Unit 3: Quantum Theory, Periodicity and Chemical Bonding

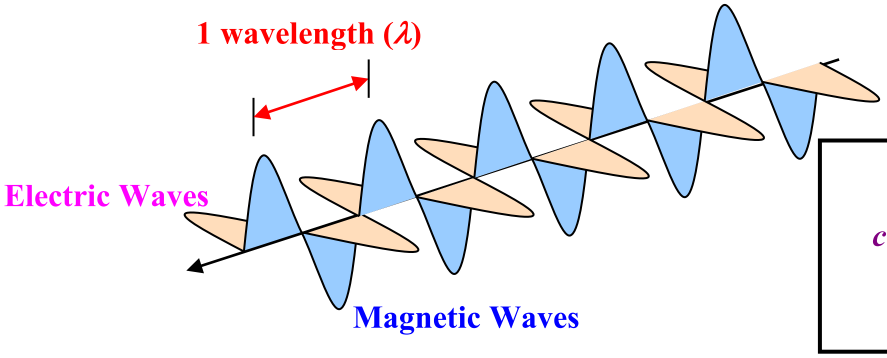
Chapter 7: The Electronic Structure of Atoms

7.1: From Classical Physics to Quantum Theory

Electromagnetic (EM) Radiation: - energy that travels at the speed of light in a form of perpendicular waves. This includes everything from cosmic rays to radio waves.

Wavelength (**λ - "*lambda*"**): - the length of a wave (from crest to crest).

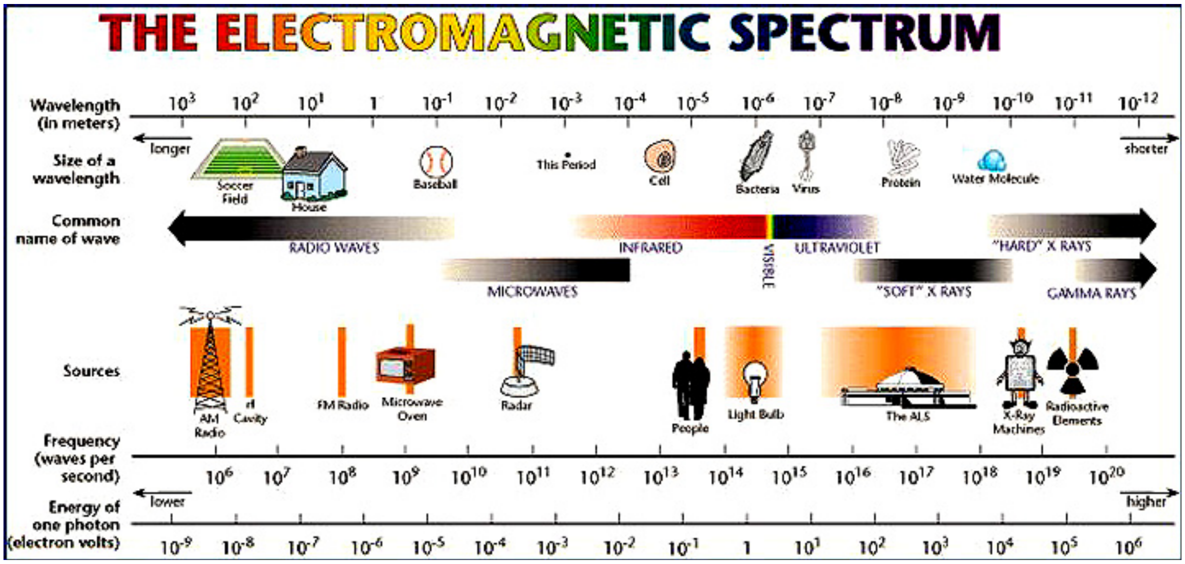
Frequency (**ν – "*nu*"**): - the number of wave in one second; measures in Hertz (Hz) or s^{-1}. (1 Hz = 1 s^{-1})



Frequency ↑ Wavelength ↓

$$c = \lambda\nu$$

c = speed of light (3.00×10^8 m/s)
λ = wavelength (m) "lambda"
ν = frequency (Hz or s^{-1}) "nu"



EM Wave	Frequency (Hz)	Wavelength (m)	EM Wave	Frequency (Hz)	Wavelength (m)
Cosmic Wave	10^{23}	10^{-15}	Infrared	10^{12}	10^{-4}
Gamma Wave	10^{20}	10^{-12}	Microwaves	10^{10}	10^{-2}
X-Ray	10^{18}	10^{-10}	FM Radio	10^{8} or (100 MHz)	1 to 10
Ultraviolet	10^{16}	10^{-8}	Shortwave Radio	10^{6} (1 MHz)	10^{2}
Visible	$(7.5 \text{ to } 4.3) \times 10^{14}$ (blue to red)	$(4 \text{ to } 7) \times 10^{-7}$ 400 nm to 700 nm (blue to red)	AM Radio	10^{4} (10 kHz)	10^{4}

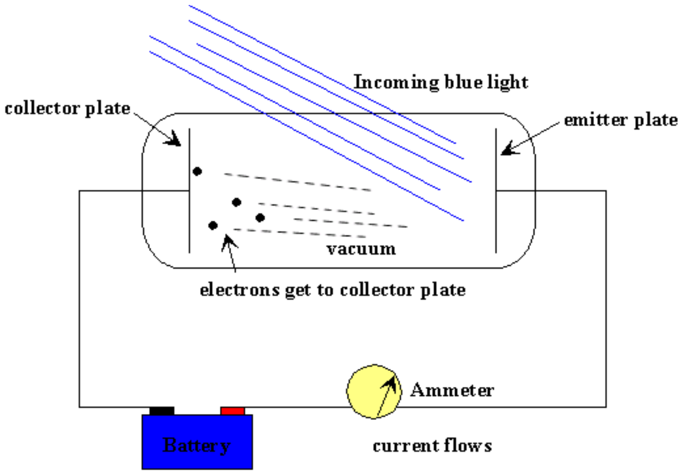
Planck's Quantum Theory

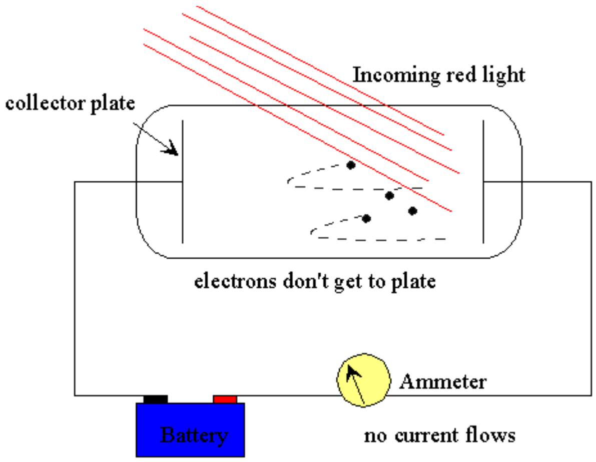
In 1900, scientists had trouble using the wave properties to account for observations that matter emits energy depend on its wavelength. Planck proposed that atoms and molecules emit or absorb energy in discrete quantities called ***quantum*.** From his equation, $E = hv$, he noticed that energy is always emitted in multiples of hv (1 hv, 2 hv, 3 hv …). This is similar to the whole number multiples of elemental charge in which, $1e^{-} = 1.602 \times 10^{-19}$ C, found by the Milliken Oil Drop Experiment.

7.2: The Photoelectric Effect

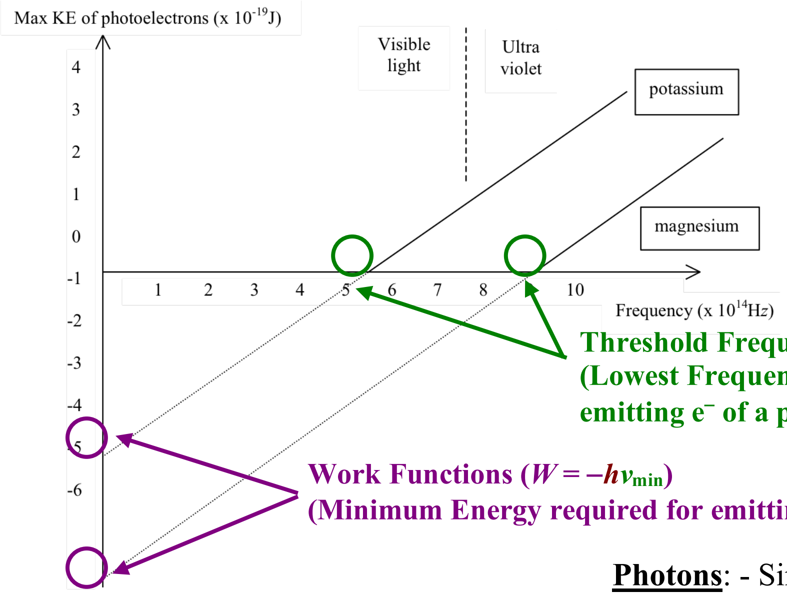
Photoelectric Effect: - Einstein's experiment with photoelectric tube found that electrons can only be emitted from a metal surface in a cathode ray tube when a threshold (minimum) frequency is directed at it. (*Intensity or Brightness of the light is not a factor*)

- the slope of amount of energy of the emitted electrons per frequency used is called the **Planck's constant (h) = 6.63×10^{-34} J s** (in honour of Max Planck who first hypothesized this relationship).





Check out the Photoelectric Effect Video at: https://www.youtube.com/watch?v=l-gwAs2ApPw



Threshold Frequencies ($v_{\min}$)
(Lowest Frequency required for emitting e⁻ of a particular metal)

Work Functions ($W = -hv_{\min}$)
(Minimum Energy required for emitting e⁻)

$$\Delta E = hv = \frac{hc}{\lambda}$$

c = speed of light (3.00×10^{8} m/s)
h = Planck's constant = 6.63×10^{-34} J s
λ = wavelength (m)
v = frequency (Hz or s^{-1})

Photons: - Since light can appear as particles, Einstein called the quantized light packet "***photons***".

Duality of Light: - the idea that light (EM-radiation) can be viewed as wave or light particles (photons).
- in some instances, we view EM-radiations as waves (reflection, refraction and diffraction).
- in other cases, we can view EM-radiations as particles (photoelectric effect, electrons transitioning in different energy levels of an atom).

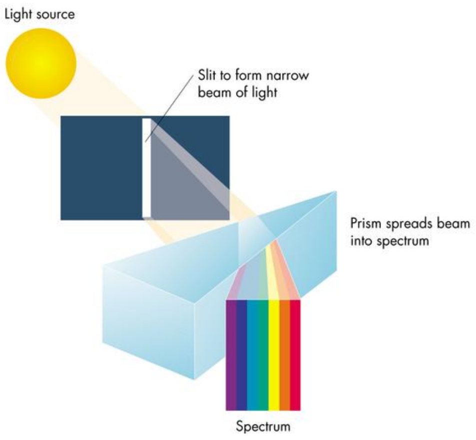
7.3: The Atomic Spectrum of Hydrogen

Quantized Energy: - because electrons can only exist at a particular orbit at one time, and never between orbits, it can only emit a certain wavelength as it comes down from an excited state to the ground state.

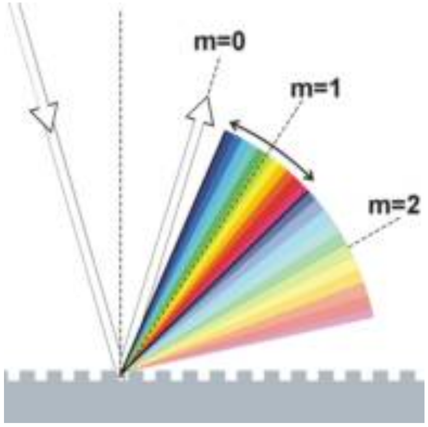
Diffraction: - as wave encountered an opening (slit), its wavelength is separated into as the wave is scattered.

Diffraction Pattern: - the pattern of bright and dark spots due to the interference of the wave front because a wave has travelled through a slit.

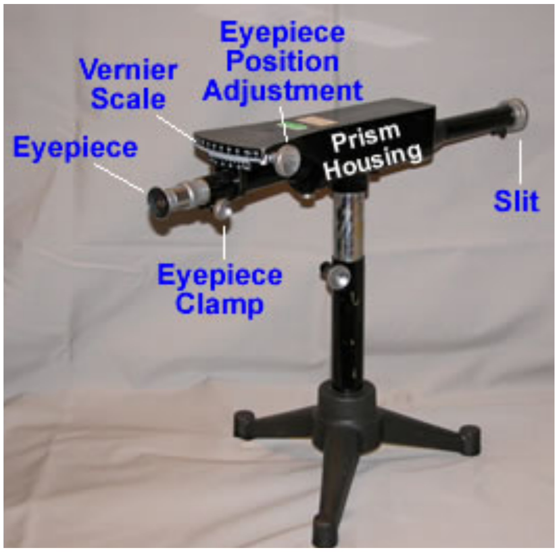
Diffraction Grating: - a surface contains a series of prisms that diffracts incoming light into their individual wavelengths.



(Left) A single prism breaks up white light into the visible spectrum. (Right) A diffraction grating is able to generate series of visible spectrum due to the uneven surface.



Spectroscope: - a device to break down light into its component colours using a diffraction grating



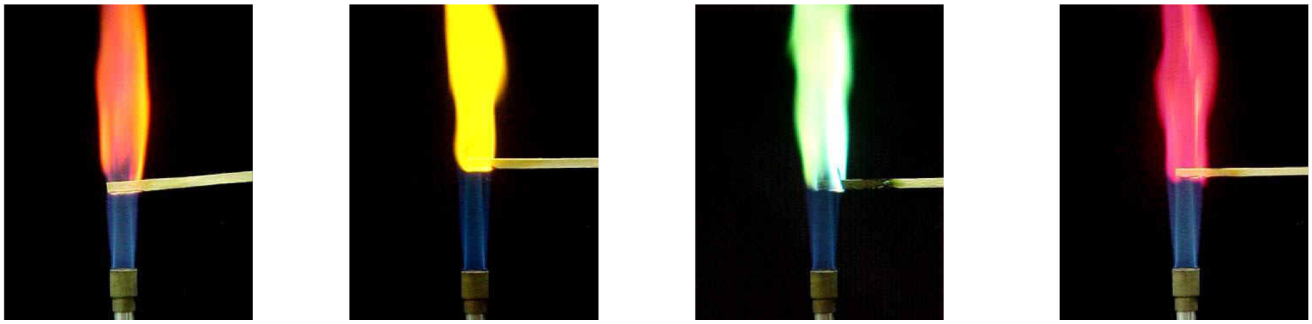
(Left) A Spectroscope. Light enters the slit and goes through the prism housing (may be replaced prism with a diffraction grating). The observer uses the eyepiece to see the image.

(Above) An image of white light diffracted through a spectroscope. Note the series of visible spectrum on either end of the central bright band.

Continuous Spectra: - as white light travelled through a prism, it is diffracted and the visible light spectrum (red to violet) is observed.

Atomic Spectrum: - when atoms of an element are given energy and become excited, they emit a distinctive glow by colours. If these colours pass through a spectroscope with diffraction grating, a series of lines will appear. These lines are unique for each element.

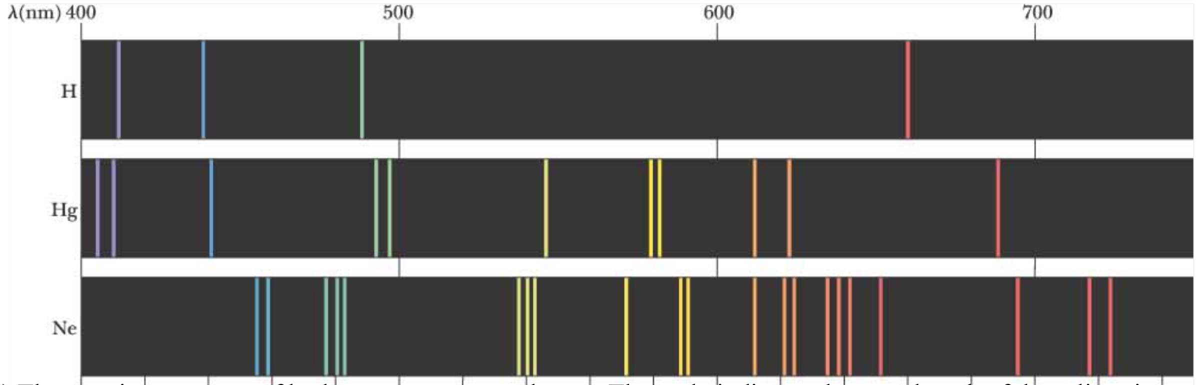
- Johann Balmer and Johannes Rydberg discovered separate series of the hydrogen atomic spectrum.



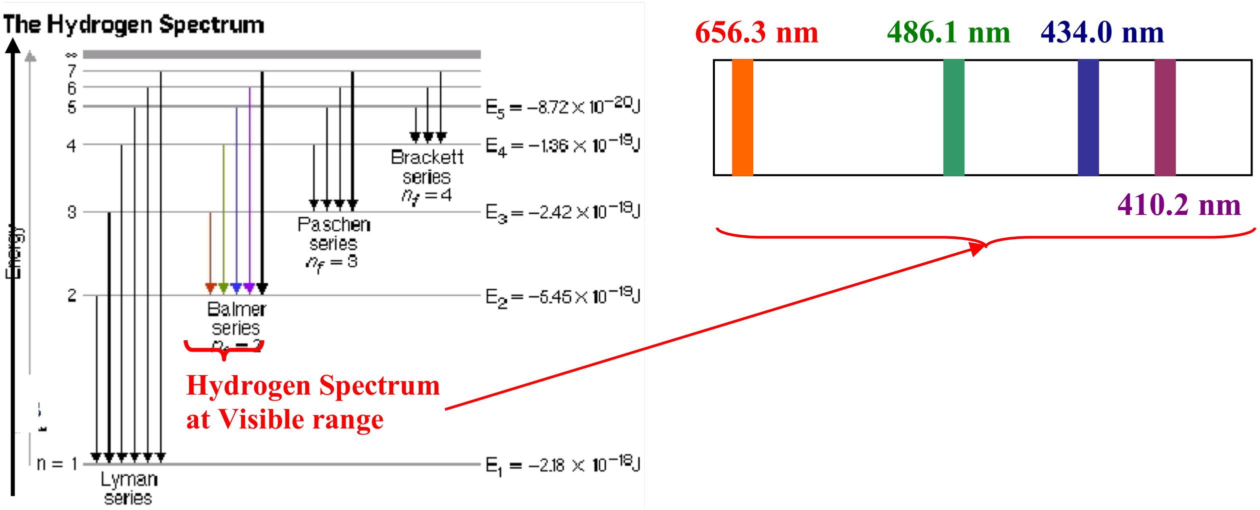
From left to right: Lithium, Sodium, Copper, and Strontium compounds produce different colours during the flame tests

Line Spectra: - when light from an excitation of a particular atom, the quantized energy is emitted as specific wavelength as it travels from higher excited orbits to the lower orbits.

Emission Spectra: - EM-frequencies that are emitted from an object that has gained energy (appears as bright lines on a dark background).

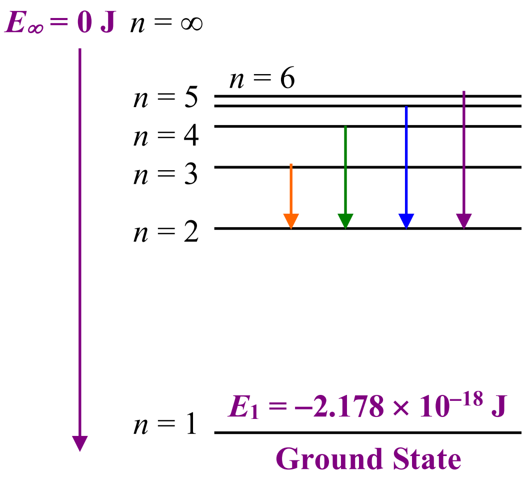


(Above) The atomic spectrums of hydrogen, mercury and neon. The scale indicates the wavelength of these lines in nanometre.



Quantum Model: - proposed by Niels Bohr, electron in hydrogen atom moves around the nucleus in specific circular orbits, which have certain energies.

- **Energy needs to be input ($\Delta E > 0$) to move up the orbits.**
- **Energy is given off as frequency ($\Delta E < 0$) to move down the orbits.**



Bohr's Hydrogen Energy Level

$$E_n = \frac{-2.178 \times 10^{-18}\text{ J}}{n^2}$$

E_n = Energy Level of a specific nth hydrogen orbit
n = the number of orbit from the nucleus
R_H = Rydberg Constant for H Atom (-2.178×10^{-18} J)

7.4: The Dual Nature of the Electron

Duality of Light: - EM-Radiation has characteristics of wave (reflection, refraction, and diffraction) and particles (momentum and kinetic energy as demonstrated by Einstein). ***Light particles are called photons***.

- Photons have no mass. But its mass equivalence can be calculated as follows.

$E = mc^2$ (Einstein's Mass Energy Conservation)

$$m = \frac{E}{c^2}$$

$$m = \frac{\left(\frac{hc}{\lambda}\right)}{c^2} = \frac{hc}{\lambda c^2} \quad \text{(Substitute } E = \frac{hc}{\lambda} \text{ and simplify)}$$

Mass Equivalence of a Photon

$$m = \frac{h}{\lambda c} \qquad (m \text{ is in kg})$$

de Broglie Wavelength:

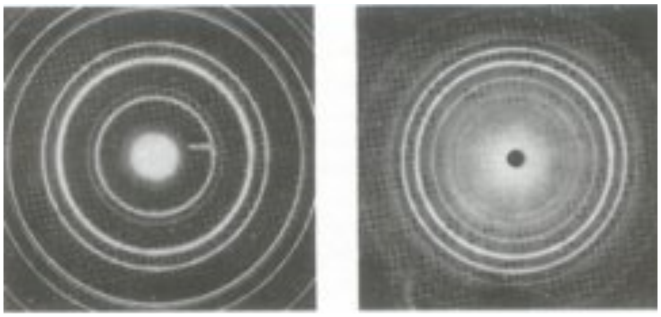
- since light can behave like particles; particles can have wave properties.
- rearranging the mass equivalence of a photon formula above and **replacing c with speed of the actual particle (nothing that has mass can travel at the speed of light – Einstein Theory of Relativity)**, we have the following,

de Broglie Wavelength

$$\lambda = \frac{h}{m\upsilon}$$

υ = speed of particle (m/s)
m = mass of particle (kg)

Further evidence for the existence of electron waves was obtained independently in 1927, by George Paget Thomson (1892-1975), son of J.J. Thomson. He passed a stream of fast moving electrons through a very thin sheet of metal and then allowed the resulting beam to fall on a photographic plate. Upon development, the plate showed a diffraction pattern consisting of a series of concentric circles, just as might have been produced by X-rays, indicating that the electrons were manifesting wave properties. (Left) Scattering of electrons by gold crystals. (Right) Scattering of X-rays by zirconium oxide crystals.



7.5: Quantum Mechanics

Heisenberg Uncertainty Principle:

It states that locating a particle in a small region of space makes the momentum of the particle (mass × velocity) uncertain; and conversely, measuring the momentum of a particle precisely makes the position uncertain. When we "observe" an electron using light (a photon), we would invariably change its position or speed (or both) due to their interactions. Hence, treating electrons as particles would create uncertainties and we could not pinpoint the speed and position of an electron in the atom. Therefore, we must employ the wave nature of particles to find their energy levels. This is why electrons are in a ***probable region of space*** where they are ***"likely" to be located***. ***In the quantum universe, we should really view electrons as waves.***

Heisenberg Uncertainty Principle $\Delta x \bullet \Delta(m\upsilon) \geq \frac{h}{4\pi}$

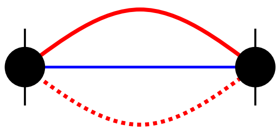
Δx = Uncertainty in particle's position **$\Delta(m\upsilon)$ = Uncertainty in particle's momentum**

As $\Delta x \downarrow$ (more certain in particle's position), $\Delta(m\upsilon) \uparrow$ (less certain in particle's momentum)

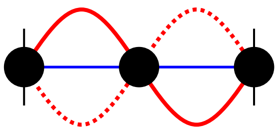
Videos and Information for Quantum Mechanics:

1. **Video on Light through Single Slit: http://www.youtube.com/watch?v=KT7xJ0tjB4A**
2. **Video on Electron through Double Slits: https://www.youtube.com/watch?v=ZqS8Jjkk1HI**
3. **History of Quantum Physics (BBC): (3 Parts)**
   - **a. https://www.youtube.com/watch?v=GOJFznzSZhM**
   - **b. https://www.youtube.com/watch?v=CYQwrAhT7HA**
   - **c. https://www.youtube.com/watch?v=KFS4oiVDeBI**
4. **Video on Properties of a Quantum Electron: http://www.youtube.com/watch?v=uq1h6jg61yI**
5. **Important People of Quantum Mechanics: http://doctortang.com/AP%20Chemistry/Historical%20Development%20of%20Quantum%20Mechanics.pdf**

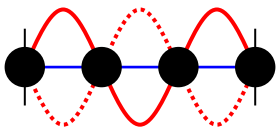
Schrödinger Wave Equation: - Schrödinger recognized that since electron can behave like waves (de Broglie), he proposed that electron could have quantized energy when it achieved a **standing wave** (wave that appears standing because it contains nodes which signifies exactly half a wavelength).



Standing Wave
(2 nodes – 1 half-λ)

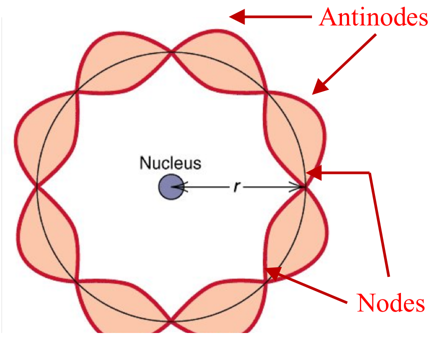


Standing Wave
(3 nodes – 2 half-λ)



Standing Wave
(4 nodes – 3 half-λ)

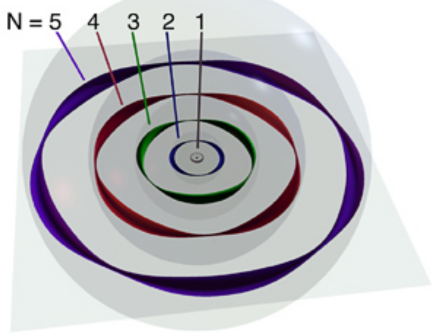
(Video at https://www.youtube.com/watch?v=wYoxOJDrZzw)



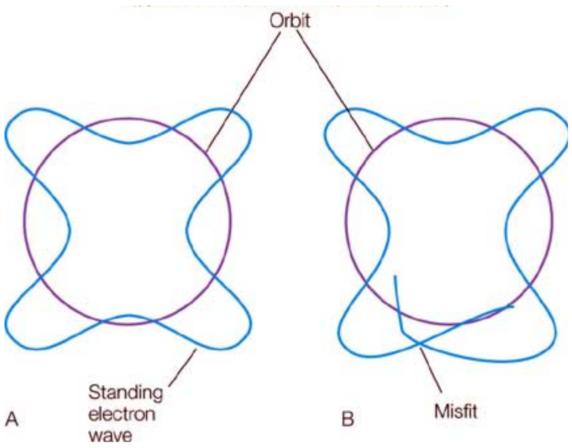
(Left) A standing electron wave with 8 nodes (or 4 λ). This would be a proper orbit for the 4th orbit or electron shell. Note that we can determine the radius by equating the circumference with natural number multiple of λ.

$$2\pi r = n\lambda$$

(where n = 1, 2, 3, 4, …)



Bohr-de Broglie electron matterwave orbits shells 1-5



(Left) (A) An allowable orbit as the standing wave forms an integral number of wavelengths (In this case, $n = 4$.). (B) A standing wave that does not have integral number of wavelengths is considered a misfit. Hence, this orbit is not allowed. (Above) Electron waves for the 5 orbits (or electron shells) of a hydrogen atom.

1-Dimensional Animations of Electron Waves in a Column
https://academo.org/demos/1D-wave-equation/
2-Dimensional Animations of Electron Waves in a Box
https://www.physicsforums.com/insights/visualizing-2-d-particle-box/

Schrödinger Wave Equation

$$\hat{H}\psi = E\psi$$

$\hat{H}$ = Hamiltonian Operator (This is not a variable, but a combination of calculation procedures like double derivatives ($\frac{-\hbar^2}{2m}$) $d^2\psi(x, y, z)/d(x, y, z)^2$ for kinetic energy and a spring potential energy function factor $U(x, y, z) = \frac{1}{2} k(x, y, z)^2$)

ψ = Wave Function **E = Total Energy (Electric Potential and Kinetic Energies)**

Note: If the wave function (ψ) remains the same after the operation by the Hamiltonian Operator ($\hat{H}$), then the coefficient of the final wave function is the total energy of the atom (E). The wave function can now be used to calculate the probability distribution of the electron around the nucleus.

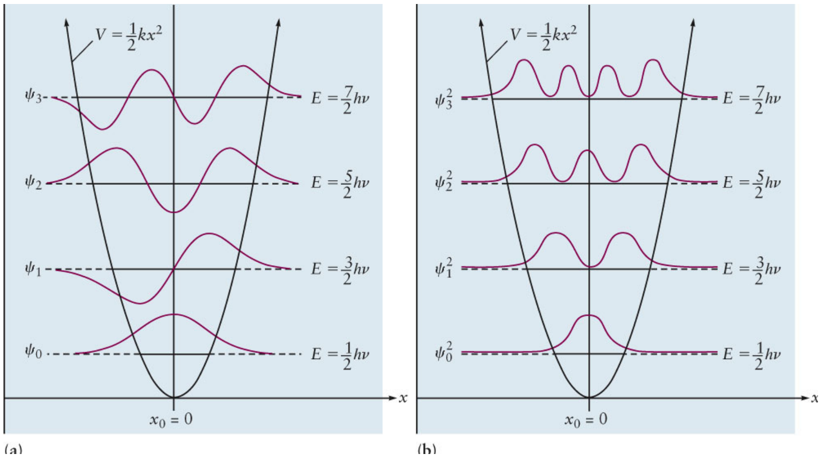
1. **Basic Schrödinger Wave Equation: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/schr.html#c1**
2. **One-Dimensional Schrödinger Wave Equation: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/scheq.html#c6**
3. **Particle in a Box: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/pbox.html#c1**
4. **Quantum Harmonic Oscillator: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/hosc.html#c1**
5. **Wikipedia Reference of Schrödinger Wave Equation: https://en.wikipedia.org/wiki/Schrödinger_equation**
6. **Schrödinger Equation (3-D) onto the H Atom: http://faculty.chas.uni.edu/~shand/Mod_Phys_Lecture_Notes/Chap10_Schrodinger_Eq_3-D_Notes_s12.pdf**

Probability Distribution (**R^2**): - the probability of the likely position of an electron around a nucleus.
- the probability distribution is equalled to the square of the wave function.

Probability Distribution

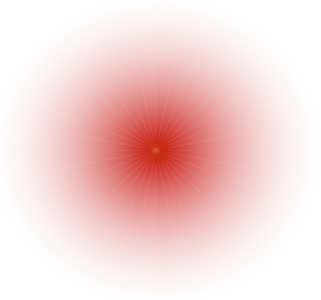
$$R^2 = [\psi(x, y, z)]^2$$

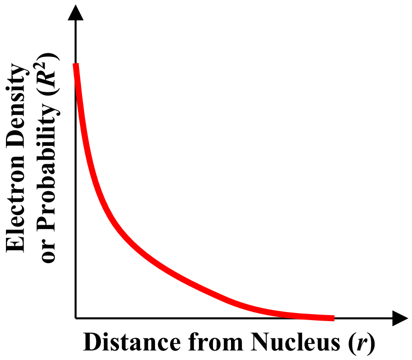
$\psi(x, y, z)$ = Wave Function in x, y, and z directions



(Right) (a) One Dimensional Schrödinger Wave Equations with their associated allowed energies. (b) Corresponding Probability Densities, $\psi_n{}^2(x)$.

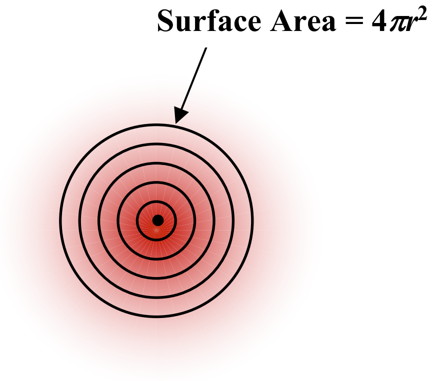
Electron Density (Probability) Map: - a diagram that shows the probability distribution of an electron around the nucleus; also called **atomic orbital**.

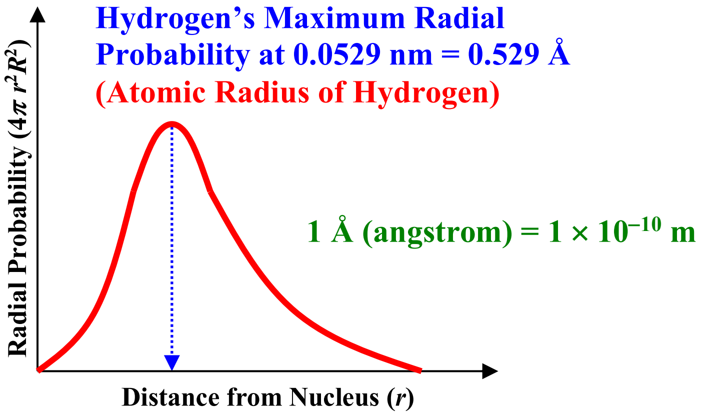




Radial Probability Distribution: - when total probability (Surface Area of a Sphere × Probability) is plotted against distance from the nucleus.

- at small radius, probability is big but surface area is small (yields low total probability).
- at large radius, probability is small but surface area is big (yields low total probability)
- at optimal radius, surface area × probability is large (maximum total probability = Atomic Radius).





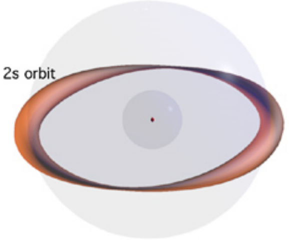
7.6 & 7.7: Quantum Numbers & Atomic Orbitals

Quantum Numbers: - a series of number that ***describe the distribution of electrons in hydrogen and other atoms***. They are derived from the *mathematical solutions of the Schrödinger Wave Equation* for the hydrogen atom. There are ***four sets of quantum numbers used to describe any single electron***.

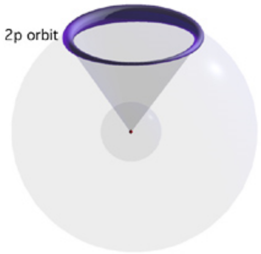
a. **Principal Quantum Number** (***n***): - natural number values {1, 2, 3, …} are used to describe the energy and size of the orbital.

b. **Angular Momentum Quantum Number** (ℓ): - whole numbers $\{0 \leq \ell \leq (n - 1)\}$ are used to indicate the shape of the atomic orbitals.

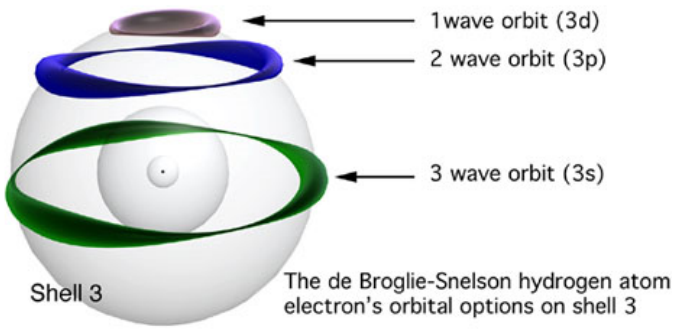
$\ell = 0$ (*s* orbital) **"sharp"**	**$\ell = 1$ (*p* orbital)** **"principal"**	**$\ell = 2$ (*d* orbital)** **"diffuse"**	**$\ell = 3$ (*f* orbital)** **"fundamental"**	**$\ell = 4$ (*g* orbital)** **(follows the alphabet after *f*)**



De Broglie 2nd energy level's original 2-wave orbit.

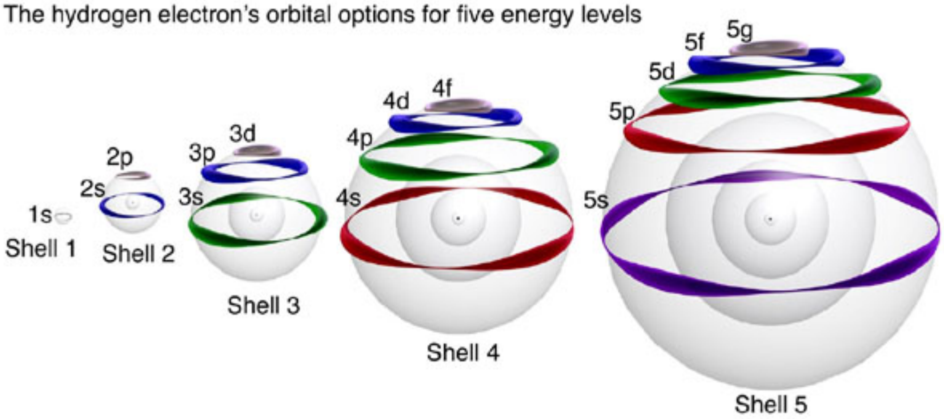


Snelson model's 2nd energy level 1-wave orbit with cone indicating its direction in space in relation to the nucleus.



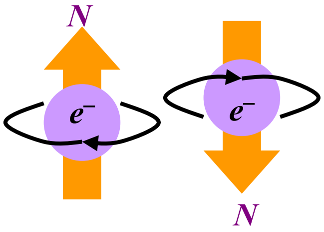
The de Broglie-Snelson hydrogen atom electron's orbital options on shell 3

The hydrogen electron's orbital options for five energy levels



c. **Magnetic Quantum Number** (***m***$_\ell$): - integral numbers $\{-\ell \leq m_\ell \leq \ell\}$ are used to show the orientation of the orbital in space relative to the other orbitals in the atom.
- each m_ℓ value represents an atomic orbital.

Electron Spin: - when electron spins clockwise, it creates a magnetic north pole in the upward direction. Conversely, when electron spins counter-clockwise, it creates a magnetic north pole in the downward direction.



d. **Electron Spin Quantum Number** (***m***$_s$): - values of ±½ to denote the electron spin direction.

Check out these websites at:

1. **Schrödinger Equation in Three Dimensions: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/sch3d.html#c1**
2. **Quantum Numbers of Hydrogen Atom: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/hydsch.html#c1**

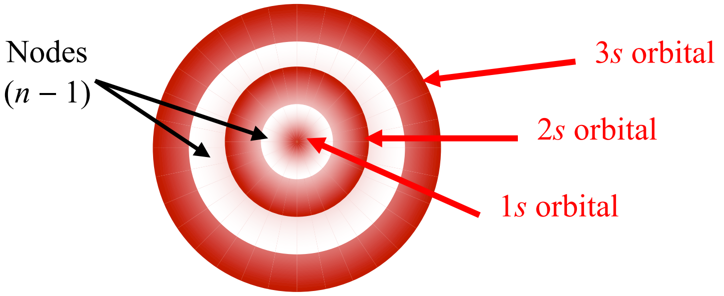
Subshells: - are electron designations as indicated by the first two quantum numbers (Principal Quantum Number (n) and the letter used for Angular Momentum Quantum Number (ℓ)).

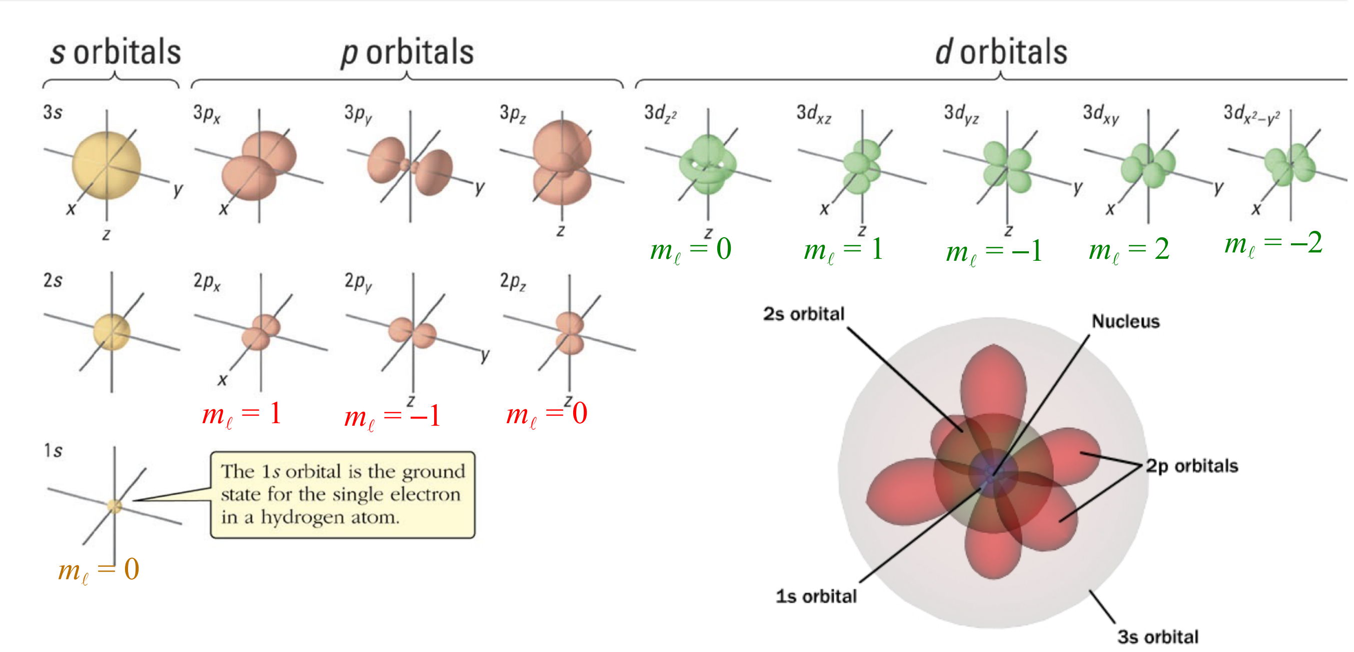
Atomic Orbitals: - are electron designations as indicated by the first three quantum numbers (Principal Quantum Number (n), the letter used for Angular Momentum Quantum Number (ℓ), and the Magnetic Quantum Number (m_ℓ)).

n	ℓ	Subshell	m_ℓ (Orientation of Orbitals)	Number of Orbitals in each Subshell	Total Number of Orbitals in each Energy Level
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1 (p_y, p_z, p_x)	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1 (p_y, p_z, p_x)	3	
	2	3*d*	−2, −1, 0, 1, 2 ($d_{x^2-y^2}$, d_{yz}, d_{z^2}, d_{xz}, d_{xy})	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1 (p_y, p_z, p_x)	3	
	2	4*d*	−2, −1, 0, 1, 2 ($d_{x^2-y^2}$, d_{yz}, d_{z^2}, d_{xz}, d_{xy})	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3 ($f_{z(x^2-y^2)}$, $f_{y(z^2-x^2)}$, f_{y^3}, f_{z^3}, f_{x^3}, $f_{x(z^2-y^2)}$, f_{xyz})	7	
5	0	5*s*	0	1	25
	1	5*p*	−1, 0, 1 (p_y, p_z, p_x)	3	
	2	5*d*	−2, −1, 0, 1, 2 ($d_{x^2-y^2}$, d_{yz}, d_{z^2}, d_{xz}, d_{xy})	5	
	3	5*f*	−3, −2, −1, 0, 1, 2, 3 ($f_{z(x^2-y^2)}$, $f_{y(z^2-x^2)}$, f_{y^3}, f_{z^3}, f_{x^3}, $f_{x(z^2-y^2)}$, f_{xyz})	7	
	4	5*g*	−4,−3, −2, −1, 0, 1, 2, 3, 4 ($g_{xy(x^2-y^2)}$, g_{zy^3}, $g_{z^2(x^2-y^2)}$ g_{z^3y}, g_{z^4}, g_{z^3x}, g_{z^2xy}, g_{zx^3}, $g_{(x^4+y^4)}$)	9	

Orbital Shapes: - from the Schrödinger wave functions, the graph the radial probability distributions in 3 dimensions forms the orbital shapes.

Nodal Surfaces (Nodes): - the areas between orbitals where there is zero probability of electron distribution.



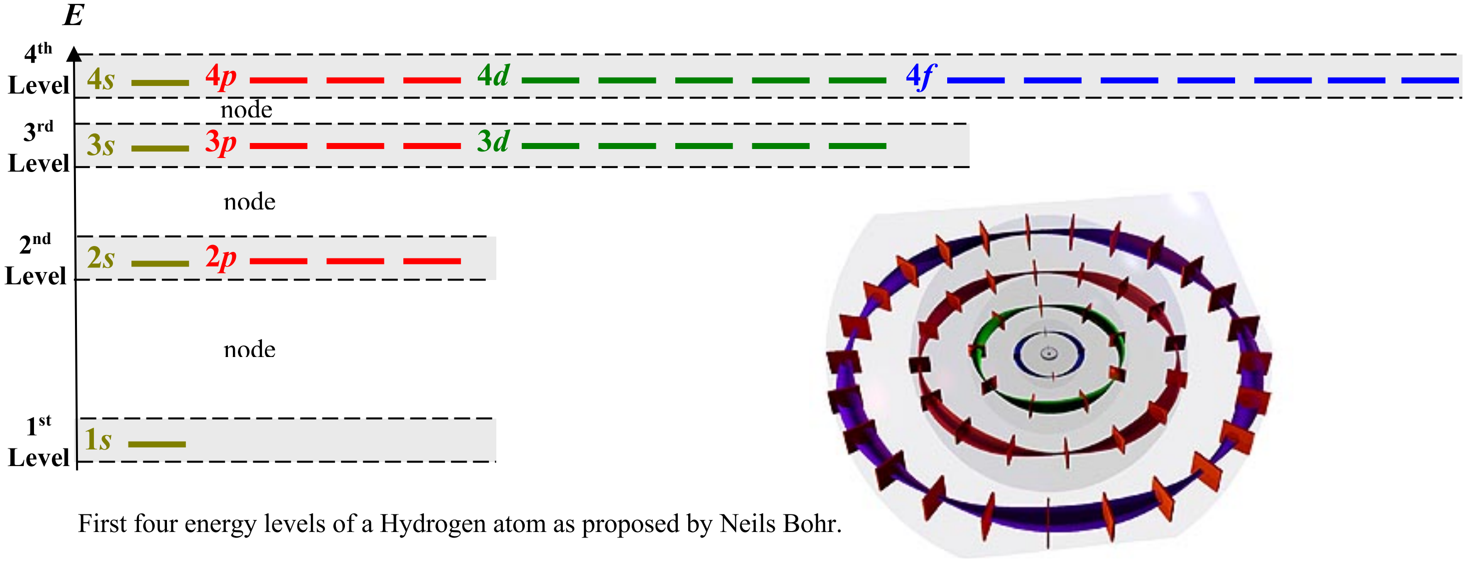


Hydrogen Atom Orbital Viewer at http://www.falstad.com/qmatom/
Pictures of *f* and *g* orbitals are at http://winter.group.shef.ac.uk/orbitron/AOs/4f/index.html

Energies of Orbitals:

Orbitals Energy Profile of Hydrogen Atom: - Neil Bohr first proposed that in the case of hydrogen atom where it consists of one electron, all orbitals of the same *n* value share the same energy level. Hence, the distance between orbitals in the same energy level is 0. We can also view the hydrogen atom as having concentric sphere as shells.

$$\boxed{E_{ns} = E_{np} = E_{nd} = E_{nf}}$$



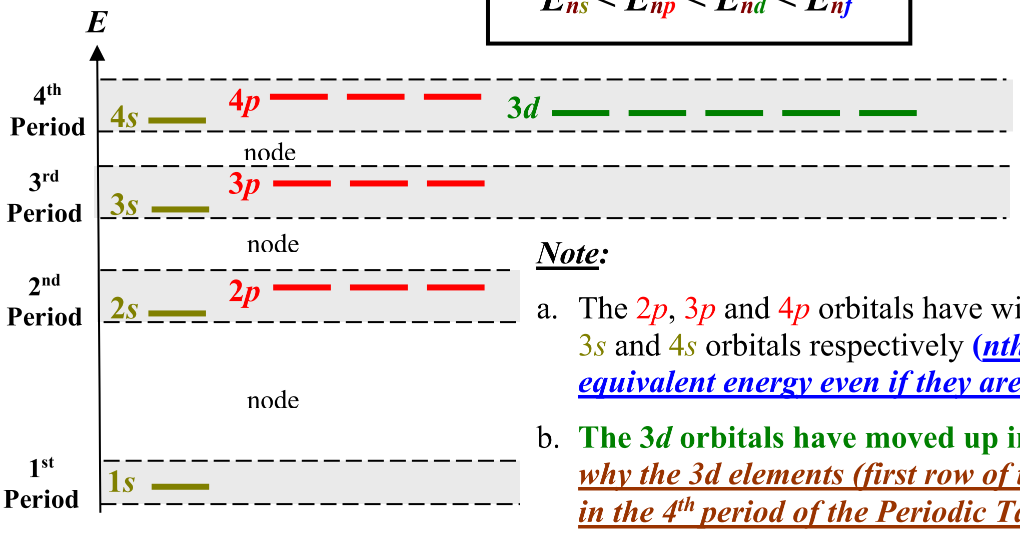
First four energy levels of a Hydrogen atom as proposed by Neils Bohr.

7.8 & 7.9: Electron Configuration & The Building-Up Principle

Polyelectronic Atoms: - atoms with more than one electron (all non-hydrogen atoms).

Electron Correction Problem:
Due to the mathematical difficulty in calculating the ***repulsion of electrons in polyelectronic atoms*** (since Heisenberg Uncertainty Principle rules out predicting the exact location and momentum of an electron), an assumption needs to be made that the valence electrons are "*screened*" or "*shielded*" from the **nuclear charge** which **composes of the inner electrons and the protons in the nucleus**. The result is the ***splitting or degenerations*** of these atomic orbitals (see notes below).

$$\boxed{E_{ns} < E_{np} < E_{nd} < E_{nf}}$$



Note:

a. The 2*p*, 3*p* and 4*p* orbitals have with up slightly from the 2*s*, 3*s* and 4*s* orbitals respectively **(*nth Orbitals no longer have equivalent energy even if they are in the same energy levels*)**.

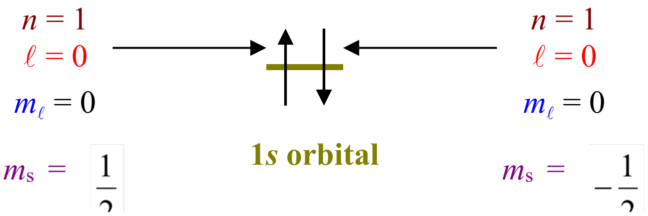
b. **The 3*d* orbitals have moved up into the 4th period.** ***That is why the 3d elements (first row of the transition metals) are in the 4th period of the Periodic Table***.

1. **Electron Configurations Applet: http://intro.chem.okstate.edu/WorkshopFolder/ElectronConfnew.html**
2. **Periodic Table with Emission Spectrums: https://www.edumedia-sciences.com/en/media/661-emission-and-absorption-spectra**

Pauli Exclusion Principle: - in a given atom, no two electrons can have exactly the same set of four quantum numbers (n, ℓ, m_ℓ, and m_s).

- an orbital can only hold two electrons with opposing spins.

Example 1: In the 1*s* orbital, the four quantum numbers for the two electrons are:



Aufbau (Building-Up) Principle: - "*Aufbau*" German for "building up"
- for each element, electrons are added up into the quantum orbitals (after taken account with the electron correction problem and the penetration effect) as protons are being added to the nucleus.

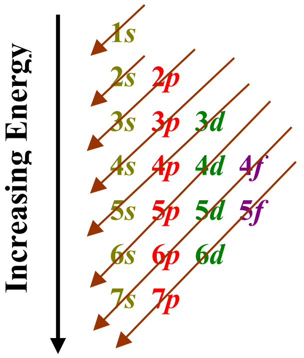
Orbital Diagram: - a diagram that shows the arrangements of electrons in quantum subshells (orbitals) in order of increasing potential energy.

Hund's Rule: - for subshells that can have more than 1 orbital (as in *p*, *d*, *f* …), the lowest energy can be achieved when the electrons are arranged so that there are a maximum number of unpaired electrons. These unpaired electrons are drawn "spinning up" (↑) in the orbital diagram.

Electron Configuration: - the arrangement of electrons in atomic subshells.

Rules in Assigning Electrons to Atomic Orbitals:

1. **Each shell or principle quantum number, *n*, contains *n* type of subshells.**
   (Example: There are 3 type of subshells (*s*, *p*, *d*) for $n = 3$ because there are three values of $\ell = 0, 1, 2$.)
2. **For each subshell of angular momentum quantum number, ℓ, there are $(2\ell + 1)$ orbitals.**
   (Example: There are 5 *d*-orbitals for $\ell = 2$.)
3. **There can be a maximum of only 2 electrons placed in each orbitals (Hund's Rule).** Hence, the maximum number of electrons is twice the number of orbitals that are used.
4. **The maximum number of electrons for each principle level, *n*, is $2n^2$.**
   (Example: For $n = 4$, there can be a maximum of $2(4)^2 = 32$ electrons.)



Order of appearance for Subshell ←

Example 2: Draw the quantum orbital diagrams and state the electron configurations for the following atoms.

Atomic #	Atom	Electron Configuration	Orbital Diagram 1*s* 2*s* 2*p*
1	H	$1s^1$	↑ __ __ __ __
2	He	$1s^2$	↑↓ __ __ __ __
3	Li	$1s^2\ 2s^1$	↑↓ ↑ __ __ __
4	Be	$1s^2\ 2s^2$	↑↓ ↑↓ __ __ __
5	B	$1s^2\ 2s^2\ 2p^1$	↑↓ ↑↓ ↑ __ __
6	C	$1s^2\ 2s^2\ 2p^2$	↑↓ ↑↓ ↑ ↑ __
7	N	$1s^2\ 2s^2\ 2p^3$	↑↓ ↑↓ ↑ ↑ ↑
8	O	$1s^2\ 2s^2\ 2p^4$	↑↓ ↑↓ ↑↓ ↑ ↑
9	F	$1s^2\ 2s^2\ 2p^5$	↑↓ ↑↓ ↑↓ ↑↓ ↑
10	Ne	$1s^2\ 2s^2\ 2p^6$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓

Core Electrons: - inner electrons that have completed a row in the Periodic Table of Elements.
- instead of writing the full electron configuration from the very beginning, we can ***abbreviate*** this process by stating the previous noble, then writing out the rest of the element's electron configuration.

Valance Electrons: - electrons in the outermost principal quantum number of an atom.
- elements in the same group or family contain the same valence electron configuration.

Example 3: Draw the quantum orbital diagrams and state the electron configurations for the following atoms.

Atomic #	Atom	Electron Configuration	Orbital Diagram									
				4*s*			3*d*				4*p*	
19	K	[Ar] $4s^1$	[Ar]	↑								
20	Ca	[Ar] $4s^2$	[Ar]	↑↓								
21	Sc	[Ar] $4s^2\ 3d^1$	[Ar]	↑↓	↑							
22	Ti	[Ar] $4s^2\ 3d^2$	[Ar]	↑↓	↑	↑						
23	V	[Ar] $4s^2\ 3d^3$	[Ar]	↑↓	↑	↑	↑					
24	***Cr**	[Ar] $4s^1\ 3d^5$	[Ar]	↑	↑	↑	↑	↑	↑			
25	Mn	[Ar] $4s^2\ 3d^5$	[Ar]	↑↓	↑	↑	↑	↑	↑			
26	Fe	[Ar] $4s^2\ 3d^6$	[Ar]	↑↓	↑↓	↑	↑	↑	↑			
27	Co	[Ar] $4s^2\ 3d^7$	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑			
28	Ni	[Ar] $4s^2\ 3d^8$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑	↑			
29	***Cu**	[Ar] $4s^1\ 3d^{10}$	[Ar]	↑	↑↓	↑↓	↑↓	↑↓	↑↓			
30	Zn	[Ar] $4s^2\ 3d^{10}$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			
31	Ga	[Ar] $4s^2\ 3d^{10}\ 4p^1$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		
32	Ge	[Ar] $4s^2\ 3d^{10}\ 4p^2$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	
33	As	[Ar] $4s^2\ 3d^{10}\ 4p^3$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
34	Se	[Ar] $4s^2\ 3d^{10}\ 4p^4$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑
35	Br	[Ar] $4s^2\ 3d^{10}\ 4p^5$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑
36	Kr	[Ar] $4s^2\ 3d^{10}\ 4p^6$	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

***From Hund's Rule, Cr and Cu can achieve lowest energy if the $4s^2$ e^- was moved to the $3d^5$ or $3d^{10}$.**

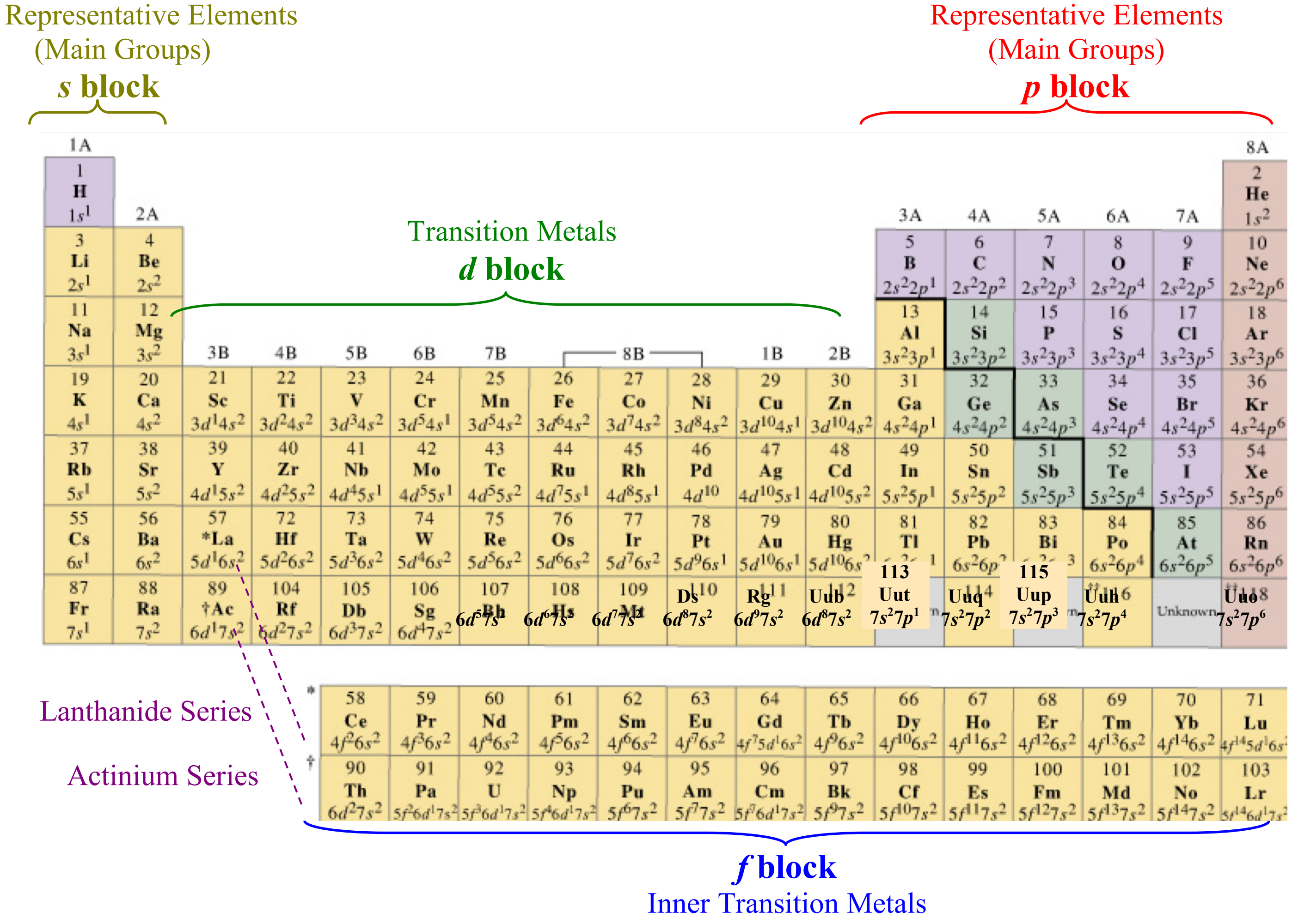
Some Exceptions in Electron Configurations:

4th Period:
Chromium ($_{24}$Cr): [Ar] $4s^1\ 3d^5$
Copper ($_{29}$Cu): [Ar] $4s^1\ 3d^{10}$

There are many more exceptions in the higher periods because the s, f and d orbitals are closer together when n increases.

5th Period:
Niobium ($_{41}$Nb): [Kr] $5s^1\ 4d^4$
Molybdenum ($_{42}$Mo): [Kr] $5s^1\ 4d^5$
Ruthenium ($_{44}$Ru): [Kr] $5s^1\ 4d^7$
Rhodium ($_{45}$Rh): [Kr] $5s^1\ 4d^8$
Palladium ($_{46}$Pd): [Kr] $4d^{10}$
Silver ($_{47}$Ag): [Kr] $5s^1\ 4d^{10}$

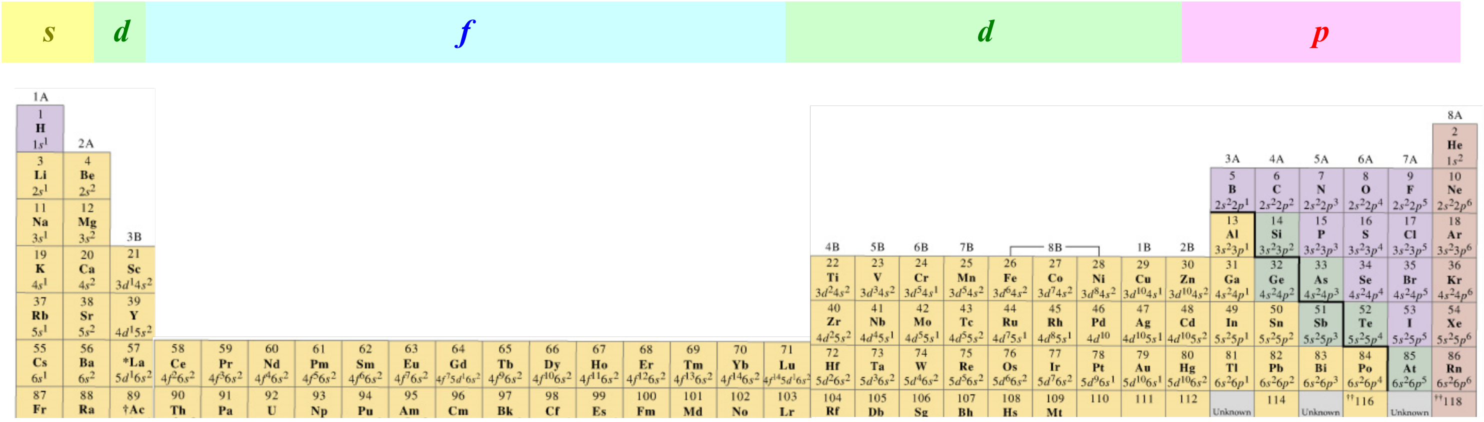
Electron Configurations in the Periodic Table of Elements



1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 H $1s^1$																	2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$	27 Co $3d^74s^2$	28 Ni $3d^84s^2$	29 Cu $3d^{10}4s^1$	30 Zn $3d^{10}4s^2$	31 Ga $4s^24p^1$	32 Ge $4s^24p^2$	33 As $4s^24p^3$	34 Se $4s^24p^4$	35 Br $4s^24p^5$	36 Kr $4s^24p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$	45 Rh $4d^85s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10}5s^1$	48 Cd $4d^{10}5s^2$	49 In $5s^25p^1$	50 Sn $5s^25p^2$	51 Sb $5s^25p^3$	52 Te $5s^25p^4$	53 I $5s^25p^5$	54 Xe $5s^25p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57 *La $5d^16s^2$	72 Hf $5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$	77 Ir $5d^76s^2$	78 Pt $5d^96s^1$	79 Au $5d^{10}6s^1$	80 Hg $5d^{10}6s^2$	81 Tl $6s^26p^1$	82 Pb $6s^26p^2$	83 Bi $6s^26p^3$	84 Po $6s^26p^4$	85 At $6s^26p^5$	86 Rn $6s^26p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89 †Ac $6d^17s^2$	104 Rf $6d^27s^2$	105 Db $6d^37s^2$	106 Sg $6d^47s^2$	107 Bh $6d^57s^2$	108 Hs $6d^67s^2$	109 Mt $6d^77s^2$	110 Ds $6d^87s^2$	111 Rg $6d^97s^2$	112 Uub $6d^87s^2$	113 Uut $7s^27p^1$	114 Uuq $7s^27p^2$	115 Uup $7s^27p^3$	116 Uuh $7s^27p^4$	Unknown	118 Uuo $7s^27p^6$

*	58 Ce $4f^26s^2$	59 Pr $4f^36s^2$	60 Nd $4f^46s^2$	61 Pm $4f^56s^2$	62 Sm $4f^66s^2$	63 Eu $4f^76s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^96s^2$	66 Dy $4f^{10}6s^2$	67 Ho $4f^{11}6s^2$	68 Er $4f^{12}6s^2$	69 Tm $4f^{13}6s^2$	70 Yb $4f^{14}6s^2$	71 Lu $4f^{14}5d^16s^2$
†	90 Th $6d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^67s^2$	95 Am $5f^77s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^97s^2$	98 Cf $5f^{10}7s^2$	99 Es $5f^{11}7s^2$	100 Fm $5f^{12}7s^2$	101 Md $5f^{13}7s^2$	102 No $5f^{14}7s^2$	103 Lr $5f^{14}6d^17s^2$

Extended Periodic Table of Elements



Assignment

7.6 & 7.7 pg. 240 to 241 #48, 57, 58, 61 to 64, 66 to 68, 70

7.8 & 7.9 pg. 241 #71, 72, 76, 77, 80, 82 to 84, 86 to 89, 91, 92

Chapter 8: The Periodic Table

8.1: Development of the Periodic Table

Johann Dobereiner: - first to discover a pattern of a group of elements like Cl, Br, and I (called triads).

John Newland: - suggested elements should be arranged in "octaves" because they repeat their properties for every eighth elements.

Demitri Mendeleev: - conceived the first modern periodic table of elements (independently worked on by Julius Lothar Meyer).
- insisted certain spots of the table be left blank until the actual element is found that matched the predicted properties. This was done to preserve the elements with similar properties called groups or families.

8.2: Periodic Classification of the Elements

Representative Elements: - also called ***Main Group Elements***.
- elements in Group IA to VIIIA (Groups 1, 2 and 13 to 18) that consists of partial or filled *s* and *p* orbitals of the same principal quantum number, *n*.
- other than helium, $1s^2$, all noble gases have ns^2np^6 as their electron configurations.

Transition Metals: - elements in Group 1B and 3B through 8B (Groups 3 to 11).
- all transition metals consists of *d* orbital electrons in their outer electron configurations. The group designation acknowledges the number of outer electrons. For examples, Mn has 7 valence electrons ($4s^23d^5$) and it is in Group 7B.
- Group 2B (Zn, Cd and Hg) are neither transition metals nor representative elements due to the fact they have filled $ns^2\ (n-1)d^{10}$ as their electron configurations.

Lanthanides and Actinides: - are elements with incompletely filled *f* subshells.
- are sometimes called **Inner Transition Elements**.

Valence Electrons: - the outer electrons of an atom that are involved in chemical bonding.
- for representative elements, it takes 8 valence electrons (ns^2np^6) to achieve stability.
- in most cases, this means having the same electron arrangement of the **nearest** noble gas, except helium (only 2 electrons to fill the first energy level), and the transition metals.

Ground State Electron Configuration: - the electron configuration of an atom at its lowest energy state.

Excited State Electron Configuration: - the electron configuration of an atom at a higher energy state.

Example 1: Identify the atom of the following electron configurations and indicate whether it is at ground state or excited state.

a. $[\text{Ar}]\ 4s^2\ 3d^2$

There are 4 valence electrons after the 3rd row of the Table of Elements (Ar). This mean the atom is at the 4th element in row 4. Hence, it is **Ti**. It is at its **ground state** because it did not indicate any electrons have gone into the 4*p* or higher orbitals than 4*s* and 3*d*.

b. $[\text{Ar}]\ 4s^2\ 3d^7\ 4p^3$

There are 12 valence electrons (2 + 7 + 3) after the 3rd row of the Table of Elements (Ar). This mean the atom is at the 12th element in row 4. Hence, it is **Zn**. It is at its **excited state** since there are three electrons in the 4*p* when the 3*d* subshell is not filled.

Electron Configurations of Ions from the Representative Elements:

- **Group 1A and 2A metals, which like to lose electrons to form cations**, they have the same electron configurations as the **noble gas of the previous row**.
- for representative elements **non-metals, which like to gain electrons to form anions**, they have the same electron configurations as the **noble gas at the end of the same row**.

Example 2: Write the electron configurations of the following.

a. Mg and Mg^{2+}

Mg: **[Ne] $3s^2$**

Mg^{2+}: **[Ne]** (lost 2 e^-)

b. P and P^{3-}

P: **[Ne] $3s^2 3p^3$**

P^{3-}: **[Ne] $3s^2 3p^6$** (gained $3e^-$) or **[Ar]**

Electron Configurations of Ions from Transition Metals:

- because the proximity between the energy levels of *ns* and $(n-1)d$ orbitals, the interactions between the electrons and nucleus of transition metals ions are quite different than their parent atoms. Hence the **transition metal atom tends to lose the *ns* electrons before the electrons in the $(n-1)d$ orbitals**.

Example: Fe atom: **[Ar] $4s^2 3d^6$**, Fe^{2+} ion: **[Ar] $3d^6$**, Fe^{3+} ion: **[Ar] $3d^5$**

Assignment

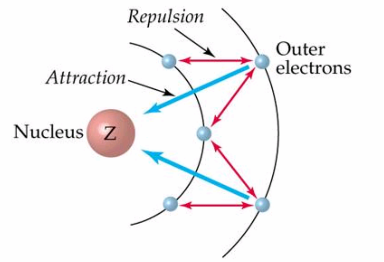
8.1 pg. 272 #1, 3, 4

8.2 pg. 272−273 #7, 11, 13, 15, 16, 18 to 20, 22 to 26, 28, 30, 32

8.3: Periodic Variation in Physical Properties

There are many different trends regarding the physical and chemical properties of the elements in the Periodic Table. However, we will limit to three atomic properties. They are atomic size, ionic radii, ionization energy, and electron affinity.

Shielding Effect: - the outer electrons are pushed away because of the repulsion between them and the core electrons. The net result is that the protons in the nucleus cannot hold on to these outer electrons as tightly as they would for the core electrons.



Effective Nuclear Charge (**Z_{eff}**): - the net nuclear charge actually experienced by an electron (the difference between the number of protons, *Z*, and the number of "shielded" core electrons).

- **the higher it is for Z_{eff}, the less shielding effect the outer electrons will experience**.

$$Z_{eff} = Z - \text{"Shield" Core Electrons}$$

Example 1: Calculate the effective nuclear charge of Na and Ar (first and last elements of period 3).

Sodium (Na): $Z = 11$ protons "Shield" Core e^- = 10 (e^- in the first two shells)

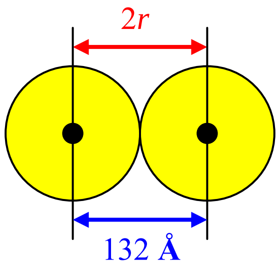
$Z_{eff} = 11 - 10$ **Z_{eff} = 1 for Na**

Argon (Ar): $Z = 18$ protons "Shield" Core e^- = 10 (e^- in the first two shells)

$Z_{eff} = 18 - 10$ **Z_{eff} = 8 for Ar**

(Ar has experience LESS shielding effect than Na)

Atomic Radius: - the size of an atom as measured by the distances between atoms in chemical compound.



Cl_2 Molecule
$2r = 132$ Å

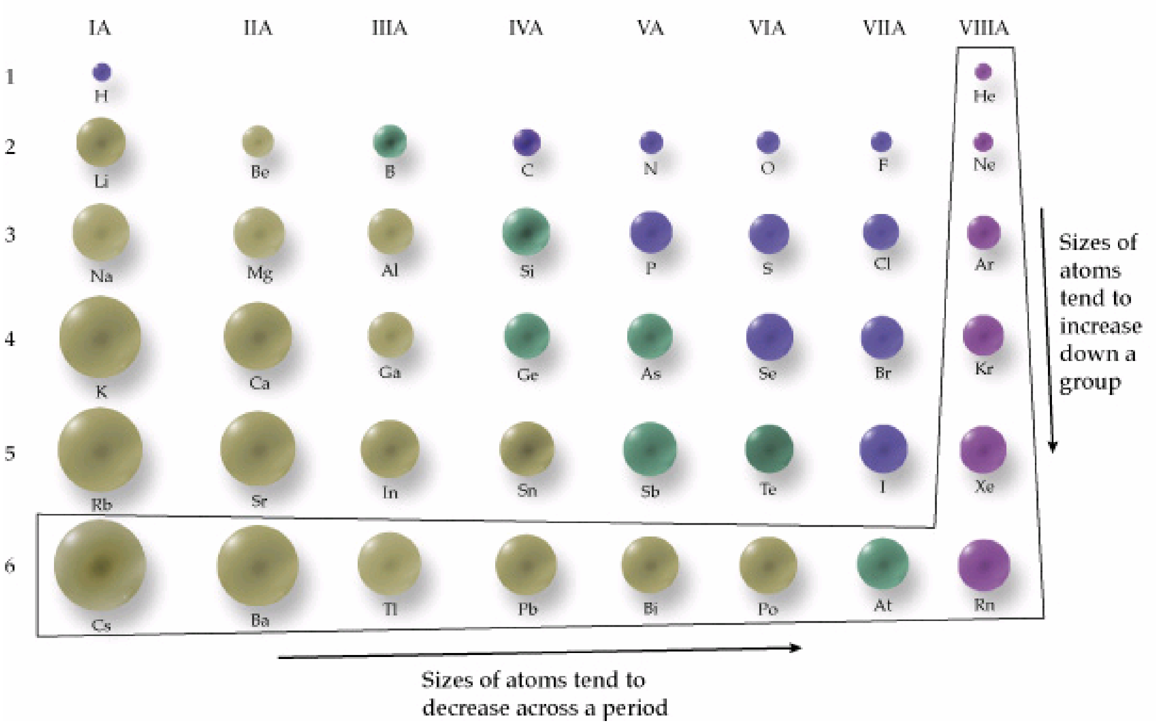
Cl Atom
$r = 66$ Å

Several Notes on Trends in Atomic Radii

1. In general, **Atomic Radii decrease as one move to the right of a period**. This is because the increases in protons in the same row increase the effective nuclear charge (the protons in the nucleus have more pull on the outer electrons, decreasing shielding), thus drawing these outer electrons closer to the nucleus, decreasing in sizes as the result.

2. **Atomic Radii INCRESES Down a Group**. This is due to the fact there are more orbitals as the number of row increases. The outer electrons are, of course, further away from the nucleus

Relative Atomic Sizes of the Representative Elements



Example 1: Order the following atoms from the smallest to the largest.

a. Te, S, Se, O

These atoms are within the same Group (column). As we move down the column, atomic size increases. Therefore,

O < S < Se < Te

b. Na, S, Mg, Cl, P

These atoms are within the same Period (row). As we move to the right, atomic size decreases. Therefore,

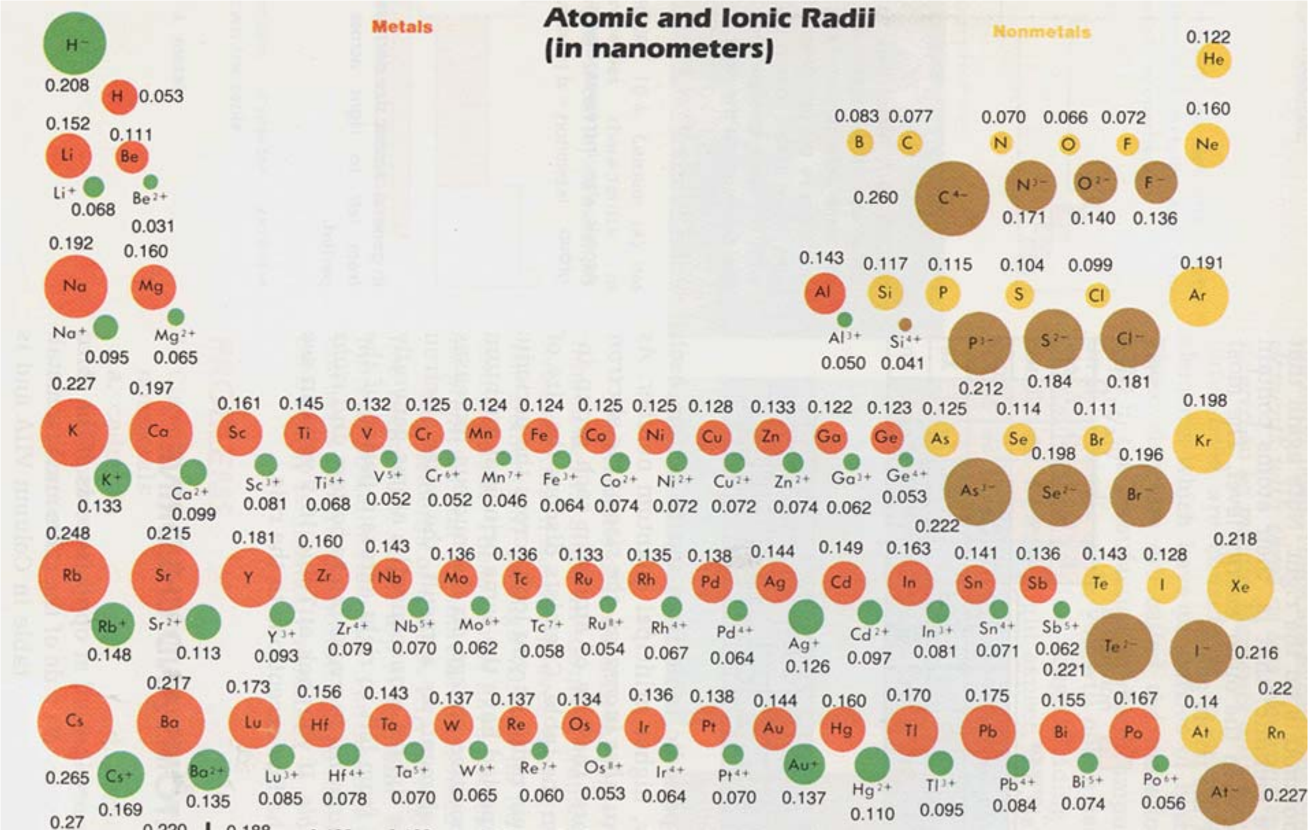
Cl < S < P < Mg < Na

Ions Sizes: - the size of cations and anions.

Isoelectronic Ions: - ions that have the same number of electrons. "iso" means same.

Several Notes on Trends in Ion Size

1. **Metal Cations are generally Smaller than Non-Metal Anions WITHIN the Same Period**. Metal cations tend to lose electrons to achieve the electron configuration of a previous noble gas. Thereby, losing an energy level in the process. **Metal Cations are always Smaller than the Parent Neutral Atoms. Non-Metal Anions are always Larger than the Parent Neutral Atoms.**
2. In general, **Ion Sizes Decrease as one move from LEFT to RIGHT of a period WITHIN the METAL GROUPS and WITHIN the NON-METAL GROUPS**. This is because the increases in protons in the same row increase the effective nuclear charge (the protons in the nucleus have more pull on the outer electrons, decreasing shielding), thus drawing these outer electrons closer to the nucleus, decreasing in sizes as the result.
3. **Ionic Radii INCRESES Down a Group**. This is due to the fact there are more orbitals as the number of row increases. The outer electrons are, of course, further away from the nucleus
4. When **Comparing Sizes of Isoelectronic Ions, the rule is that the Ion with the MOST PROTONS is the SMALLEST Ions**. The increase amount of protons have pull the electrons inward, decreasing the general size.



Example 2: Order the following ions from the smallest to the largest.

a. Te^{2-}, S^{2-}, Se^{2-}, O^{2-}

These anions are within the same Group (column). As we move down the column, ion size increases. Therefore,

$$O^{2-} < S^{2-} < Se^{2-} < Te^{2-}$$

b. Na^{+}, Mg^{2+}, P^{3-}, S^{2-}, Cl^{-}

These ions are within the same Period (row). As we move to the right, ion size <u>decreases within each of the metal and non-metal groups</u>. Therefore,

$$Mg^{2+} < Na^{+} < Cl^{-} < S^{2-} < P^{3-}$$

c. Ca^{2+}, K^{+}, Cl^{-}, S^{2-}, V^{5+}

These ions are isoelectronic (all have 18e^{-}). Since they have the same number of core and valence electrons in their various energy levels, <u>the ions with the largest atomic number (number of protons)</u> exerts more "pull" on these electrons. This in turn would <u>make the size of the ion smaller</u>.

$$\underset{(23\ p^{+})}{V^{5+}} < \underset{(20\ p^{+})}{Ca^{2+}} < \underset{(19\ p^{+})}{K^{+}} < \underset{(17\ p^{+})}{Cl^{-}} < \underset{(16\ p^{+})}{S^{2-}}$$

<u>Assignment</u>

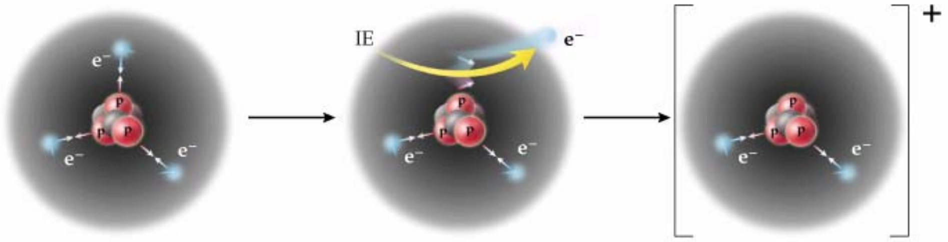
8.3 pg. 273–274 #34, 36, 38, 40, 42 to 48

8.4 & 8.5: Ionization Energy & Electron Affinity

<u>Ionization Energy</u>: - the energy needed to completely remove an electron from a gaseous atom or gaseous ion (plasma).

<u>First Ionization Energy</u>: - the ionization energy required to remove the highest-energy electron from an atom.

$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$ $Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-}$ $I_1 = 495$ kJ/mol (energy is required)



Negative electrons cannot leave the atom unless energy is supplied to overcome their attraction to the nucleus.

Ionization energy (IE) kicks an electron out of the atom.

The resulting surplus of one proton gives the atom an overall +1 charge. The atom has been ionized and is now a cation.

<u>Second Ionization Energy</u>: - the ionization energy required to remove the second highest-energy electron from the ion.

$X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-}$ $Na^{+}_{(g)} \rightarrow Na^{2+}_{(g)} + e^{-}$ $I_2 = 4560$ kJ/mol

Successive Ionization Energies (kJ/mol) for Elements in Row 3 of the Periodic Table

First Ionization Energies generally INCREASE within a Period. ($I_{Na} < I_{Mg} > I_{Al} < I_{Si} < I_P > I_S < I_{Cl} < I_{Ar}$)

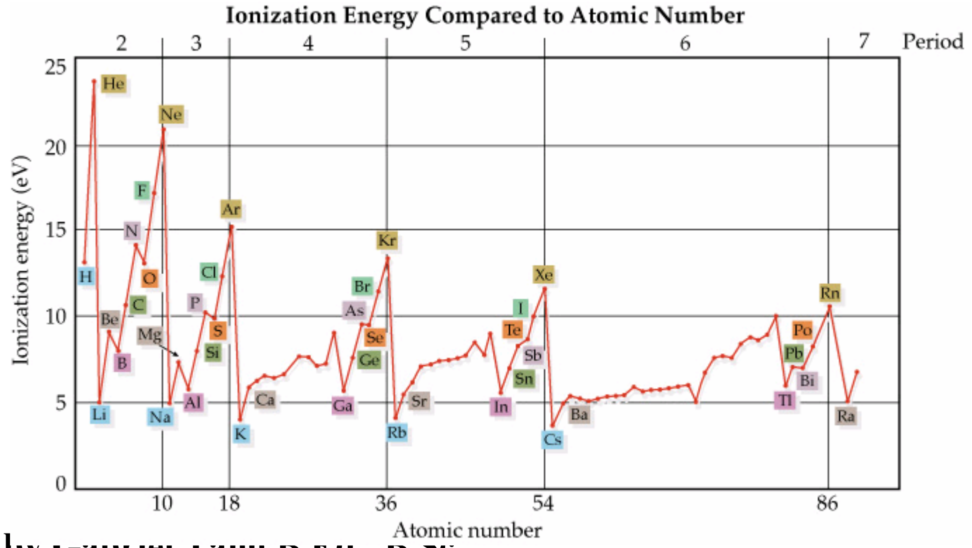
Elements	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	**735**	1445	7730				
Al	**580**	**1815**	2740	11600			
Si	780	**1575**	3220	4350	16100		
P	**1060**	1890	2905	4950	6270	21200	
S	**1005**	2260	3375	4565	6950	8490	27000
Cl	1255	2295	3850	5160	6560	9360	11000
Ar	1527	2665	3945	5770	7230	8780	12000

Core Electrons

Successive Ionization Energies INCREASES within each element. ($I_1 < I_2 < I_3 < \ldots$)

Several Notes on Trends in Ionization Energies

1. There is an **Increase in Successive Ionization Energies** because each successive electron has to jump from a lower level. Besides, these successive electrons are bind more tightly with the nucleus because they are closer to the protons.
2. **Ionization Energies Decrease Down a Group**. This is due to the fact as the atom has more orbitals, it is increasing in size. It is easier (takes less energy) to take away a valence electron because the protons are having a more difficult time to "hold on" to the electron.
3. In general, **Ionization Energies Increase as one move from Left to the Right of a Period**. This is because the increases in protons in the same row increase the effective nuclear charge (the protons in the nucleus have more pull on the outer electrons, decreasing shielding), thus requiring more energy to ionize them.
4. The notable exceptions to the above statement is between Mg and Al along with P and S. In the case between magnesium and aluminum, the I_1 decreases because of the change in subshells ([Ne] $3s^2$ and [Ne] $3s^2\ 3p^1$). It is easier to remove a $3p^1$ electron than an electron in $3s^2$. Between P and S, the electron configuration changes between [Ne] $3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$ to [Ne] $3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$. Again, it is easier to remove an electron from a $3p_x^2$ orbital because of Hund's Rule (the lowest energy state is achieved when all electrons in the subshell is unpaired).



Electron Affinity: - the change in energy associates with an addition of an electron to a gaseous atom.
- the larger negative electron affinity, the more stable the anion formed.

$$X_{(g)} + e^- \rightarrow X^-_{(g)}$$

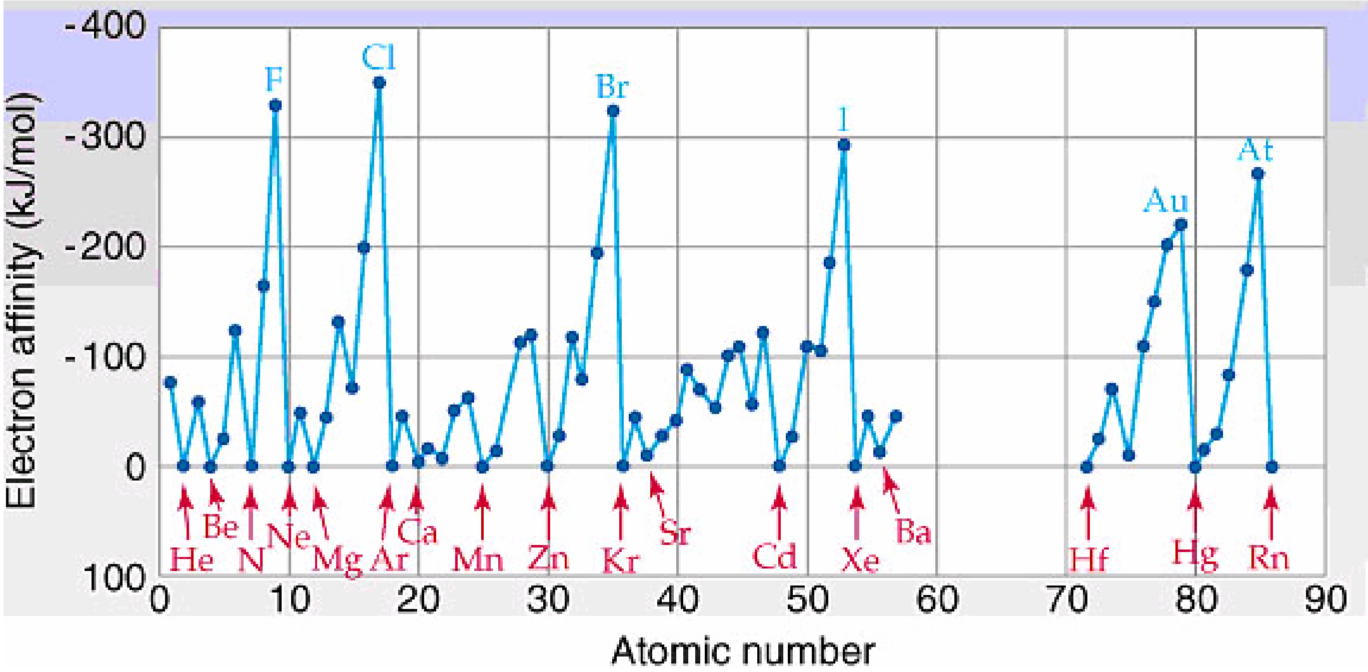
$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad \Delta EA = -348.7 \text{ kJ/mol} \qquad (348.7 \text{ kJ/mol is released})$$

Several Notes on Trends in Electron Affinities

1. In general, **Electron Affinity DECRESES Down a Group (less energy is released)**. This is due to the fact there are more orbitals as the number of row increases. Since the protons in the nucleus cannot attract another electron as effectively due to the increase distance involved, less energy is released. **The trend holds except for row 2. The reason is because of the small size of the 2*p* orbitals. Electron repulsion cause smaller values of electron affinities than expected for row 2.**

2. In most cases, **Electron affinity INCRESASES (becomes more negative) across the Period from Left to Right up to the Halogen group (more energy is released)**. Metals have $EA > 0$ because they like to form cations (low ionization energy). Non-metals have $EA < 0$ because they like to form anions in order to form a stable octet.

3. **Exceptions can be found in the 2A and 5A Groups**. With the 2A Alkaline Earth Group, it is more difficult to add an electron into the *s* orbital such that it will be filled to $ns^2\ np^1$. This is because the 2A Group already has an electron configuration of ns^2 (subshell is already filled). Therefore, they have a more positive (less negative) electron affinity. In the case of the 5A Group, the atoms find themselves difficult to add another electron because this will mean a np^4 configuration, which contains a paired electron from three unpaired electrons in np^3. Again, Hund's Rule frowns on such arrangement because it is not of the lowest energy state. Thus, Group 5A tends to have a more positive (less negative) electron affinity.



Assignment

8.4 pg. 274 #49 to 52, 54

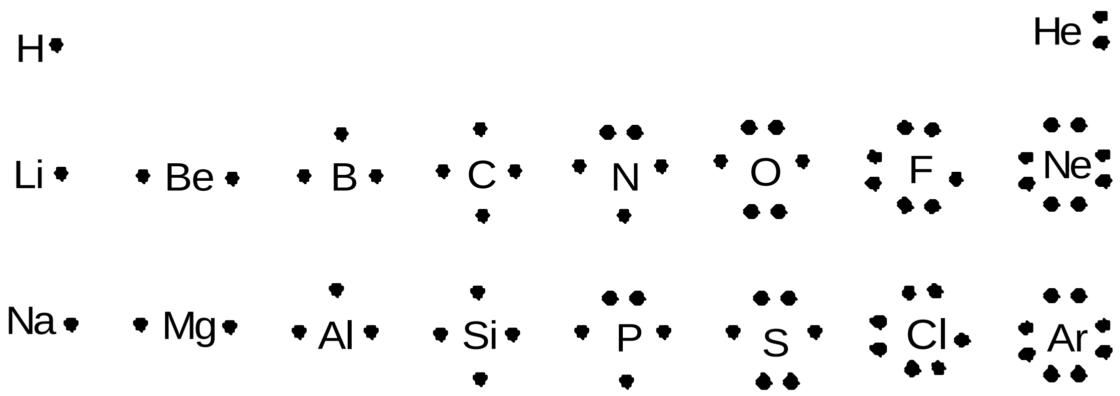
8.5 pg. 274 #57 to 62

Chapter 9: Chemical Bonding I: General Concepts

9.1: Lewis Dot Symbols

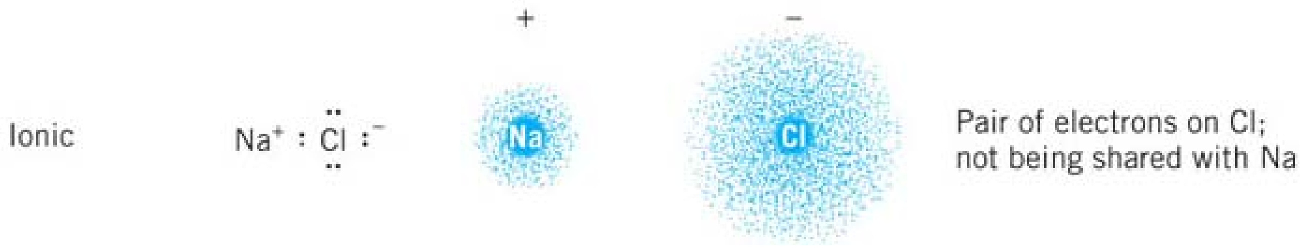
Lewis Structure: - sometimes refer to as Lewis Dot Diagram.
- shows electrons of valence electron (*s* and *p* orbitals) as dots for all atoms of representative elements (Groups IA to VIIIA).
- max of eight electrons around each atomic symbol, and hence Lewis structure cannot be used on transition metals.

Lewis Structure for Atoms in the First Three Rows of the Periodic Table of Elements



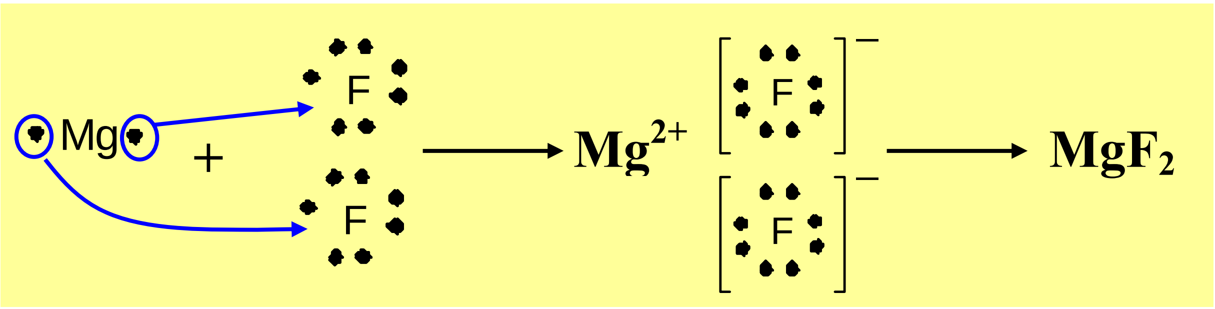
9.2: The Ionic Bond

Ionic Bonds: - a chemical bond (attraction) that is characterized by the **transfer of electrons** to form ions between metals and non-metals.
- the resulting attraction between the cation(s) and anion(s) is the ionic bond within an ionic compound.

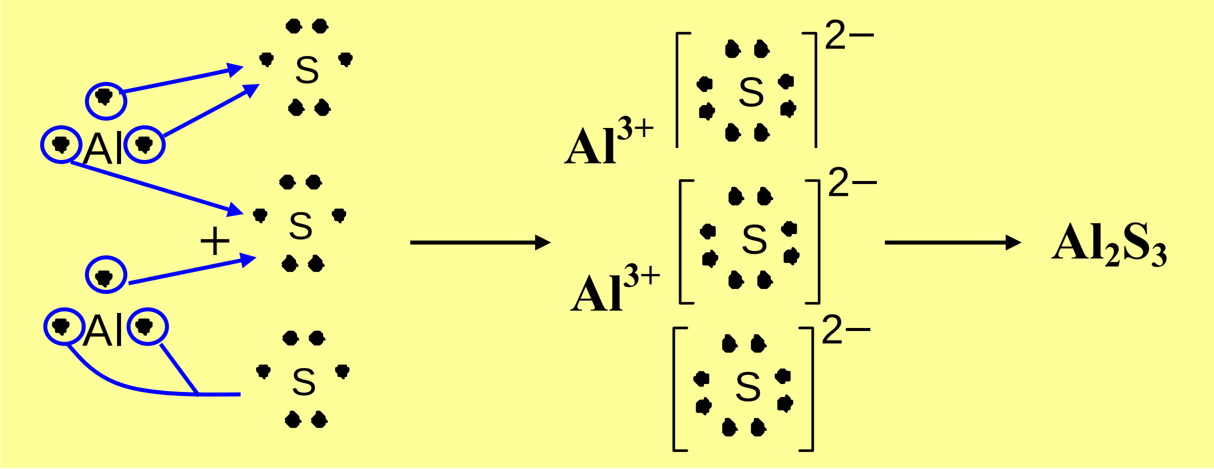


Example 1: For each ionic compound, draw the Lewis dot diagram for each atom and ion involved.

a. Mg and F

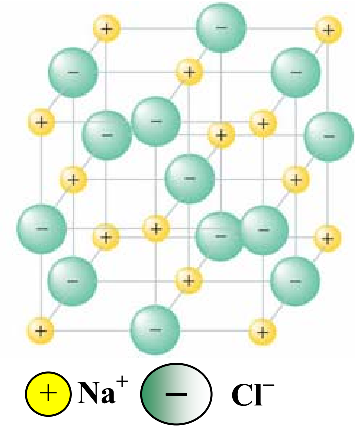


b. Al and S

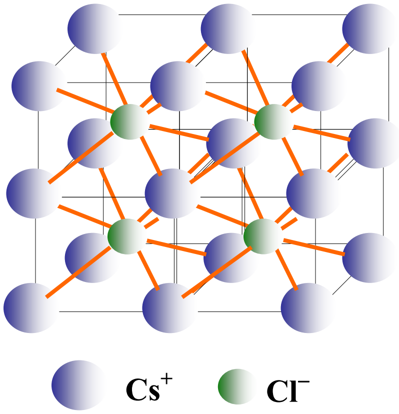


Properties of Ionic Crystalline Solids

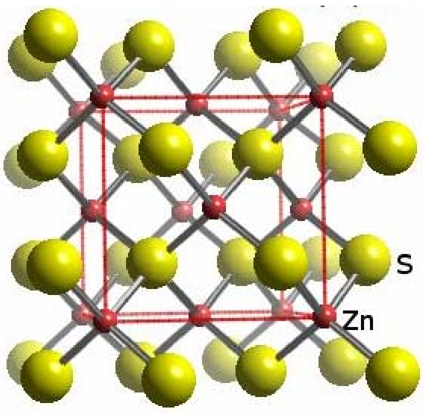
1. **Ionic Compounds have a definite Crystalline Structure and are Poor Conductors of Electricity and Heat in their Solid Form.** Conduction of electricity and heat requires ions to move freely within the solid. The lattice structures of the solid ionic compounds do not allow ions to move freely.



Simple Cubic Unit Crystalline Structure of NaCl



Body Centred Cubic Unit Crystalline Structure of CsCl



Face Centred Cubic Unit Crystalline Structure of ZnS

2. **Ionic solids are generally High Melting Points (typically 300°C to 1000°C).** Since a strong force can only shatter the crystal but not bend it as in metals, **the energy needed to completely break up the lattice structure (lattice energy)** is very large and it is the same energy needed to melt the ionic compounds.

3. **Ionic solids are Hard and Brittle.** The lattice structure of all ionic compounds holds the ions in definite positions. When the compound encountered a strong force, the close proximity of the ions stay close together. This causes the crystal to **shatter**, not bent like metal solid would.

4. **Ionic solids can be Melted to form Liquids that are Electrical Conductors.** Ionic solids melt when the ions gain enough energy to break the lattice structure. They are move freely and can carry electrical charge through the liquid. This explains why a molten ionic substance conducts electricity, but a solid ionic material doesn't. The ions move through the liquid can carry charge from one place to another.

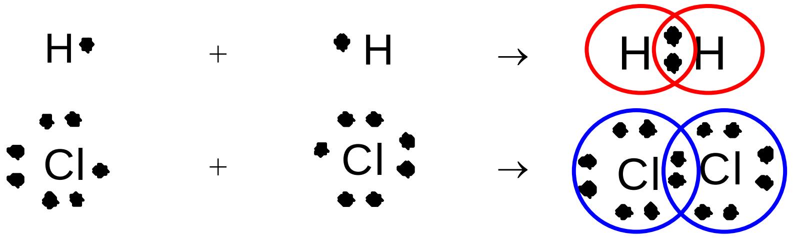
5. **Soluble ionic solids dissolve to form solutions that are Electrical Conductors. (Not all ionic substances are soluble in water.)** Soluble ionic compounds form **electrolytes (ions in aqueous from)** that allow the conduction of electricity.

Assignment

9.1 pg. 306 #1 and 5; 9.2 pg. 306−307 #7, 9, 10, 13, 15, 16, 18, 20

9.4: The Covalent Bond

Covalent Bond: - an attraction force between two non-metal elements where the sharing of valence electrons is taken place so each atom can achieve the stable duet (for hydrogen) or octet (for other representative elements – ns^2np^6) conditions.



2 valence e^- around each H atom (duet rule)

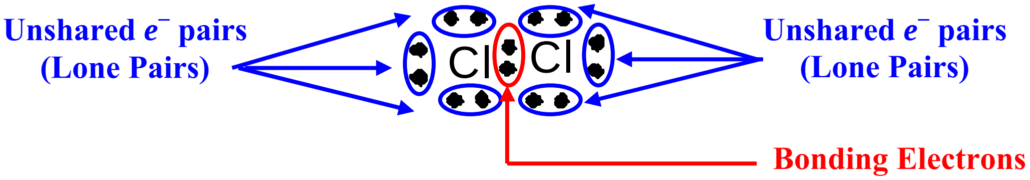
8 valence e^- around each Cl atom (octet rule)

Covalent Compound: - a compound that consists of only covalent bonds.
- sometimes refers to as **molecular compound**.

Types of Covalent Chemical Bonds:

1. **Single Covalent Bond**: - covalent bond where there are only **two valence electrons** being shared between two atoms (also refer to as **bonding electrons**).

Unshared Electron Pairs (Lone Pairs): - pairs of electrons **not** involving in the **covalent bond**.

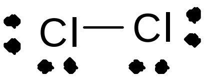


Unshared e^- pairs (Lone Pairs)

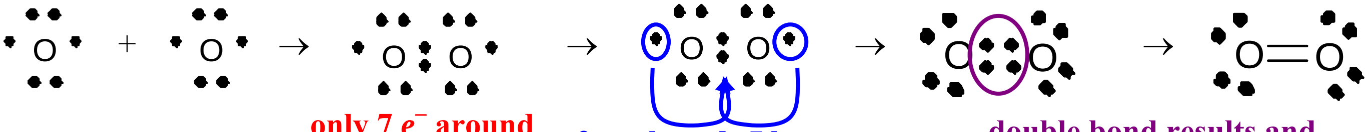
Unshared e^- pairs (Lone Pairs)

Bonding Electrons

Structural Formula: - a Lewis dot diagram of a molecule where the bonding electrons are replaced by a short line.



2. **Double Covalent Bond**: - covalent bond where there are only **four valence electrons** being shared between two atoms.
- denotes by a double line in the structural formula.

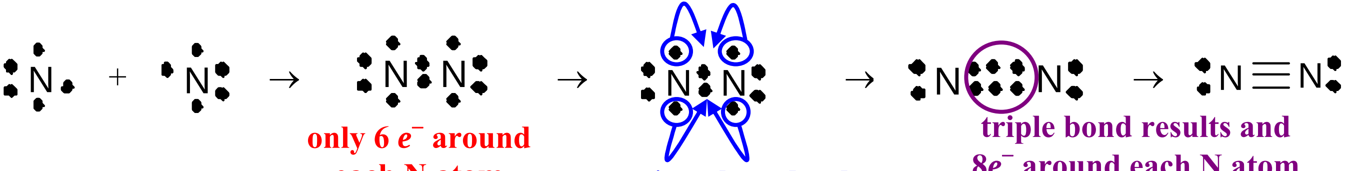


only 7 e^- around each O atom

2 unshared e^- become another bonding pair

double bond results and 8e^- around each O atom

3. **Triple Covalent Bond**: - covalent bond where there are only **six valence electrons** being shared between two atoms.
- denotes by a triple line in the structural formula.



only 6 e^- around each N atom

4 unshared e^- become 2 other bonding pairs

triple bond results and 8e^- around each N atom

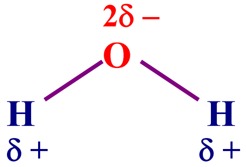
Coordinate Covalent Bond: - where an atom contributes an unshared electron pair (lone pair) to form double or triple bonds to achieve a stable octet around both atoms.
- sometimes refer to as **multiple bond**.

***Note*: In general, bond length decreases with multiple bonds.**

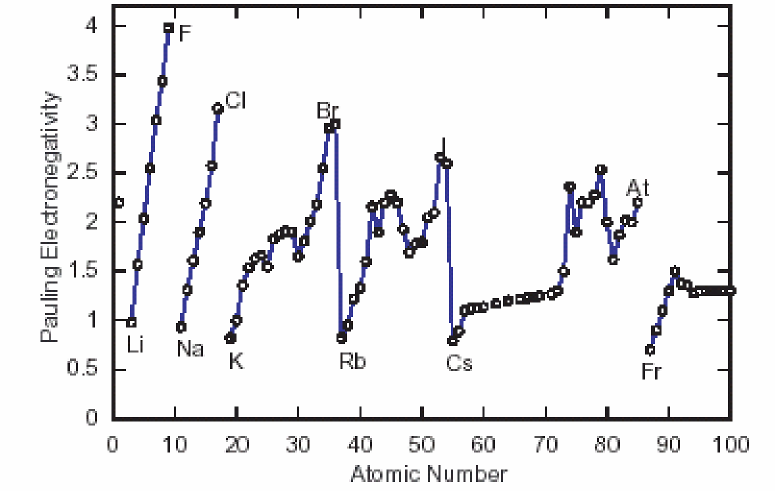
Bond and Bond Type	Bond Length (pm)
C – C (single bond)	154
C = C (double bond	134
C ≡ C (triple Bond)	120

9.5: Electronegativity

Polar Covalent Bond: - a covalent bond where electrons are not evenly distributed, resulting in localized charges at either end.



Electronegativity: - first determined by **Linus Pauling**, it is a measure of the **capability of an atom within a molecule to attract shared electrons around itself**.
- the better the atom is able to attract electrons, the higher the electronegativity value.
- electronegativity of noble gases is 0 as their outer orbitals are filled and do not attract electrons.



Several Notes on Trends in Electronegativity

1. In general, **Electronegativities INCREASE as one move to the right of a period (up to and including halogens)**. This is because of the increase in electron affinity of the non-metals. These non-metals like to form anions to fill the valence orbitals. Metals tend to the high ionization energy because they like to give away electrons to form cations.
2. **Electronegativities DECRESE Down a Group**. This is due to the fact there are more orbitals as the number of row increases. The outer electrons are, of course, further away from the nucleus. Hence, it is more difficult for the protons of the nucleus to attract electrons into the valence orbitals.

Relative Bond Polarity: - the difference in electronegativity in a molecule.

1. **Ionic Bonds have High Bond Polarity.**
2. **Non-Polar Covalent Bonds have No Bond Polarity.**
3. **Polar Covalent Bonds have Some Bond Polarity.**

Example 1: Using Figure 9.5 of the textbook, determine the relative bond polarity of Cl_2, HCl, and LiCl. Order them from least to greatest and classify them.

Cl — Cl **3.2 3.2**	**Difference in Electronegativity = 0 (Non-Polar Covalent Bonds – No Bond Polarity)**
H — Cl **2.2 3.2**	**Difference in Electronegativity = 1 (Polar Covalent Bonds – Some Bond Polarity)**
Li — Cl **1.0 3.2**	**Difference in Electronegativity = 2.2 (Ionic Bonds – High Bond Polarity)**

Assignment

9.4 pg. 307 #29 and 30

9.5 pg. 307 #32, 34, 35, 37, 38

9.6: Writing Lewis Structures

Procedure to draw Lewis Dot Diagram

1. **Add up all the valence electrons available from all atoms and extra charges from complex ions (ex: charge of 1– means one more electron; charge of 1+ means one less electron).**
2. **Decide on the central atom. Usually, it is the atom with the most available bonding sites (carbon and silicon has the most bonding site – 4 valence e^-) or it is element with the least number of atom. Place a pair of electrons to form a single bond between each atom.**
3. **Arrange any remaining electrons around all atoms such that the octet rule is followed for the second and third period atoms and duet rule is satisfied for the first period atoms. This may sometimes mean setting up multiple bonds (moving lone pairs to the central atom so that it satisfies the octet rule).**
4. **Final Lewis structure of Polyatomic Ion must include a big square bracket and the indication of net charge.**

Example 1: Draw the Lewis structure for the following molecules and polyatomic ions.

a. H_2

$2e^-$ (2 H atoms)
$2e^-$ Total
– $2e^-$ (1 bond)
$0e^-$

H H

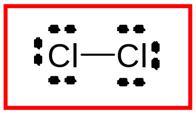
H – H

b. Cl_2

$14e^-$ (2 Cl atoms)
$14e^-$ Total
– $2e^-$ (1 bond)
$12e^-$ Left
– $12e^-$ (6 lone pairs on Cl's for octets)
$0e^-$

Cl Cl

Cl – Cl

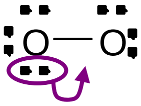


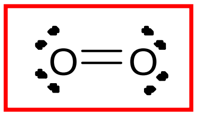
c. O_2

O O

O – O

$12e^-$ (2 O atoms)
$12e^-$ Total
– $2e^-$ (1 bond)
$10e^-$ Left
– $6e^-$ (3 lone pairs on one O for octet)
– $4e^-$ (2 lone pair on other O)
$0e^-$





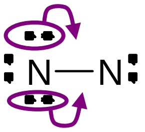
Need to move a lone pair between the atoms because the oxygen to the right does not have enough e^- for an octet.

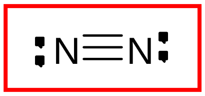
d. N_2

N N

N – N

$10e^-$ (2 N atoms)
$10e^-$ Total
– $2e^-$ (1 bond)
$8e^-$ Left
– $6e^-$ (3 lone pairs on one N for octet)
– $2e^-$ (lone pair on other N)
$0e^-$





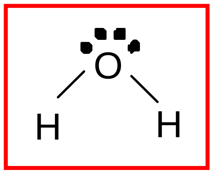
Need to move two lone pairs between the atoms because the nitrogen to the right does not have enough e^- for an octet.

e. H_2O

H O H

H – O – H

$2e^-$ (2 H atoms)
+ $6e^-$ (1 O atom)
$8e^-$ Total
– $4e^-$ (2 bonds)
$4e^-$ Left
– $4e^-$ (2 lone-pairs on O for octet)
$0e^-$



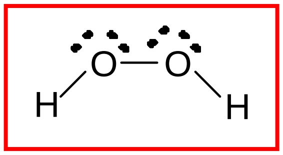
Reason for why the H_2O structure is bent will be explained in section 10.2

f. H_2O_2

H O O H

H – O – O – H

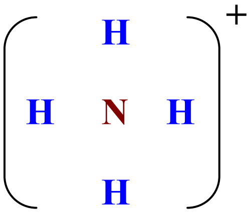
$2e^-$ (2 H atoms)
+ $12e^-$ (2 O atoms)
$14e^-$ Total
– $6e^-$ (3 bonds)
$8e^-$ Left
– $8e^-$ (4 lone-pairs on O's for octet)
$0e^-$

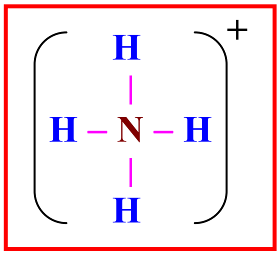


Since H can only form 1 bond each, both oxygen atoms are the central atoms

g. NH_4^+

$5e^-$ (1 N atom)
+ $4e^-$ (4 H atoms)
– $1e^-$ (+1 charge of NH_4^+)
$8e^-$ Total
– $8e^-$ (4 bonds)
$0e^-$



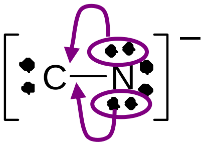


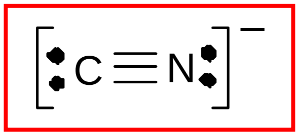
h. CN^-

$[C\ \ N]^-$

$[C – N]^-$

$5e^-$ (1 N atom)
+ $4e^-$ (1 C atom)
+ $1e^-$ (–1 charge of CN^-)
$10e^-$ Total
– $2e^-$ (1 bond)
$8e^-$ Left
– $6e^-$ (2 lone pairs on N for octet)
– $2e^-$ (last lone pair on C)
$0e^-$





There are only 4 e^- around C. Nitrogen atoms need to contribute 2 lone pairs to form a triple bond.

Assignment
9.6 pg. 307 #41

9.9: Exceptions to the Octet Rule

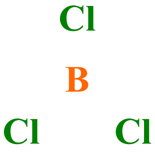
1. **In the second row, due to the 2*s* and the 2*p* orbitals, C, N, O, and F should always follow the octet rule. Overall, the second period elements will never exceed the octet rule.**
2. **However, because Be is a metal and B is a metalloid, they are most likely to have fewer than eight electrons around them. Thus, these compounds are fairly reactive due to their electron-deficiency. This phenomenon is referred to as the Incomplete Octet.**
3. **In the third period, heavier atoms towards the right of the Table often satisfy the octet rule. This being said, there are times that they can use the empty 3*d* orbitals to exceed the 8 electrons limit. (Examples: P can have $10e^-$ rule; S and Cl can have $10e^-$ or $12e^-$ rule) – Expanded Octet**
4. **Elements in higher row can definitely exceed the octet rule. This sometimes applies to larger noble gases as well. (Examples: Br, I, Xe, Rn can have $10e^-$ or $12e^-$) – Expanded Octet**

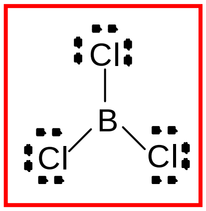
Note: **For atoms that deviate from the octet and duet rules, Formal Charges will have to be assigned to each atom in a molecule to assess all possible Lewis structures**. This will be discussed in following section.

Example 1: Draw the Lewis structure for the following molecules and polyatomic ions.

a. BCl_3

$3e^-$ (B atom)
$+ 21e^-$ (3 Cl atoms)
$24e^-$ Total
$- 6e^-$ (3 bonds)
$18e^-$ Left
$- 18e^-$ (lone-pairs on Cl's for octet)
$0e^-$





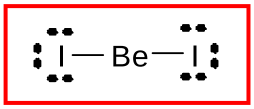
B follows $6e^-$ rule. There is no need to bring a lone pair from a Cl atom to form a double bond for B to have an octet.

b. BeI_2

$2e^-$ (Be atom)
$+ 14e^-$ (2 I atoms)
$16e^-$ Total
$- 4e^-$ (2 bonds)
$12e^-$ Left
$- 12e^-$ (lone-pairs on I's for octet)
$0e^-$

I Be I

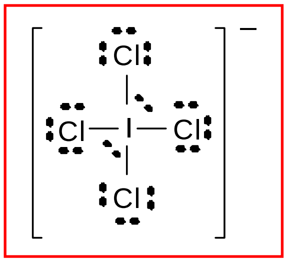
I – Be – I



Be follows $4e^-$ rule. There is no need to bring two lone pairs from the I atoms to form a double bond for Be to have an octet.

c. ICl_4^-

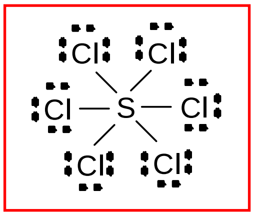
$7e^-$ (I atom)
$+ 28e^-$ (4 Cl atoms)
$+ 1e^-$ (–1 charge of ICl_4^-)
$36e^-$ Total
$- 8e^-$ (4 bonds)
$28e^-$ Left
$- 24e^-$ (lone pairs on Cl's for octet)
$- 4e^-$ (lone pairs on I)
$0e^-$



I follows $12e^-$ rule in this case. We have extra electrons left over after filling the octet of the outside Cl atoms.

d. SCl_6

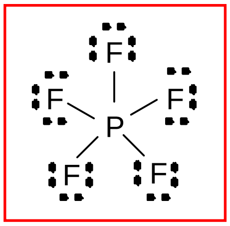
$6e^-$ (S atom)
$+ 42e^-$ (6 Cl atoms)
$48e^-$ Total
$- 12e^-$ (6 bonds)
$36e^-$ Left
$- 36e^-$ (lone-pairs on Cl's for octet)
$0e^-$



S follows $12e^-$ rule in this case. (There are 6 bonds from the central S atom.)

e. PF_5

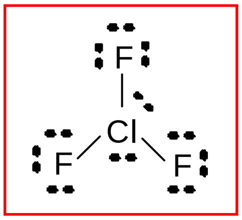
$5e^-$ (P atom)
$+ 35e^-$ (5 Cl atoms)
$40e^-$ Total
$- 10e^-$ (5 bonds)
$30e^-$ Left
$- 30e^-$ (lone-pairs on F's for octet)
$0e^-$



P follows $10e^-$ rule in this case. (There are 5 bonds from the central P atom.)

f. ClF_3

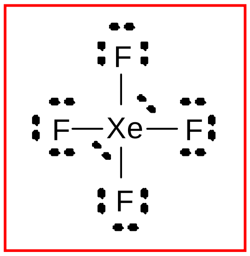
$7e^-$ (Cl atom)
$+ 21e^-$ (3 F atoms)
$28e^-$ Total
$- 6e^-$ (3 bonds)
$22e^-$ Left
$- 18e^-$ (lone-pairs on F's for octet)
$- 4e^-$ (lone pairs on I)
$0e^-$



Cl follows $10e^-$ rule in this case. We have extra electrons left over after filling the octet of the outside F atoms.

g. XeF_4

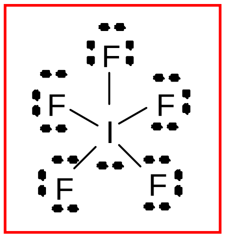
8e^- (Xe atom)
+ 28e^- (4 F atoms)
36e^- Total
– 8e^- (4 bonds)
28e^- Left
– 24e^- (lone-pairs on F's for octet)
– 4e^- (lone pairs on Xe)
0e^-



Xe follows 12e^- rule. We have extra electrons left over after filling the octet of the outside F atoms.

h. IF_5

7e^- (I atom)
+ 35e^- (5 F atoms)
42e^- Total
– 10e^- (5 bonds)
32e^- Left
– 30e^- (lone-pairs on F's for octet)
– 2e^- (lone pair on I)
0e^-



I follows 12e^- rule. We have extra electrons left over after filling the octet of the outside F atoms.

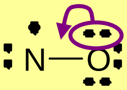
Odd Electron Molecules: - when the sum of all valence electrons and any net charges yields an odd number of electrons available.
- odd electron molecules do not fit well with the localized electron model because the model deals with pairs of electrons. Hence, **odd electron molecules are very unstable and very reactive**.

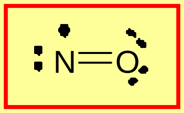
Example 2: Draw all the possible Lewis structures for NO and NO_2. Comment on the stability of each compound.

For NO:
5e^- (N atom)
+ 6e^- (O atom)
11e^- Total (Odd)
– 2e^- (1 bond)
9e^- Left
– 6e^- (lone-pair on O for octet)
– 3e^- (lone-pair & a radical e^- on N)
0e^-

N O

N – O



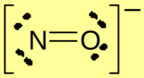


Need to move a lone pair from oxygen to between the atoms because the nitrogen does not have enough e^- for an octet.

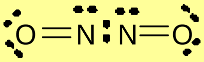
Note that we cannot bring another lone pair in from the oxygen atom because it means nitrogen would exceed the octet rule (9e^- around N).

The overall **NO molecule is unstable** because nitrogen has odd number of electrons (7e^-) around itself.

Remedy #1: Pick up an electron and form a polyatomic ion – hyponitrite (NO^-)



Remedy #2: Bond with another NO molecule to form a dimer – dinitrogen dioxide (N_2O_2)



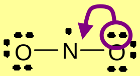
Remedy #3: Decomposition back into N_2 and O_2 using a catalyst.

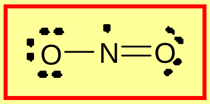
$$2\,NO_{(g)} \rightarrow N_{2\,(g)} + O_{2\,(g)}$$

For NO_2:
5e^- (N atom)
+ 12e^- (2 O atoms)
17e^- Total (Odd)
– 4e^- (2 bonds)
13e^- Left
– 12e^- (lone-pair on O's for octet)
– 1e^- (a radical e^- on N)
0e^-

O N O

O – N – O



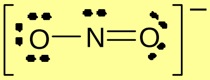


Need to move a lone pair from oxygen to between the atoms because the nitrogen does not have enough e^- for an octet.

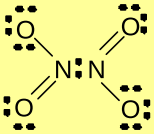
Note that we cannot bring another lone pair in from the oxygen atom because it means nitrogen would exceed the octet rule (9e^- around N).

The overall **NO_2 molecule is unstable** because nitrogen has odd number of electrons (7e^-) around itself.

Remedy #1: Pick up an electron and form a polyatomic ion –nitrite (NO_2^-)



Remedy #2: Bond with another NO_2 molecule to form a dimer – dinitrogen tetraoxide (N_2O_4)



Remedy #3: Decomposition back into N_2 and O_2 using a catalyst.

$$2\,NO_{2\,(g)} \rightarrow N_{2\,(g)} + 2\,O_{2\,(g)}$$

Assignment
9.9 pg. 308 #55, 57, 61 to 64

9.7 & 9.8: Formal Charges and the Concept of Resonance

Resonance: - occurs when more than one Lewis structure exists for a molecule.

Resonance Structure: - different variations of a resonance molecule can be drawn using a double headed arrow, ↔, between the diagrams.

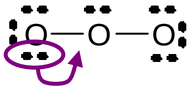
Example 1: Draw the Lewis structure for the following molecules or polyatomic ions.

a. O_3

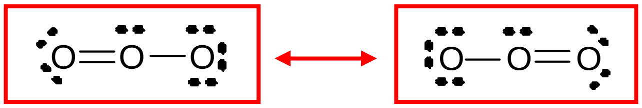
$18e^-$ (3 O atoms)
$18e^-$ Total
– $4e^-$ (2 bonds)
$14e^-$ Left
– $12e^-$ (6 lone pairs on outside O's for octet)
– $2e^-$ (lone pair on central O)
$0e^-$

O O O

O – O – O



There are only 6 e^- around the central O atom. An outside O atom needs to contribute a lone pair to form a double bond.



The double bond can be on either the left or right side of the central oxygen atom (resonance).

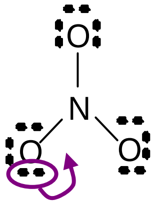
b. NO_3^-

$5e^-$ (1 N atom)
+ $18e^-$ (3 O atoms)
+ $1e^-$ (−1 charge of NO_3^-)
$24e^-$ Total
– $6e^-$ (3 bonds)
$18e^-$ Left
– $18e^-$ (lone pairs on O's for octet)
$0e^-$

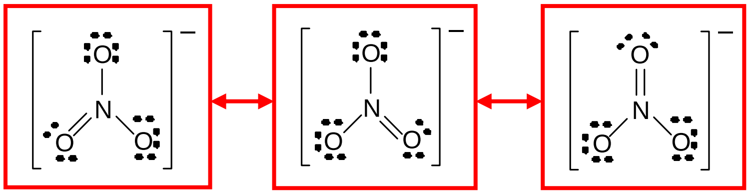
O

N

O O



There are only 6 e^- around the central N atom. An outside O atom needs to contribute a lone pair to form a double bond.

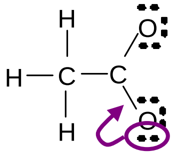


The double bond can come from any one of the O atoms (resonance).

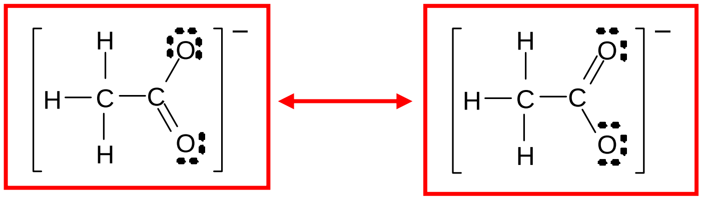
c. CH_3COO^-

$8e^-$ (2 C atoms)
+ $3e^-$ (3 H atoms)
+ $12e^-$ (2 O atoms)
+ $1e^-$ (−1 charge)
$24e^-$ Total
– $12e^-$ (6 bonds)
$12e^-$ Left
– $12e^-$ (lone pairs on O's for octet)
$0e^-$

C atoms are the central atoms – most bonding capacity (can make 4 single bonds). Note the structure is like how the formula is written.



There are only 6 e^- around the one of the C atoms. An outside O atom needs to contribute a lone pair to form a double



The double bond can be on either the top or bottom side of the second carbon atom (resonance).

Formal Charge: - the difference between the number of valence electron of the original atom and the number of valence electron actually assigned to the atom in the Lewis structure.
- in cases where molecules have **more than one possible Lewis structure, the one with the Formal Charges CLOSEST to ZERO has the Lowest Energy. Hence, it is more stable than the other ones.**

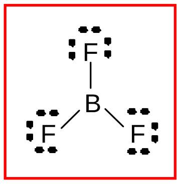
For **EACH atom in a molecule**, its **Formal Charge** is calculated by

$$\text{Formal Charge} = \#\text{ of } e^-_{\text{valence}} - \#\text{ of } e^-_{\text{unshared}} - \frac{1}{2}\left(\#\text{ of } e^-_{\text{bonding}}\right)$$

Example 2: Draw all the possible Lewis structures for each of the following molecule or polyatomic ion. Determine the formal charge of the central atom and decide which structure is more favourable.

a. BF_3

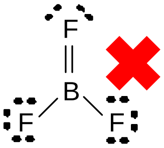
$3e^-$ (B atom)
+ $21e^-$ (3 F atoms)
$24e^-$ Total
− $6e^-$ (3 bonds)
$18e^-$ Left
− $18e^-$ (lone-pairs on F's for octet)
$0e^-$



✓

Formal Charge (B)
= $3e^-$ − $0e^-$ − $\frac{1}{2}(6e^-)$
(val.) (lone pair) (bonding)

Formal Charge (B) = 0
(Correct Structure)



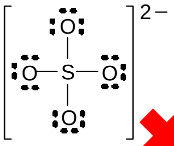
✗

Formal Charge (B)
= $3e^-$ − $0e^-$ − $\frac{1}{2}(8e^-)$
(val.) (lone pair) (bonding)
Formal Charge (B) = −1
(incorrect structure)

This is why B follows $6e^-$ rule. There is no need to bring a lone pair from a F atom to form a double bond for B to have an octet.

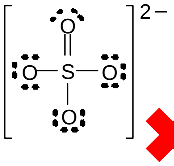
b. SO_4^{2-}

$6e^-$ (S atom)
+ $24e^-$ (4 O atoms)
+ $2e^-$ (−2 charge)
$32e^-$ Total
− $8e^-$ (4 bonds)
$24e^-$ Left
− $24e^-$ (lone-pairs on O's for octet)
$0e^-$



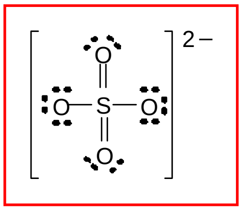
✗

Formal Charge (S)
= $6e^-$ − $0e^-$ − $\frac{1}{2}(8e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 2
(incorrect structure)



✗

Formal Charge (S)
= $6e^-$ − $0e^-$ − $\frac{1}{2}(10e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 1
(incorrect structure)



✓

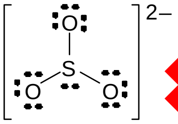
Formal Charge (S)
= $6e^-$ − $0e^-$ − $\frac{1}{2}(12e^-)$
(val.) (lone pair) (bonding)

Formal Charge (S) = 0
(Correct structure)

This is why S sometimes follows $12e^-$ rule. Both S=O bonds are opposite to each other to maximize symmetry of the polyatomic ion.

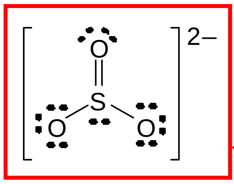
c. SO_3^{2-}

$6e^-$ (S atom)
+ $18e^-$ (3 O atoms)
+ $2e^-$ (−2 charge)
$26e^-$ Total
− $6e^-$ (3 bonds)
$20e^-$ Left
− $18e^-$ (lone-pairs on O's for octet)
− $2e^-$ (lone pair on central S)
$0e^-$



✗

Formal Charge (S)
= $6e^-$ − $2e^-$ − $\frac{1}{2}(6e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 1
(incorrect structure)



✓

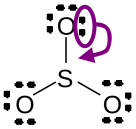
Formal Charge (S)
= $6e^-$ − $2e^-$ − $\frac{1}{2}(8e^-)$
(val.) (lone pair) (bonding)

Formal Charge (S) = 0
(Correct structure)

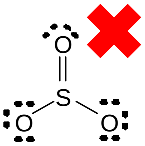
This is why S sometimes follows $10e^-$ rule (as the formal charge is now minimized to zero).

d. SO_3

$6e^-$ (S atom)
+ $18e^-$ (3 O atoms)
$24e^-$ Total
− $6e^-$ (3 bonds)
$18e^-$ Left
− $18e^-$ (lone-pairs on O's for octet)
$0e^-$

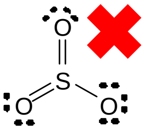


There are only 6 e^- around the central S atom. An outside O atom needs to contribute a lone pair to form a double bond.



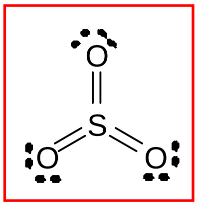
✗

Formal Charge (S)
= $6e^-$ − $0e^-$ − $\frac{1}{2}(8e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 2
(incorrect structure)



✗

Formal Charge (S)
= $6e^-$ − $0e^-$ − $\frac{1}{2}(10e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 1
(incorrect structure)



✓

Formal Charge (S)
= $6e^-$ − $0e^-$ − $\frac{1}{2}(12e^-)$
(val.) (lone pair) (bonding)

Formal Charge (S) = 0
(Correct structure)

This is why S sometimes follows $12e^-$ rule (as the formal charge is now minimized to zero).

Assignment
9.7 & 9.8 pg. 307−308 #40, 42 to 44, 49 to 54

Chapter 10: Chemical Bonding II – Molecular Geometry & Intermolecular Forces

10.1: Molecular Geometry

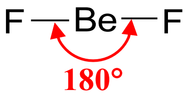
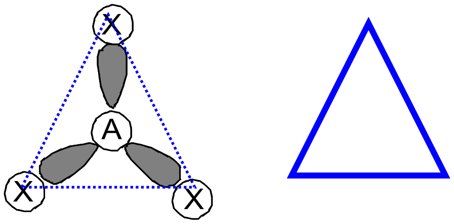
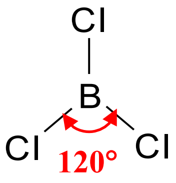
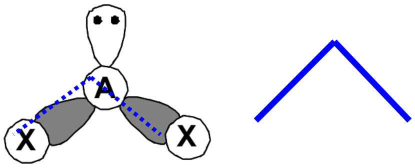
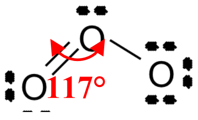
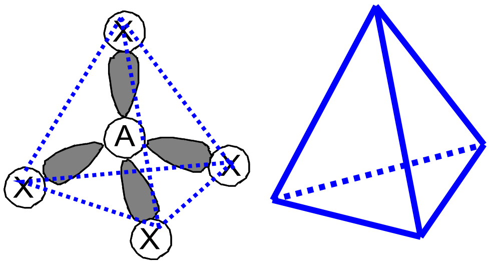
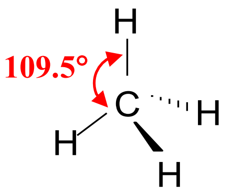
Molecular Structure: - the three-dimensional arrangement of atoms in a molecule.

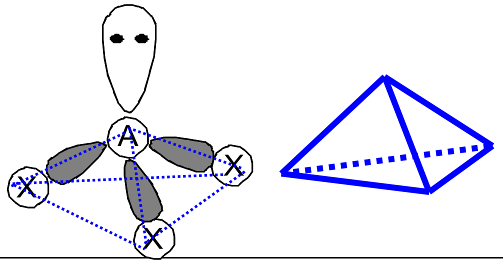
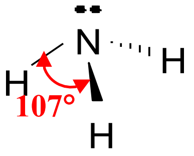
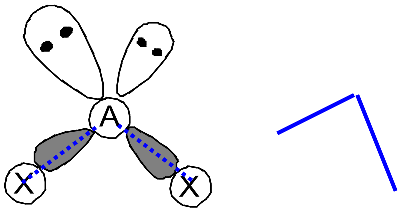
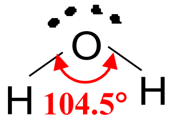
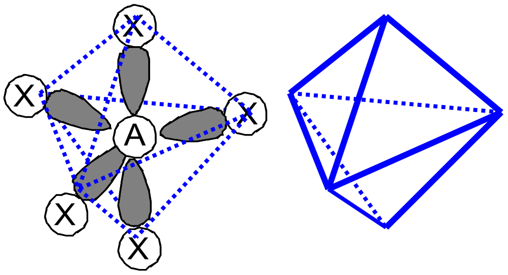
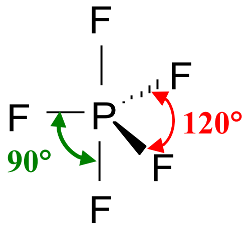
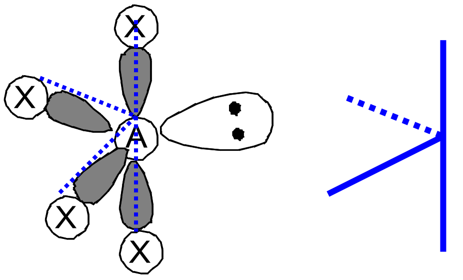
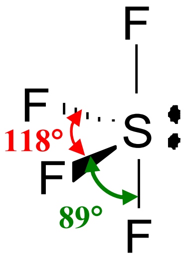
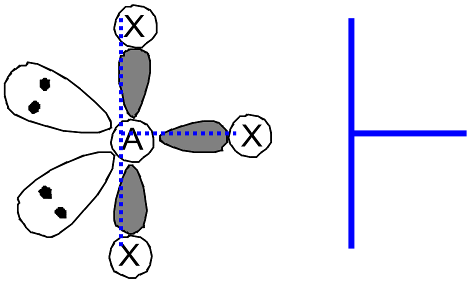
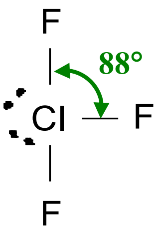
Valence Shell Electron-Pair Repulsion (VSEPR) Model:
- ***the best structure for a molecule is one that minimizes electrons lone pairs repulsion***.
- most often used to predict molecular structures involving non-metals.

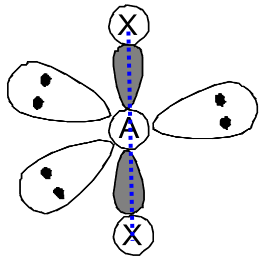
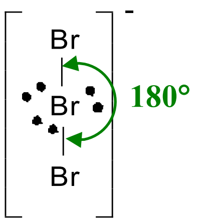
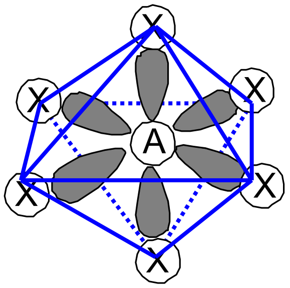
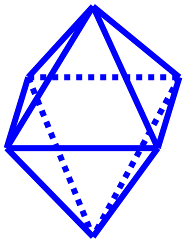
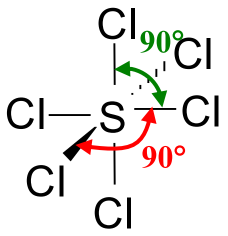
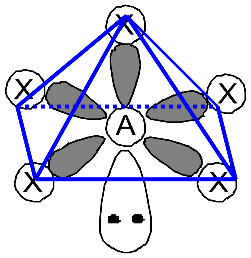
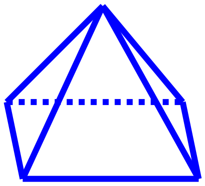
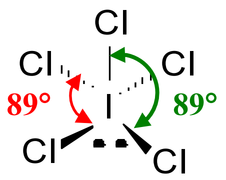
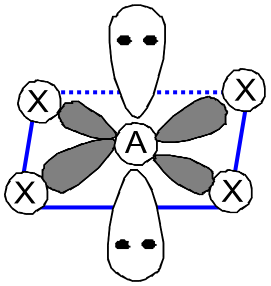
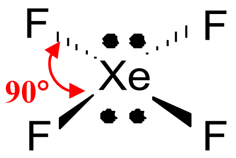
Example: For molecules with a total of 4 e^- pairs, the bond angles decreases from 109.5° as more lone pairs added. (Repulsion of Lone Pair(s) with bond electrons pushed the angle down.)

Effective Electron Pairs: - sometimes refer to as **substituents.**
- the number of lone pairs on the central atom of a molecule and the number of connections between the central atom with the outer atom(s). Each set of Multiple Bond (like double and triple bonds) count as one connection or one effective electron pair.

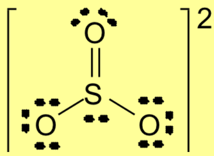
Summary of Geometrical Shape of Covalent Molecules

Around Central Atom		**Molecular Structures**	**Geometrical Shape**	**Example and Bond Angles**
Total # of Eff. e^- Pairs	**# of Lone Pairs**			
2	0		Linear	BeF_2 
3	0		Trigonal planar	BCl_3 
3	1		V-Shape (Bent)	O_3 
4	0		Tetrahedral	CH_4 

Around Central Atom		Molecular Structures	Geometrical Shape	Example and Bond Angles
Total # of Eff. e^- Pairs	# of Lone Pairs			
4	1		Trigonal pyramid	NH_3 
4	2		V-Shape (Bent)	H_2O 
5	0		Trigonal bipyramid	PF_5 
5	1		See-saw	SF_4 
5	2		T-Shape	ClF_3 

Around Central Atom		Molecular Structures	Geometrical Shape	Example and Bond Angles
Total # of Eff. e^- Pairs	# of Lone Pairs			
5	3	 	Linear	Br_3^- 
6	0	 	Octahedral	SCl_6 
6	1	 	Square pyramid	ICl_5 
6	2	 	Square planar	XeF_4 

Example 1: From Example 2c. of Sections 9.7 & 9.8, determine the geometrical shape of SO_3^{2-}. What is the possible bond angle in this polyatomic ion?



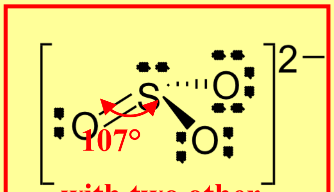
2-dimensional Lewis structure

Around the central atom (S):

1 S = O bond (1 effective e^- pair)
2 S − O bonds (2 effective e^- pairs)
1 lone pair (1 effective e^- pair)

Around S, there are 4 effective e^- pairs with 1 lone pair.

(3-Dimensional Shape – Trigonal Pyramid)

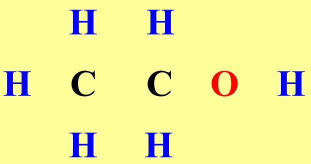


with two other resonance structures

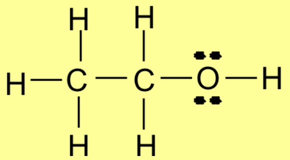
Molecular Geometry of More than One Central Atom: - describe the geometry for each central atom.

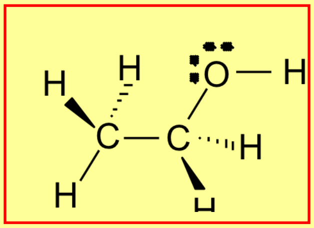
Example 2: Determine the geometrical shape of ethanol around each central atom. What are the possible bond angles in this molecule?

Ethanol (C_2H_5OH)
$8e^-$ (2 C atoms)
+ $6e^-$ (6 H atoms)
+ $6e^-$ (1 O atom)
$20e^-$ Total
− $16e^-$ (8 bonds)
$4e^-$ Left
− $4e^-$ (lone-pairs on O for octet)
$0e^-$



Note that the chemical formula, C_2H_5OH eludes how the atoms are arranged in the molecule.



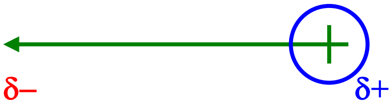


Around each central atom (C), **there are 4 effective e^- pairs (4 single bonds) and no lone pair.** *(Geometrical Shape – Tetrahedral around each central C)*

Around the O atom, **there are 4 effective e^- pairs (2 single bonds with two lone pairs).** *(Geometrical Shape – Bent around each O)*

10.2: Dipole Moments

Dipole Moments (Dipolar): - the direction of the charge distribution of a polar molecule.
- the length of the vector indicates the strength of the relative bond polarity, whereas the arrow head indicates the direction of the higher electronegative atom (negatively shifted).

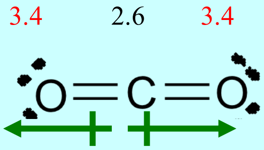


δ– **Negative Pole (More Electronegative)**

δ+ **Positive Pole (Less Electronegative)**

Example 1: Draw the molecular structures. Determine the dipole moments (if any) and their overall polarity of the following molecules.

a. CO_2

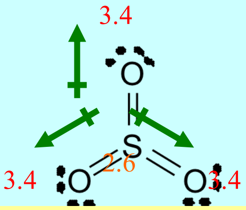


Electronegativities
C = 2.6 O = 3.4

Dipole Moment
C=O Bond = 3.4 − 2.6
C=O Bond = 0.8

Overall, CO_2 is Non-Polar. Both dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.

b. SO_3



Electronegativities
S = 2.6 O = 3.4

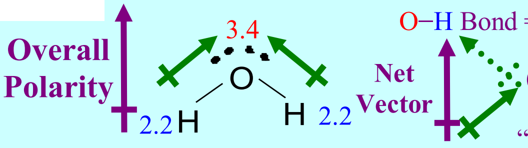
Dipole Moment
S=O Bond = 3.4 − 2.6
S=O Bond = 0.8

Overall, SO_3 is Non-Polar. All dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.

c. H_2O

Electronegativities
H = 2.2 O = 3.4

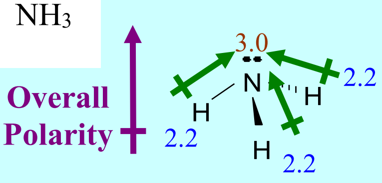
Dipole Moment
O−H Bond = 3.4 − 2.2
O−H Bond = 1.2



Vectors (arrows) are added by "head to tail".

Overall, H_2O is Polar. Both dipole moments are the same, **but** there are two lone pairs on the central atom. The dipole moments do **NOT** cancel out due to the **bent** geometry of the molecule. The overall polarity of H_2O points towards the oxygen atom.

d. NH_3



Electronegativities
H = 2.2 N = 3.0

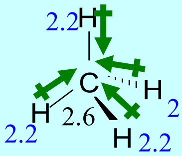
Dipole Moment
N−H Bond = 3.0 − 2.2
N−H Bond = 0.8

Overall, NH_3 is Polar. All dipole moments are the same, **but** there is a lone pair on the central atom. The dipole moments do **NOT** cancel out due to the **trigonal pyramid** geometry of the molecule. The overall polarity of NH_3 points towards the nitrogen atom.

e. CH_4

Electronegativities
H = 2.2 C = 2.6

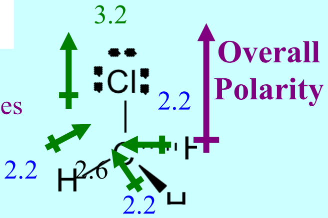
Dipole Moment
C−H Bond = 2.6 − 2.2
C−H Bond = 0.4



Overall, CH_4 is Non-Polar. All dipole moments are the same **and** the central atom has no lone pair. Hence, the dipole moments cancel out.

f. CH_3Cl

Electro-negativities
H = 2.2
C = 2.6
Cl = 3.2



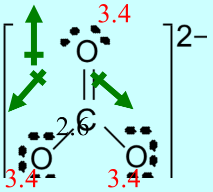
Dipole Moments
C−H Bond = 2.6 − 2.2
C−H Bond = 0.4

C−Cl Bond = 3.2 − 2.6
C−Cl Bond = 0.6

Overall, CH_3Cl is Polar. The central atom has no lone pair, **but** not all dipole moments are the same (C−Cl bond has a different dipole moment than C−H bonds). The dipole moments do **NOT** cancel out even though it has a **tetrahedral** geometry. The overall polarity of CH_3Cl points towards the chlorine atom.

g. CO_3^{2-}

Electro-negativities
C = 2.6
O = 3.4



Dipole Moments
C=O Bond = 3.4 − 2.6
C=O Bond = 0.8

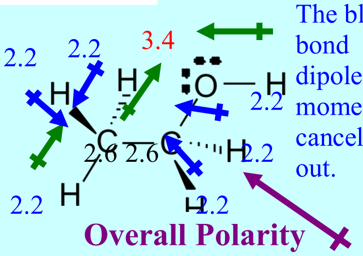
C−O Bond = 3.4 − 2.6
C−O Bond = 0.8

Overall, CO_3^{2-} is Non-Polar. All dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.
Note: A polyatomic ion does *NOT* automatically mean that it is polar! The negative charges in this case are spread evenly over the entire structure.

Assignment
10.1 pg. 349−350 #2 to 5, 7 to 12
10.2 pg. 350 #14, 15, 20 to 22

h. C_2H_5OH

Electronegativities: C = 2.6, H = 2.2, O = 3.4



The blue bond dipole moments cancel out.

Dipole Moments
C−H Bond = 2.6 − 2.2
C−H Bond = 0.4

C−O Bond = 3.4 − 2.6
C−O Bond = 0.8

O−H Bond = 3.4 − 2.2
O−H Bond = 1.2

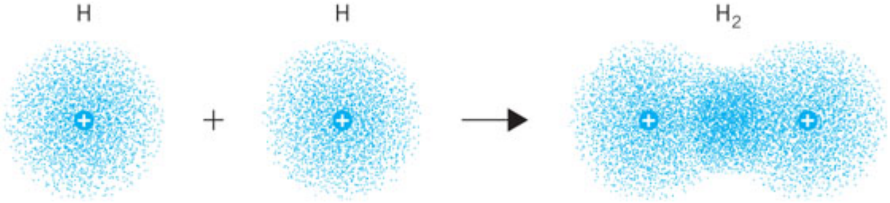
Overall, C_2H_5OH is Polar. The central C atoms have no lone pair, **but** not all dipole moments are the same (C−H bonds have a different dipole moment than C−O bond as well as O−H bond). In addition, there are two lone pairs on the oxygen atom (which can be viewed as a kind of a central atom as well). The dipole moments do **NOT** cancel out even though it has a **tetrahedral** geometry. (It **has a bent geometry** around the oxygen atom.) The overall polarity of C_2H_5OH points towards the oxygen atom.

12.2: Intermolecular Forces

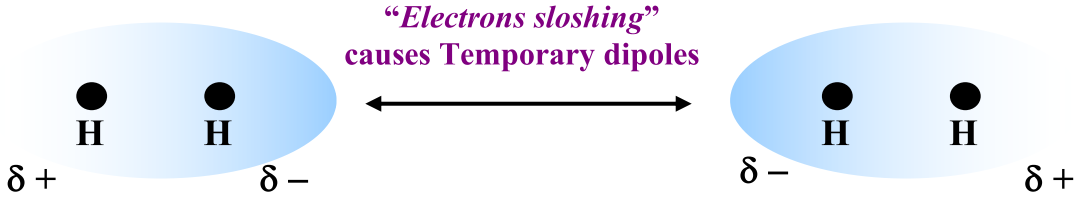
Intermolecular Forces: - attraction forces between molecules in a compound
- **the strengths of the intermolecular forces explain the physical properties of compounds (solubility, boiling and freezing points).**

a. **van der Waals Forces**: - Johannes van der Waals studied real gases and molecular interactions.
- there are two kinds of van der Waals forces.
- they are **Dispersion Forces** and **Dipole-Dipole Interactions**.

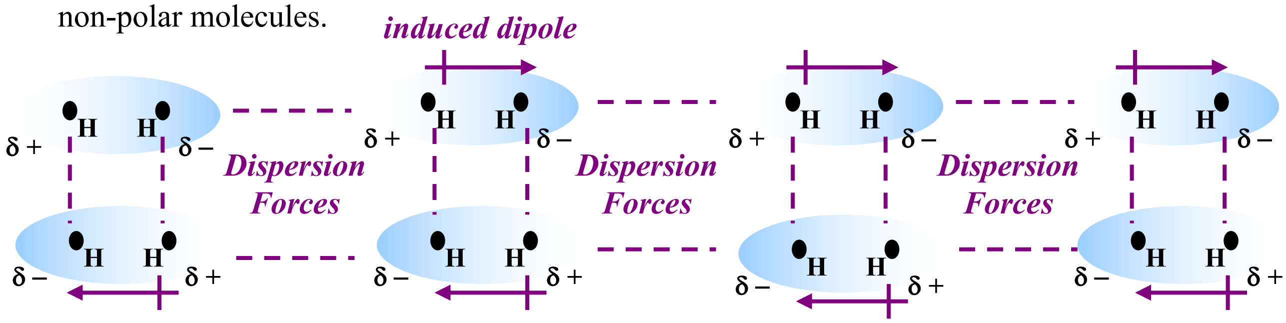
i. **Dispersion Forces**: - also known as **London Dispersion Forces** (named after Fritz London who first proposed how this force works).
- on average, the non-polar molecules do not have any permanent dipoles like polar molecules



- the "*dispersion*" is the **temporary dipole** that forms within the molecules even in non-polar molecules due the constant motions of electrons. In one instance, they can move to one side of the molecule making it temporary polar. In another instance, electrons will move and the direction of this temporary dipole will switch.



- **This constant "sloshing around" of electrons causes non-polar molecules to have these temporary dipoles**. These temporary "*induced*" dipoles are what cause the attractions between non-polar molecules.



- even monoatomic element like Neon has London Forces.
  (Check out video at https://www.youtube.com/watch?v=3t1Jn_jrsQk)

- in general, ***the higher the molar mass or the more electrons there are in a molecule*, *the stronger the London Dispersion Force* (attraction between molecules – intermolecular force). *This causes an increase in melting and boiling points of the chemical*.**

-*Note:* All molecules have electrons. Hence, ALL molecules have London Dispersion Force.

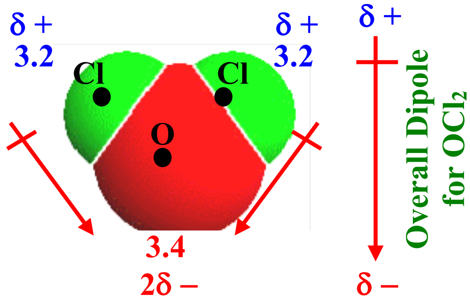
# of e^- or molar mass in atom or molecule ↑, London Dispersion Force ↑, Melting and Boiling Point ↑

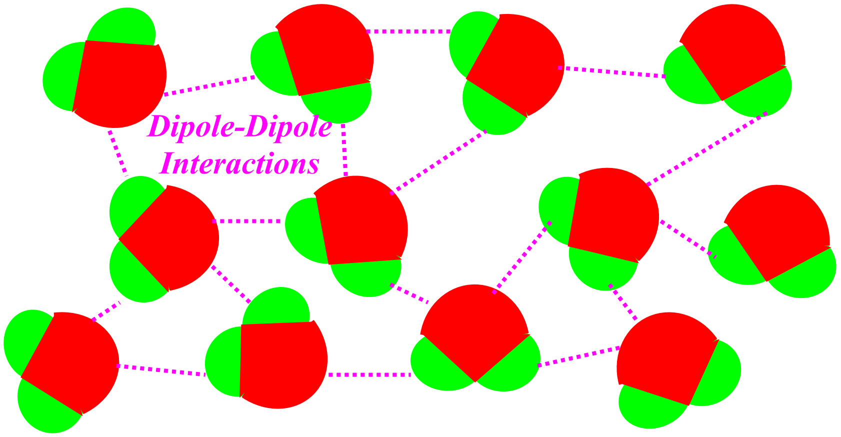
Example 1: Explain the boiling points and the melting points of the noble gases.

Noble Gases	# of e^-	Molar Mass (g/mol)	Melting Point	Boiling Point
He	2	4.00	–272°C (1 K)	–269°C (4 K)
Ne	10	20.18	–249°C (24 K)	–246°C (27 K)
Ar	18	39.95	–189°C (84 K)	–186°C (87 K)
Kr	36	83.80	–157°C (116 K)	–153°C (120 K)
Xe	54	131.29	–112°C (161 K)	–108°C (165 K)
Rn	86	222.00	–71°C (202 K)	–62°C (211 K)

All atoms of noble gases are monoatomic non-polar. The only intermolecular force that governs the melting and boiling points is the London Dispersion Force. As the number of electrons in the noble gases increase, London dispersion force makes the attraction between the atoms greater. This in turn has an effect of increasing the boiling and melting point of the noble gas as one goes down the column.

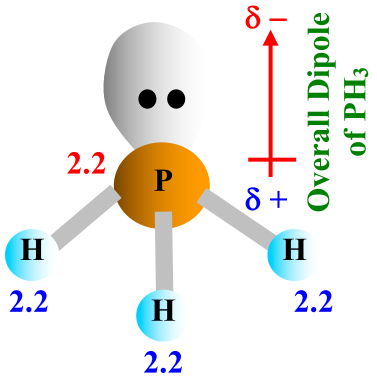
ii. **Dipole-Dipole Interaction**: - also known as simply **Dipole Interaction** or Dipole-Dipole Force
- intermolecular forces resulted from polar molecules.
- dipole interaction is **much stronger than Dispersion Force**.

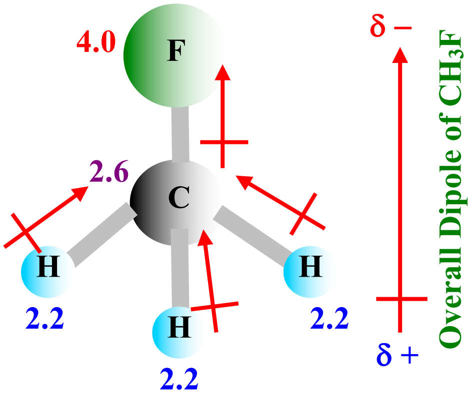




Example 2: Order the boiling points from the least to greatest for the following compounds with similar molar mass. PH_3 (34.00 g/mol), CH_3F (34.04 g/mol), and SiH_4 (32.13 g/mol)

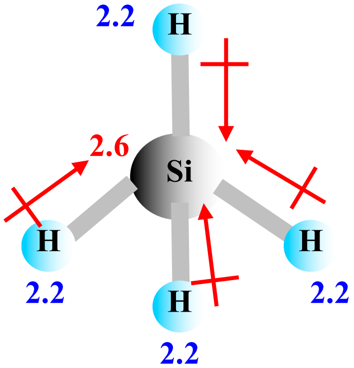
Since PH_3, CH_3F and SiH_4 have similar molar mass; any differences in boiling points cannot be due to London Dispersion forces. Since dipole-dipole interactions exist in polar molecules, we have to examine the molecular geometry and structure of each compound.





PH_3 has a trigonal pyramid geometry (VSEPR) and is Polar. Even though the P−H bonds have no polarity (electronegativities of P and H are the same), the lone pair on one end of the P atom causes an uneven distribution of electrons.

CH_3F has a tetrahedral geometry and is very polar. The C−F bond along with the C−H bonds has strong polarity. The overall dipole moment for the molecule has electrons around the F atom.



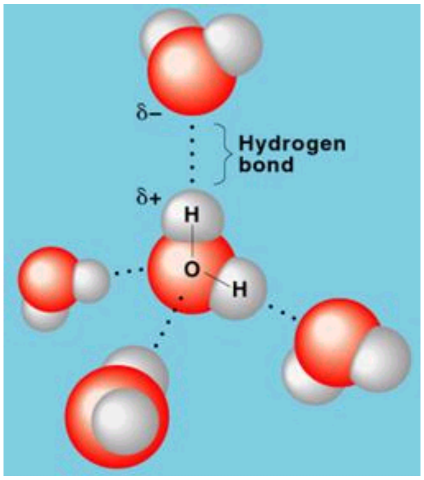
SiH_4 has a tetrahedral geometry with equal dipoles of Si−H bonds cancels out all bond polarities. Hence, SiH_4 is Non-Polar.

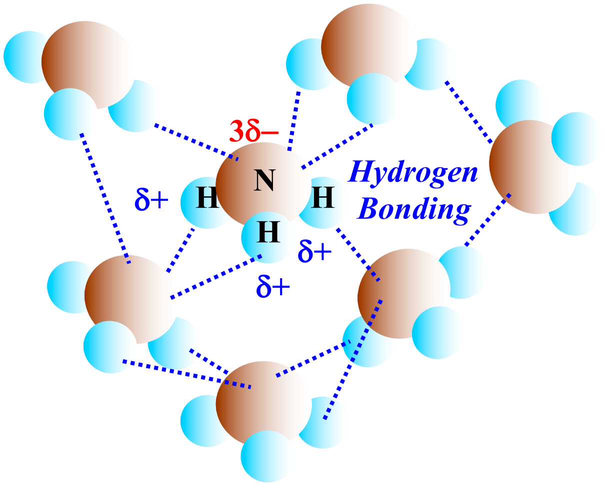
Since non-polar molecules have no dipole interactions, SiH_4 should have the lowest boiling point. PH_3 is less polar than CH_3F due to the difference in electronegativities between P−H bond and C−F with C−H bonds. Therefore, CH_3F must have the highest boiling point.

Boiling Point: $SiH_4 < PH_3 < CH_3F$

b. **Hydrogen Bonds**: - are intermolecular bonds that involve **hydrogen atom with very electronegative atom that also consists of lone pairs**.

- these **include O–H, N–H, and H–Cl and H–F bonds**.
- the resulting molecule is always polar. Therefore, **all hydrogen bonding molecules also have dipole interactions**.
- hydrogen bond is the **STRONGEST** of the intermolecular bonds **amongst molecular compounds**.



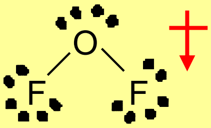


(Check out the Hydrogen Bond Animation at http://www.northland.cc.mn.us/biology/Biology1111/animations/hydrogenbonds.html)

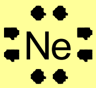
Example 3: Account for the differences in the boiling points of the compounds listed below.

Chemical	**Molar Mass (g/mol)**	**London Dispersion Forces**	**Dipole Interactions**	**Hydrogen Bonds**	**Boiling Point**
OF_2	54.00	✓	✓	✗	**–145°C (128 K)**
Ne	20.18	✓	✗	✗	**–246°C (27 K)**
HF	20.01	✓	✓	✓	**19°C (292 K)**
H_2O	18.02	✓	✓	✓	**100°C (373 K)**
NH_3	17.04	✓	✓	✓	**–33°C (240 K)**
CH_4	16.05	✓	✗	✗	**–161°C (112 K)**

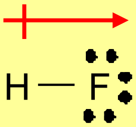
Again, we need to draw the structural formulas of these molecules and compare their polarities.



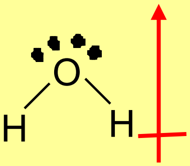
OF_2 is polar with dipole interactions



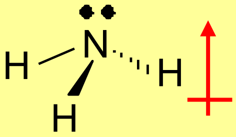
Ne is non-polar with dispersion forces only



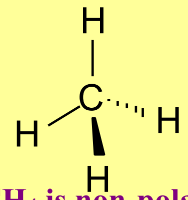
HF is polar with hydrogen bonds



H_2O is polar with hydrogen bonds



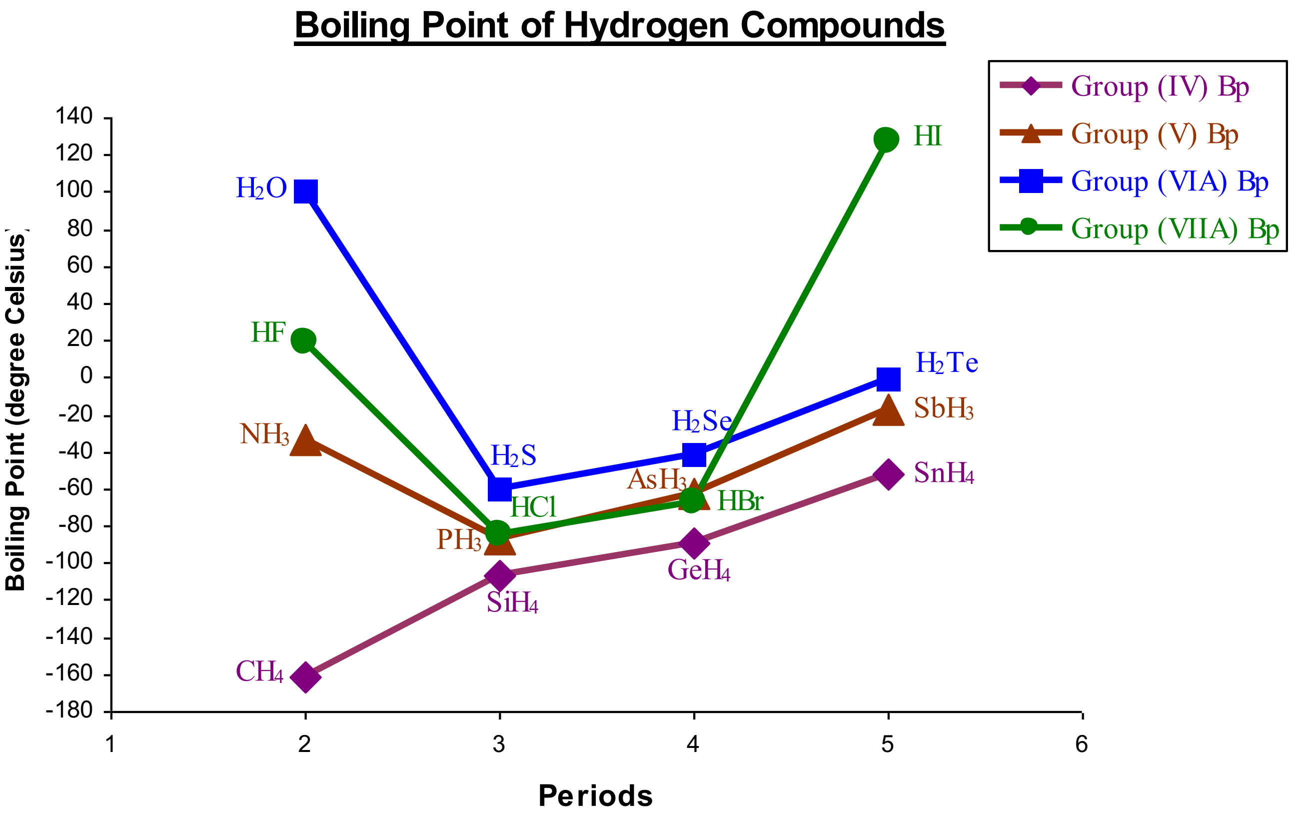
NH_3 is polar with hydrogen bonds



CH_4 is non-polar with dispersion forces only

Notice that the hydrogen bond molecules (HF, H_2O and NH_3) have boiling points much higher than molecule with just dipole interactions (OF_2) and the ones with only London Dispersion Forces (Ne and CH_4).

Example 4: Given the graph below on the boiling points of hydrogen compounds with different group series, explain the following using the concepts of chemical bonding.



Boiling Point of Hydrogen Compounds

a. The hydrogen compounds in the Group (VIA) series have higher boiling points than hydrogen compounds in the other series.

b. The first hydrogen compounds in Groups (VA), (VIA) and (VIIA), namely NH_3, H_2O and HF, have higher boiling points than most other hydrogen compounds in their respective series. On the other hand CH_4 has a lowest boiling point in its own Group (IVA) series.

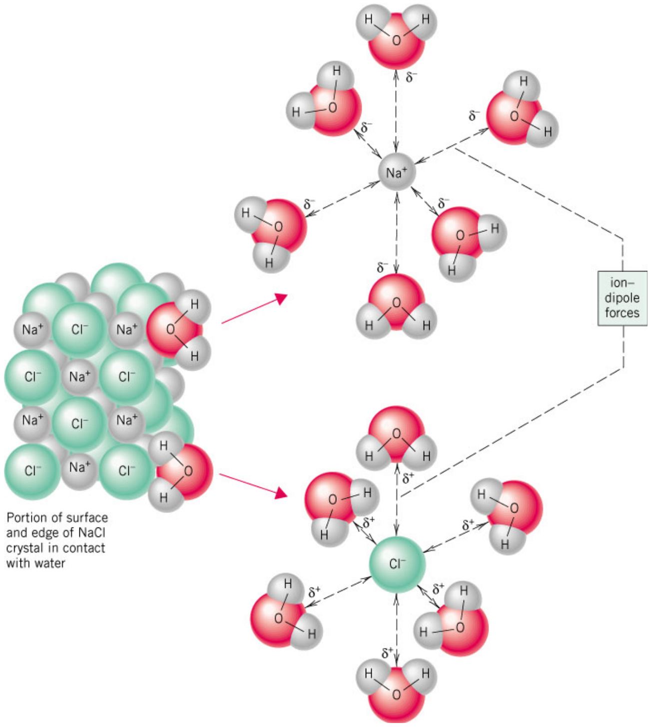
a. All hydrogen compounds in the Group (VIA) series are very polar and most have hydrogen bonds. The V-shape molecules characterized in Group (VIA) create a greater dipole moment than other series (Group (VA) with its trigonal pyramid shape and Group (VIIA) with its linear form). On the other hand, all hydrogen compounds in the Group (IVA) series are non-polar and only have London dispersion forces. Since hydrogen bonds are stronger intermolecular forces than London dispersion forces, the hydrogen compounds in the Group (IVA) series have the lowest boiling points than the counterparts in the other series.

b. NH_3, HF and H_2O have stronger hydrogen bonds than most other hydrogen compounds in their series. The difference between the electronegativities with H is the greatest in row 2 (Electronegativities increase from left to right and from bottom to top of the Table). This huge difference in electronegativities in NH_3, HF and H_2O is what causes their boiling points to *buckle the trend*. After NH_3, HF and H_2O the rest of the hydrogen compounds in the respective series follow the effect of London dispersion forces, the higher the molar mass, the stronger the dispersion forces, and the increase in boiling points is the result.

CH_4 in the Group (IVA) series do not buckle the trend because the entire series are non-polar. The only intermolecular force at work is the London dispersion force. Hence, CH_4 has a lower boiling point than SiH_4.

c. Ion-Dipole Force: - when ionic compounds dissolve in water, the cation and anion components separate from one another. These ions are then attracted by the polar water molecules.
- ion-dipole force is the **STRONGEST of all intermolecular forces.**

Example: Sodium Chloride (Salt) $\mathrm{NaCl}_{(s)} \xrightarrow{H_2O} \mathrm{Na}^+_{(aq)} + \mathrm{Cl}^-_{(aq)}$



Summary of Intermolecular Forces

1. **Intermolecular Forces involve in a compound explain its physical properties such as solubility (“*like dissolves like*”), boiling and melting points (energy involved in physical phase change).**
2. **van der Waals Forces consist of London Dispersion forces (apply to all molecules) and Dipole Interactions (apply to polar molecules).**
3. **Hydrogen Bond** is the **STRONGEST** of the intermolecular bonds **amongst molecular compounds**
4. **Ion-Dipole Force is the *strongest* of all intermolecular bonds.**

Strength of Intermolecular Forces

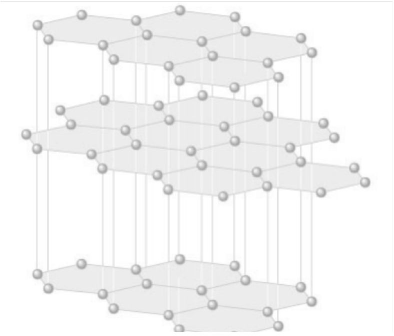
$$\text{Ion-Dipole Force} > \text{Hydrogen Bond} > \overbrace{\text{Dipole Interaction} \gg \text{London Dispersion Force}}^{\text{van der Waals Forces}}$$

>> (much stronger than)

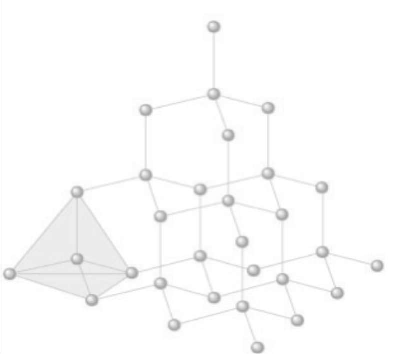
Properties of Covalent Crystalline Solids *(Metalloid Network Covalent)*

1. **Metalloids**: - consists of elements near the "*staircase*" of the Table (Examples are carbon in a form of diamond and silicon dioxide in a form of quartz crystal).
2. **Three-Dimensional Network Solids** as they **form giant molecules by directional covalent bonding** (contains **no discrete molecular units where an array or network of atoms are held together by conventional covelent bonds,** which are directional with dipoles **of neighboring atoms**.
3. **Covalent Compounds / Elements are Hard and have High Melting Points.** This is due to a more organized crystalline structure and covalent bonds are strong intramolecular bonds.
4. **Covalent Compounds are Relatively Poor Heat and Electric Conductors (or Good Heat or Electric Insulators).** Covalent compounds do not have any charge particles like ions. Therefore, they cannot conduct heat and electricity well. *An exception is silicon elements*. (Silicon has smaller networks than diamonds, allowing some electrons to pass through. Hence, **silicon is called a semiconductor**.)

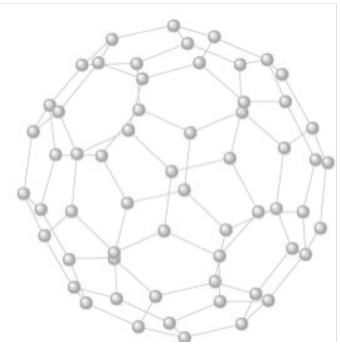
Example: Alloptropes of Carbon



Carbon as *Graphite* has *weak layered with delocalized bonding network* (only some carbon atoms are connected – for each layer is $2sp^2$ hybridized which explains its hardness and brittleness). The layers are connected by weak van der Waal forces and hence, graphite can be slippery to the touch. For this reason, we can use it as a lubricant.



Carbon as *Diamond* has *strong tetrahedral network* ($2sp^3$) where all four bonding sites of each carbon atoms are connected. Hence, diamond is the hardest material known, and it has an extremely high melting point (3550°C).



Carbon Network as C_{60}, *Buckminsterfullerene*, was discovered in 1985. *Fullerenes* are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane.

Properties of Molecular Crystalline Solids

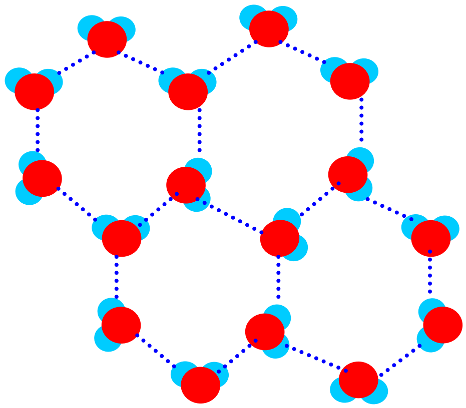
1. **Molecular Compounds tend to have much Lower Boiling and Melting Points than ionic compounds.** This is because solid molecular compounds use **weak intermolecular forces to form their lattice structures**, which does not take much energy to break them. Their boiling points are lower than ionic compounds because there are **no ion interactions in liquid state, only intermolecular forces**.
2. **Molecular Compounds are Soft.** Again, molecular compounds **have a weak lattice structure made of intermolecular bonds** that makes them soft.

3. **Some Molecular Compounds and Elements tend to be More Flammable than ionic compound.** This is due to the some non-metals like sucrose and sulfur, which **combine readily with oxygen in combustion reactions**.

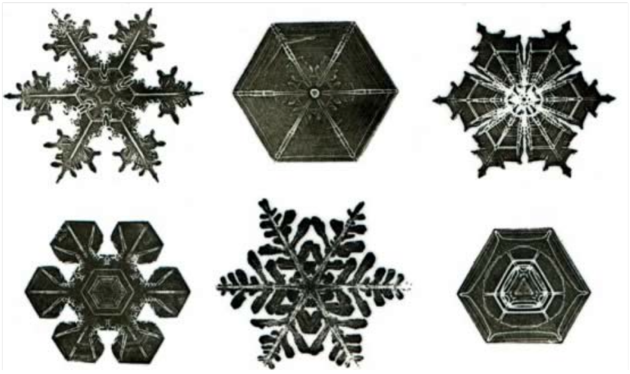
4. **Most Molecular Compounds are Insoluble in Water.** Because **water is very polar,** and it has lots of hydrogen bonds, it can only dissolve molecular compounds that are polar as well "***Like Dissolves Like***". Since **most molecular compounds are fairly non-polar**, they do not dissolve in polar water well.

5. **Molecular Compounds do NOT Conduct Electricity in their Solid States** due to a lack of delocalized electrons.

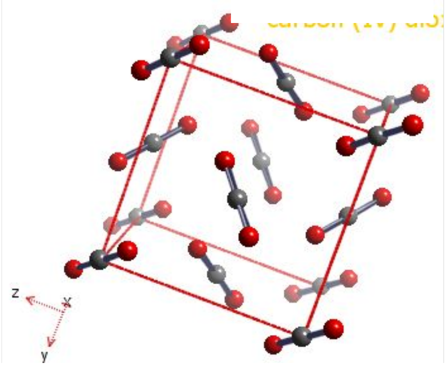
6. **Soluble Molecular Compounds do NOT Conduct Electricity in Water.** This is simply due to the fact that molecular compounds **do not dissociate into ions or electrolytes** like soluble ionic compounds do.



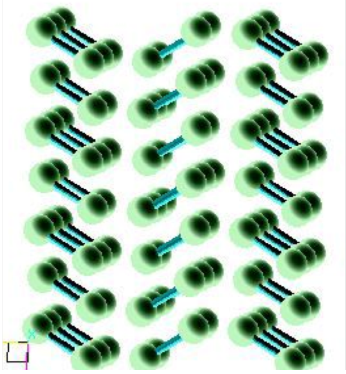
Due to the hydrogen bonds in water, it forms a *honeycomb shape* and expands in volume when it crystallizes into ice.



Even though no two snowflakes are alike, all of them have a basic hexagonal shape as dictated by the bent shape of water molecule and its hydrogen bonds.



Dry Ice, $CO_{2\,(s)}$, is a covalent compound that has a crystalline structure.



Even a halogen like $I_{2\,(s)}$ has a crystalline structure.

Phosphorus, $P_{4\,(s)}$ can form crystalline structure.

Assignment

12.2 pg. 418–422 #2, 3, 6 to 10, 12 to 19, 31, 32, 63, 64, 101; pg. 448 #9