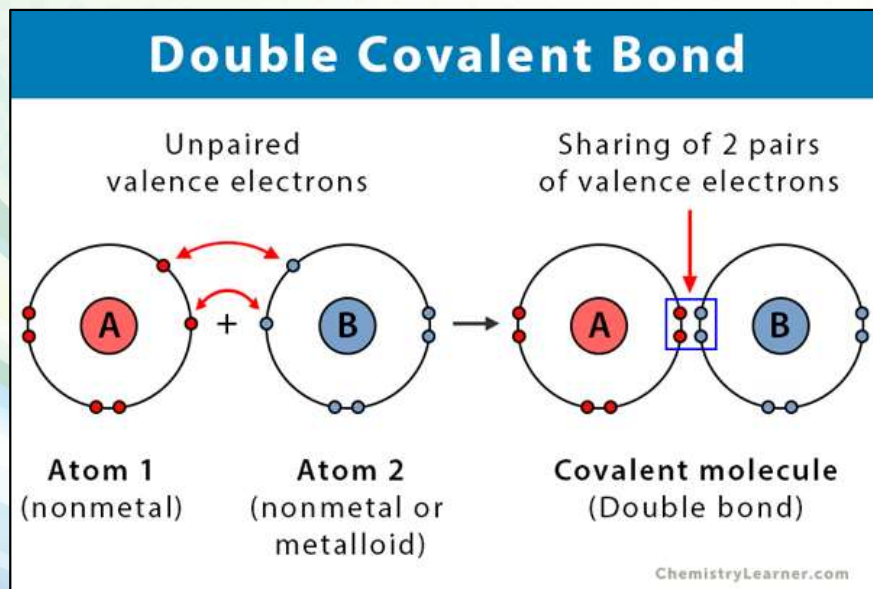


4. Ammonia

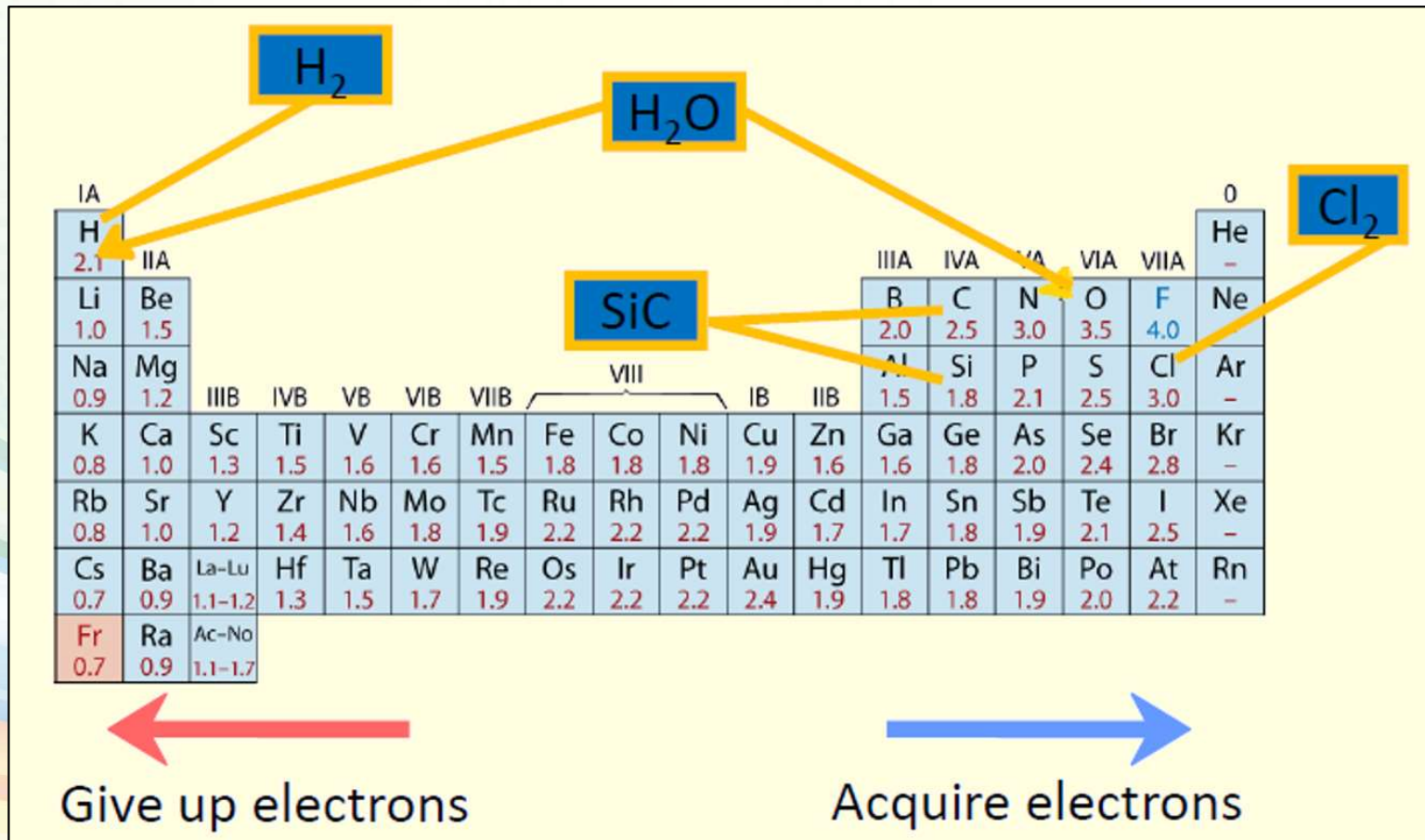


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Covalent Bonding



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

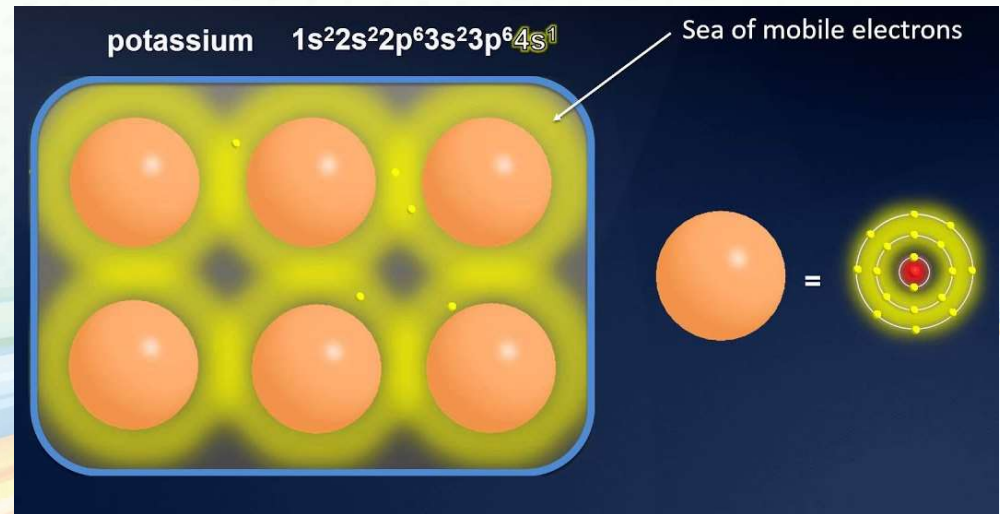
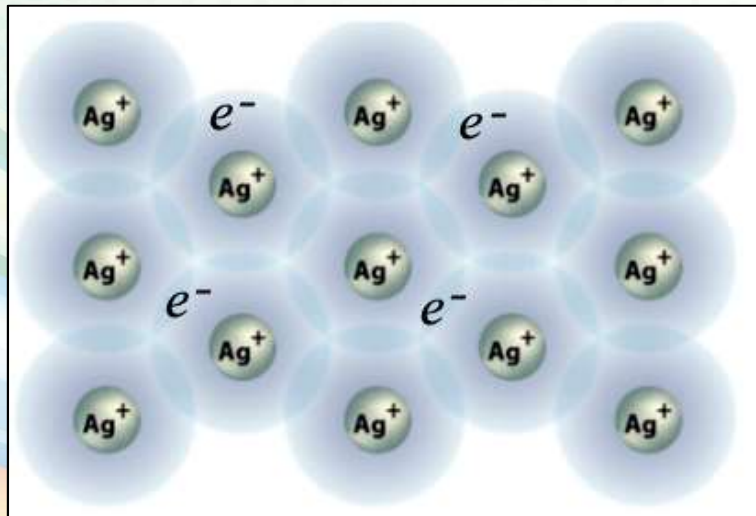
- *Covalent compounds generally have much lower melting and boiling points than ionic compounds.*
- *Covalent compounds are soft and squishy (compared to ionic compounds).*
- *Covalent compounds tend to be more flammable than ionic compounds.*
- *Covalent compounds don't conduct electricity in water.*
- *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

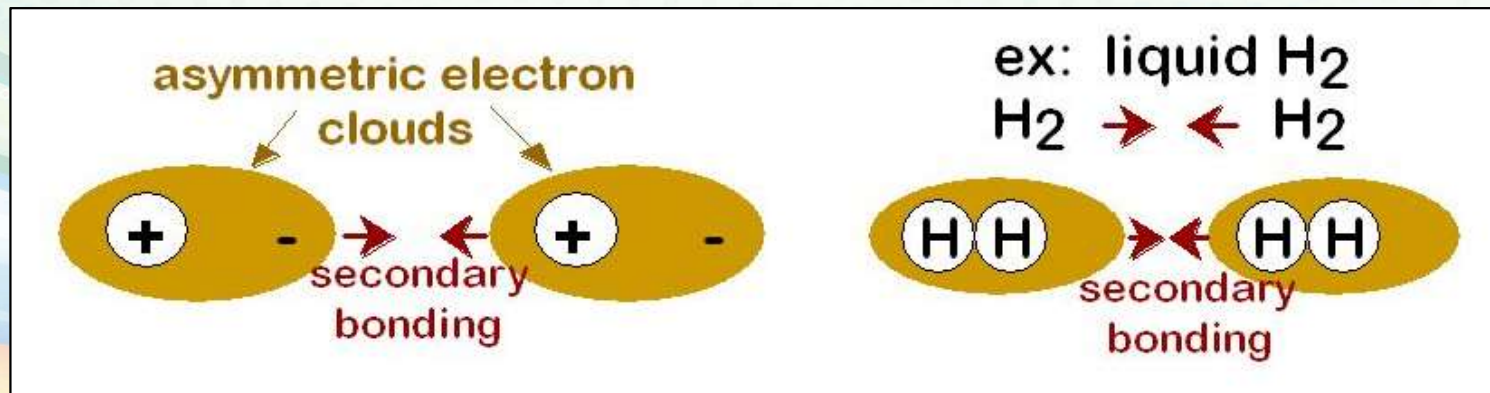
- *The strong bonding generally results in dense, strong materials with high melting and boiling points.*
- *Metals are good conductors of electricity because these 'free' electrons carry the charge of an electric current when a potential difference (voltage) is applied across a piece of metal.*
- *Metals 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*

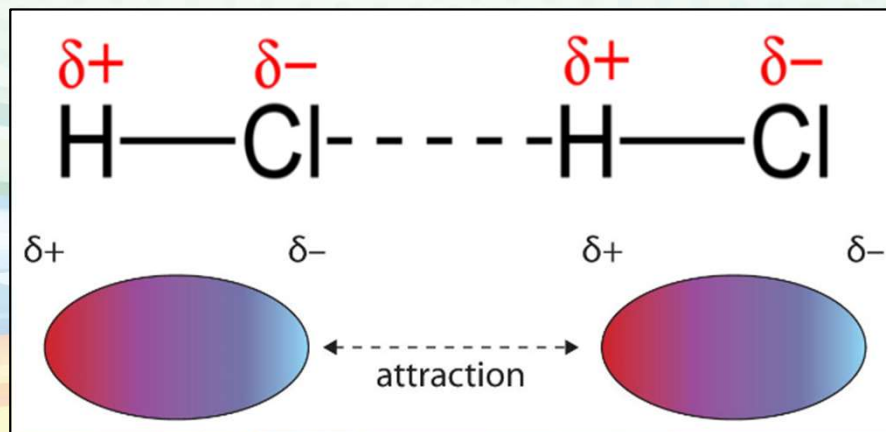
Fluctuating induced dipoles

- 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.



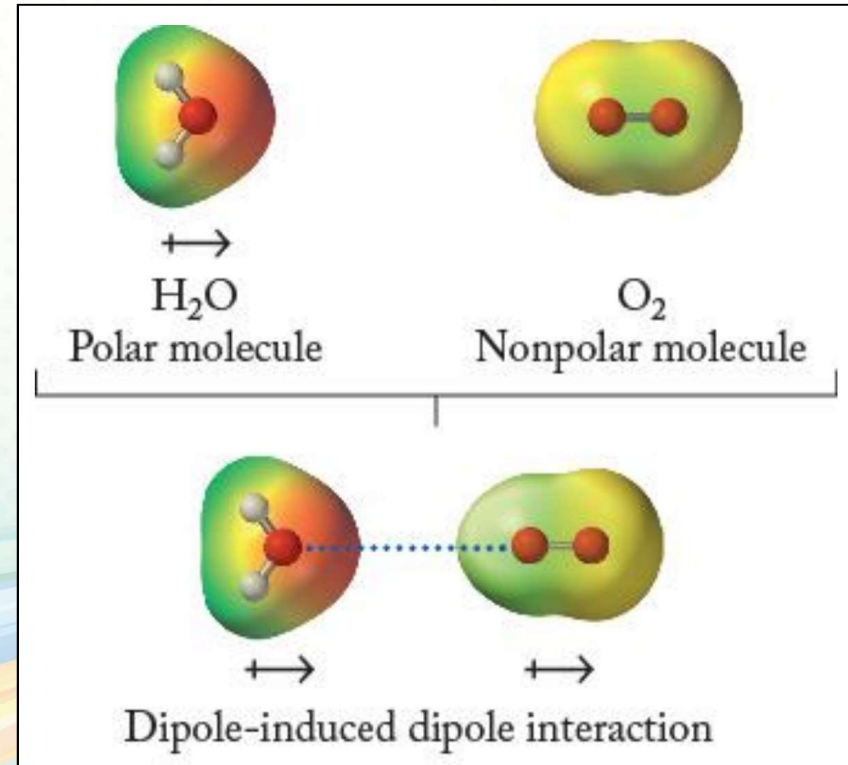
Permanent dipoles

- *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

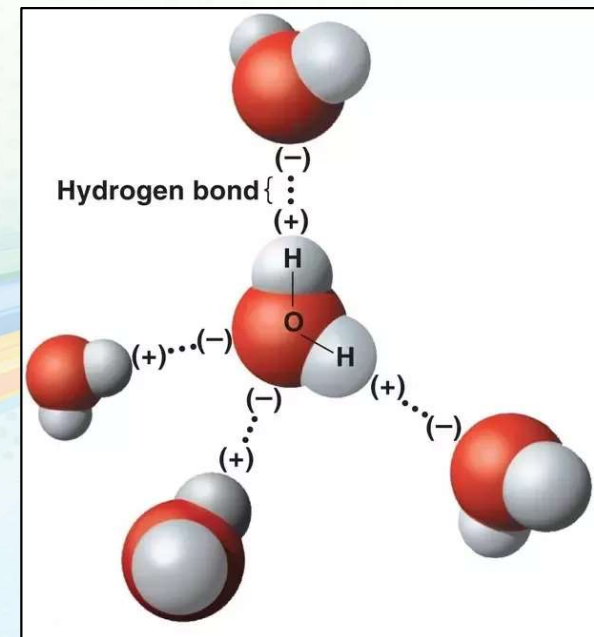


Hydrogen bonding

- 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 H_2O molecule (the O side of the H_2O dipole)



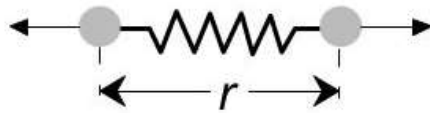
<i>Type</i>	<i>Bond Energy</i>	<i>Comments</i>
<i>Ionic</i>	<i>Large</i>	<i>Nondirectional (ceramics)</i>
<i>Covalent</i>	<i>Variable Large-Diamond Small-Bismuth</i>	<i>Directional (semiconductors, ceramics, polymer chains)</i>
<i>Metallic</i>	<i>Variable Large-Tungsten Small-Mercury</i>	<i>Nondirectional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

Bonding and materials properties

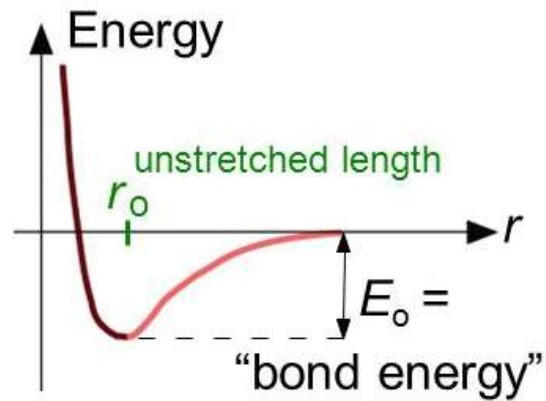
- *Materials with large bonding energies usually have high melting temperatures.*
- *There is a correlation between the magnitude of the bonding energy and the state of materials*
 - ✓ *Solids have large bonding energies*
 - ✓ *Liquids tend to have relatively lower energies*
- *The expansion/contraction 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

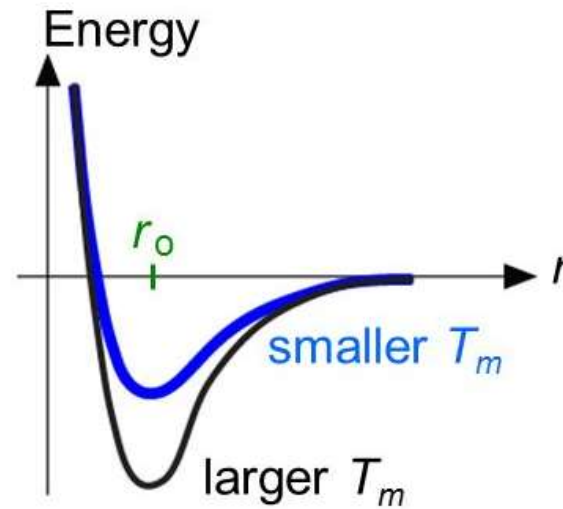
- Bond length, r



- Bond energy, E_o



- Melting Temperature, T_m



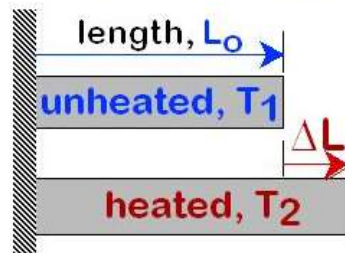
T_m is larger if E_o is larger.

Properties From Bonding: T_m

Bonding Energies and Melting Temperatures for Various Substances				
<i>Bonding Type</i>	<i>Substance</i>	<i>Bonding Energy</i>		<i>Melting Temperature (°C)</i>
		<i>kJ/mol</i>	<i>eV/Atom, Ion, Molecule</i>	
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 ₂ O	51	0.52	0

Properties From Bonding: α

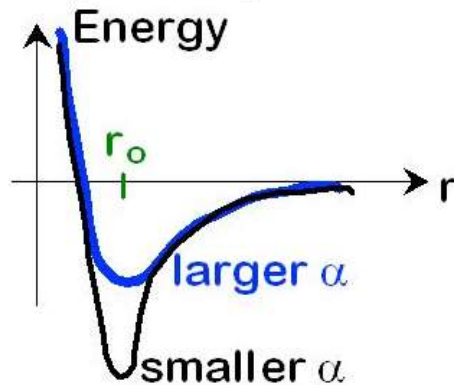
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_0} = \alpha (T_2 - T_1)$$

- $\alpha \sim$ symmetry at r_0



α is larger if E_0 is smaller.

Example

For a K^+ - Cl^- ion pair, attractive and repulsive energies E_A and E_R , 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 E_N is just the sum of the two expressions above. Determine:

- (i) The equilibrium spacing r_0 between the K^+ and Cl^- ions.*
- (ii) The magnitude of the bonding energy E_0 between the two ions.*