Unit 2: Chemical Bonding and Organic Chemistry

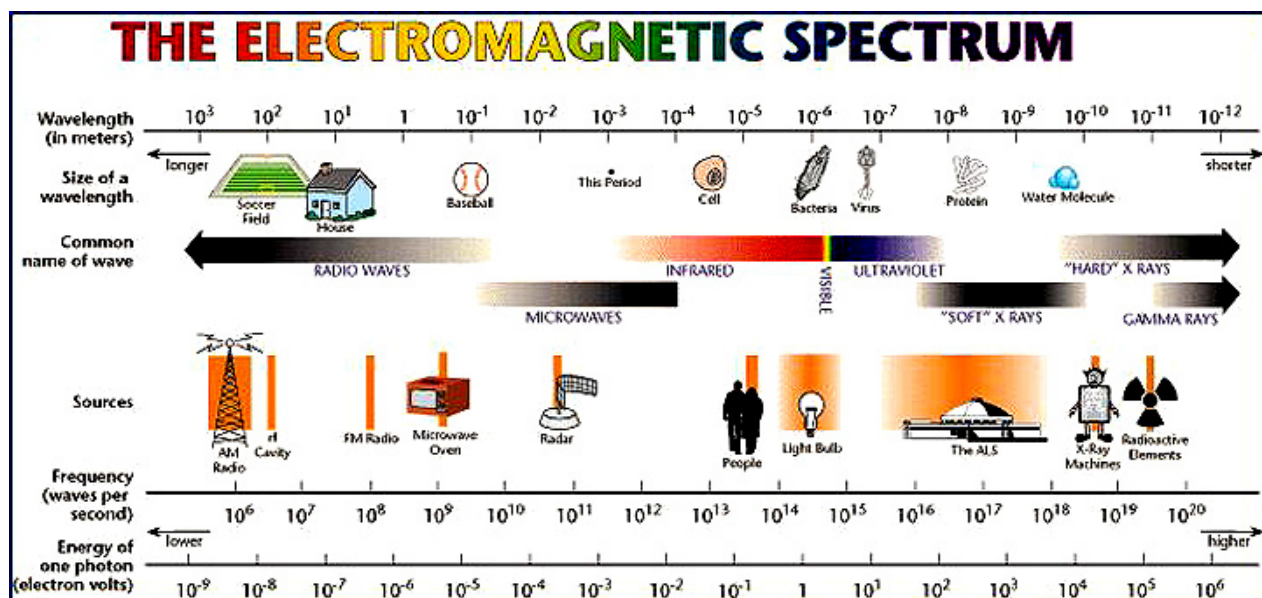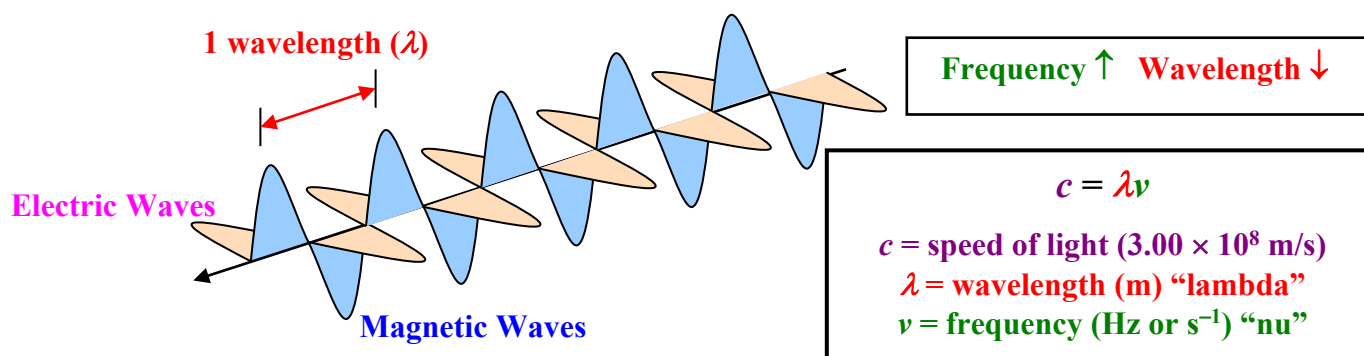## Chapter 7: Quantum Theory and the Electronic Structure of Atoms

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

1 wavelength (λ)

Electric Waves

Magnetic Waves

Frequency ↑ Wavelength ↓

$$c = \lambda v$$

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

THE ELECTROMAGNETIC SPECTRUM

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

Example 1: One of the spectral lines of hydrogen has a wavelength of 410. nm. Determine its frequency.

$c = 3.00 \times 10^8$ m/s

$\lambda = 410.$ nm $= 410 \times 10^{-9}$ m

$v = ?$

$c = \lambda v$

$v = \dfrac{c}{\lambda} = \dfrac{(3.00 \times 10^8 \text{ m/s})}{(410. \times 10^{-9} \text{ m})}$

$v = 7.32 \times 10^{14}$ s^{-1} (Hz)

Example 2: What is the wavelength being broadcast by a radio station with a frequency of 102.1 MHz?

$c = 3.00 \times 10^8$ m/s

$v = 102.1$ MHz $= 102.1 \times 10^6$ s^{-1}

$\lambda = ?$

$c = \lambda v$

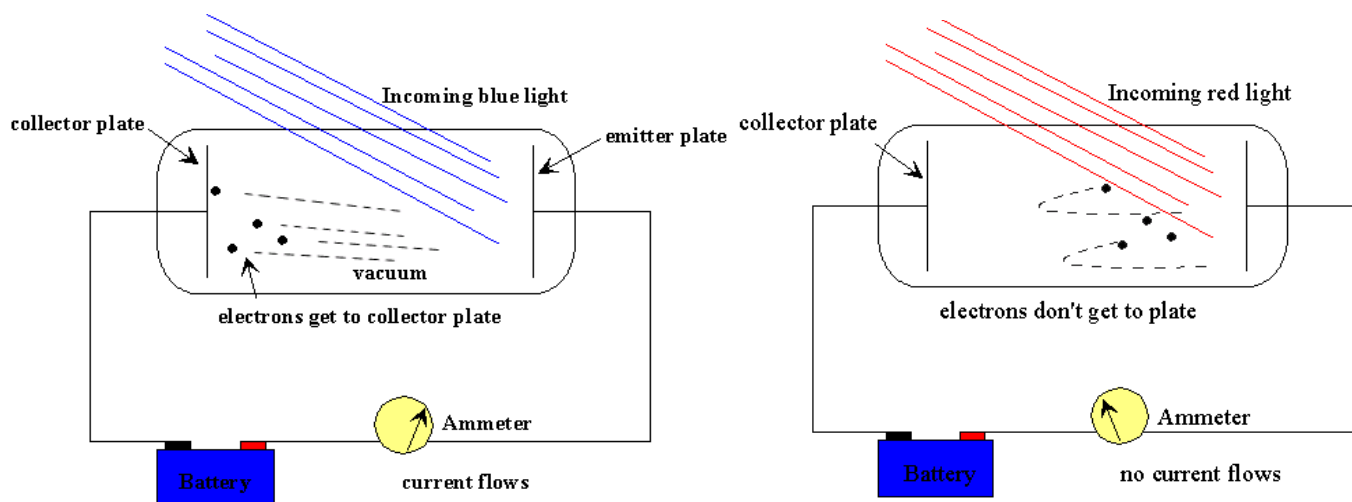$\lambda = \dfrac{c}{v} = \dfrac{(3.00 \times 10^8 \text{ m/s})}{(102.1 \times 10^6 \text{ s}^{-1})}$

$\lambda = 2.94$ m
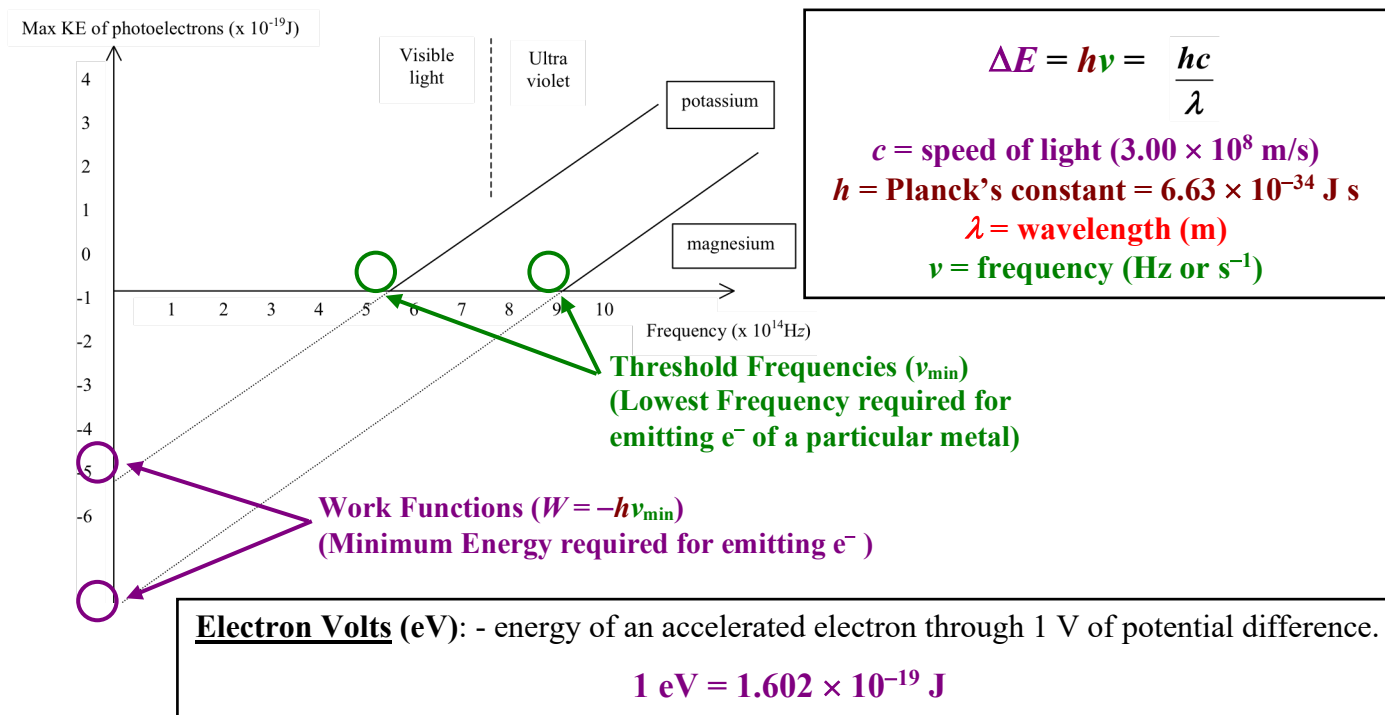
Planck's Quantum Theory

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 $\times$ 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**

Max KE of photoelectrons (x 10^{-19}J)

Visible light

Ultra violet

potassium

magnesium

Frequency (x 10^{14}Hz)

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 × 10⁸ m/s)
h = Planck's constant = 6.63 × 10⁻³⁴ J s
λ = wavelength (m)
v = frequency (Hz or s⁻¹)

Electron Volts (eV): - energy of an accelerated electron through 1 V of potential difference.

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

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

Example 1: Calculate the energy change (in J and eV) associated with the longest spectral line of hydrogen at 656 nm.

$c = 3.00 \times 10^8$ m/s
$h = 6.63 \times 10^{-34}$ J s
$\lambda = 656$ nm $= 656 \times 10^{-9}$ m
$\Delta E = ?$

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{(656 \times 10^{-9} \text{ m})}$$

$$\Delta E = 3.03 \times 10^{-19} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}$$

$$\boxed{\Delta E = 3.03 \times 10^{-19} \text{ J}}$$

$$\boxed{\Delta E = 1.89 \text{ eV}}$$

Example 2: What is the minimum frequency needed if it takes 450. kJ to remove one mole of electrons from a metal surface of a photoelectric tube?

$h = 6.63 \times 10^{-34}$ J s
$\Delta E_{min} = W = -450.$ kJ/mol
(negative because of energy input)

$v_{min} = ?$

$$\Delta E_{min} = -450. \times 10^3 \text{ J/mol} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ e}^-} = -7.47 \times 10^{-19} \text{ J}$$

$$W = -hv_{min} \qquad v_{min} = \frac{W}{h} = \frac{(-7.47 \times 10^{-19} \text{ J})}{(6.63 \times 10^{-34} \text{ J s})}$$

$$\boxed{v_{min} = 1.13 \times 10^{15} \text{ s}^{-1}}$$

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).

Assignment
**7.1 pg. 312–313 #2, 4, 8, 10, 12**
7.2 pg. 313 #14 to 20 (even)

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.
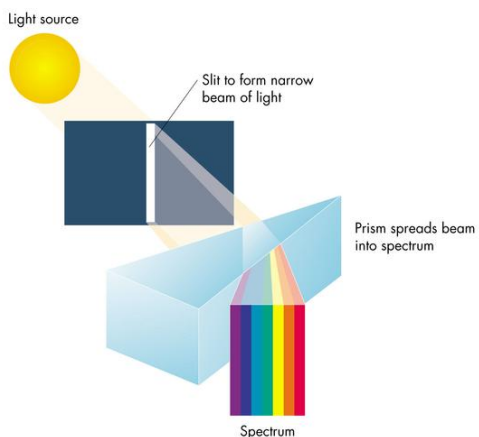
(Left) A single prism breaks up white light into the visible spectrum. (Right) A diffraction grating is able to generate series of visible spectrum due to the uneven surface.
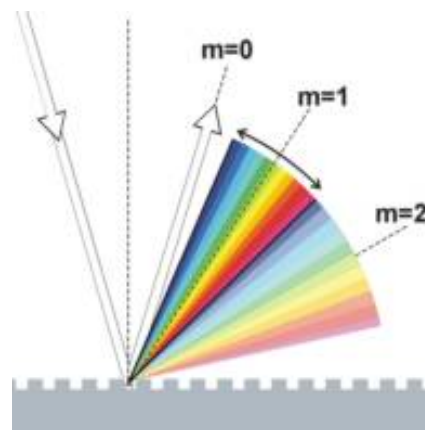
Spectroscope: - a device to break down light into its component colours using a diffraction grating

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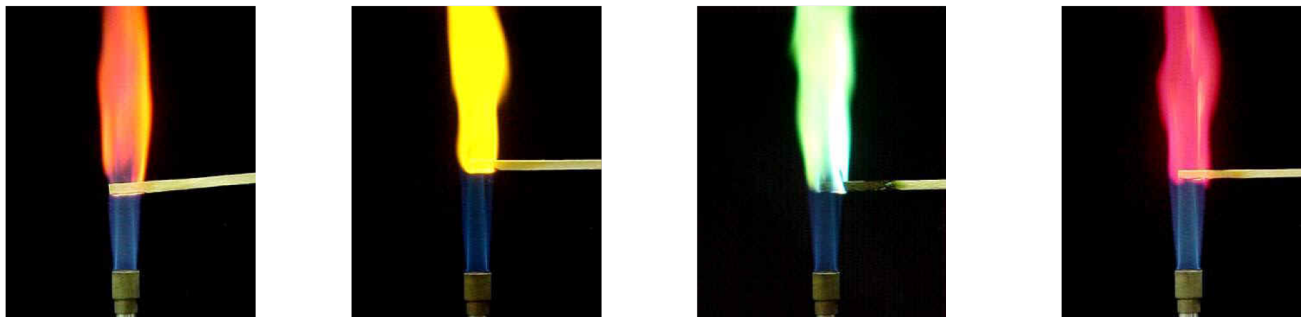
From left to right: Lithium, Sodium, Copper, and Strontium compounds produce different colours during the flame tests

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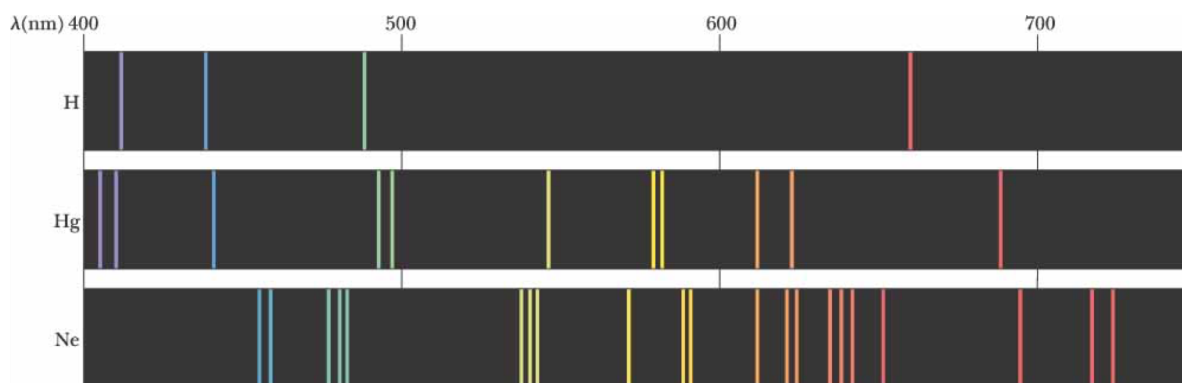
(Above) The atomic spectrums of hydrogen, mercury and neon. The scale indicates the wavelength of these lines in nanometre.

The Hydrogen Spectrum

$E_5 = -8.72 \times 10^{-20} \text{J}$

$E_4 = -1.36 \times 10^{-19} \text{J}$

Brackett series $n_f = 4$

Paschen series $n_f = 3$

$E_3 = -2.42 \times 10^{-19} \text{J}$

$E_2 = -5.45 \times 10^{-19} \text{J}$

Balmer series $n_f = 2$

Hydrogen Spectrum at Visible range

$E_1 = -2.18 \times 10^{-18} \text{J}$

Lyman series $n_f = 1$

656.3 nm   486.1 nm   434.0 nm

410.2 nm
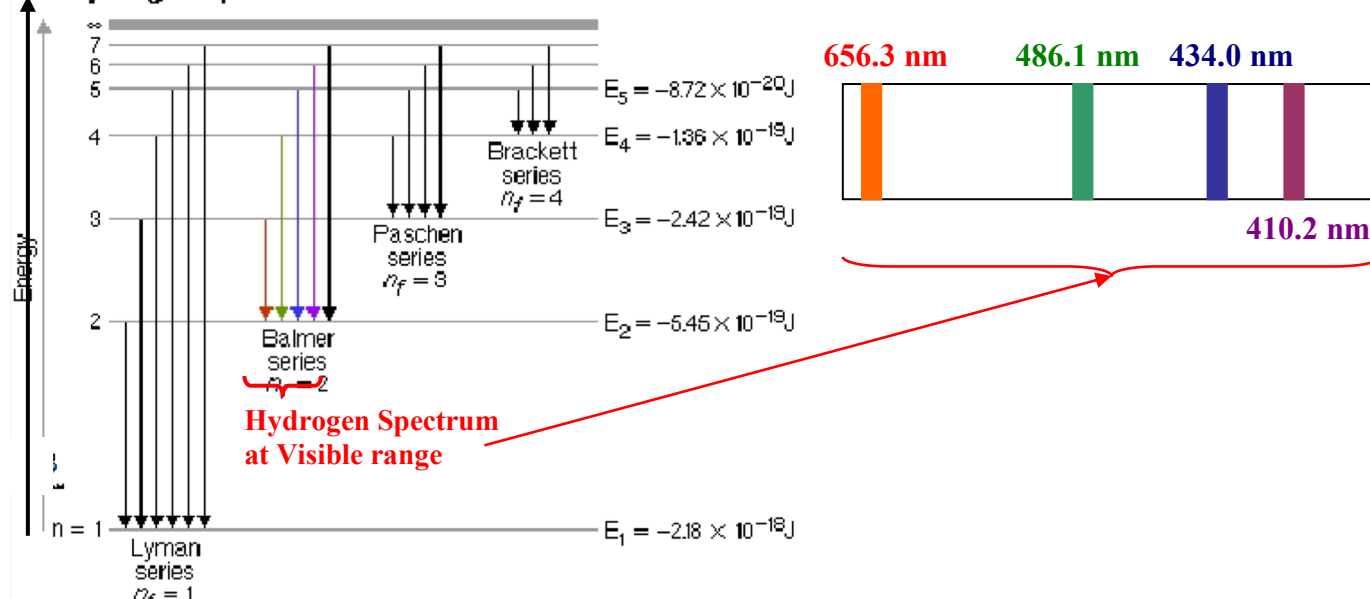
Absorption Spectra: - EM-frequencies that are absorbed by an object from a continuous source of energy (appears as dark lines on a multi-color background).
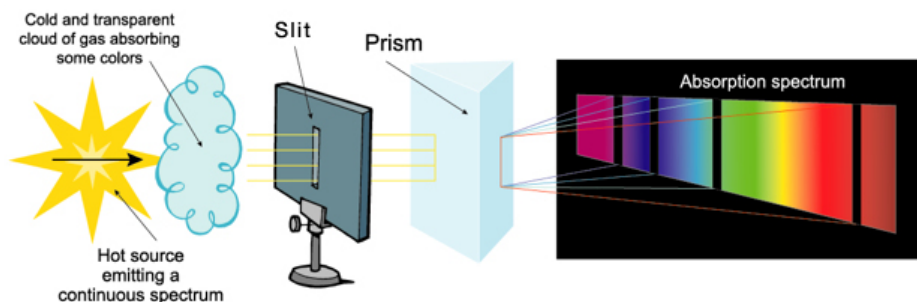
Quantum Model: - proposed by Niels Bohr, electron in hydrogen atom moves around the nucleus in specific circular orbits, which have certain energies.

- **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.**

$E_\infty = 0$ J $n = \infty$

$n = 6$
$n = 5$
$n = 4$
$n = 3$
$n = 2$

$E_1 = -2.178 \times 10^{-18}$ J
$n = 1$ **Ground State**
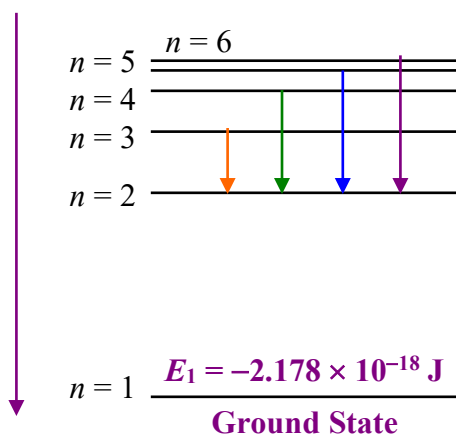
Bohr's Hydrogen Energy Level

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

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)**

Example 1: Verify that the blue line (434.0 nm) of the visible part of the hydrogen spectrum is indeed from the emission of energy of an electron moving from the 5th orbit to the 2nd orbit.

$\Delta E = E_f - E_i$

$\Delta E = \dfrac{-2.178 \times 10^{-18} \text{ J}}{n_f^2} - \dfrac{-2.178 \times 10^{-18} \text{ J}}{n_i^2}$

$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\dfrac{1}{n_f^2} - \dfrac{1}{n_i^2} \right)$

$\Delta E_{5 \to 2} = -2.178 \times 10^{-18} \text{ J} \left(\dfrac{1}{2^2} - \dfrac{1}{5^2} \right)$

$\Delta E_{5 \to 2} = -4.5738 \times 10^{-19}$ J ($\Delta E < 0$ means energy is released)

$\Delta E_{5 \to 2} = \dfrac{hc}{\lambda}$

$\lambda = \dfrac{hc}{\Delta E_{5 \to 2}}$

$\lambda = \dfrac{(6.63 \times 10^{-34} \text{ J s})(3.00 \times 10^8 \text{ m/s})}{(4.5738 \times 10^{-19} \text{ J})}$
(Using net energy change)

$\lambda = 4.3487 \times 10^{-7}$ m   **$\lambda = 434.9$ nm**

(It is fairly close to the measured value of 434.0 nm.)

Example 2: Determine the ionization energy (from ground state to infinity) of hydrogen in J and in eV. Explain the meaning of the sign in the calculated value.

$$\Delta E = E_f - E_i$$

$$\Delta E = \frac{-2.178 \times 10^{-18}\,\text{J}}{n_f^2} - \frac{-2.178 \times 10^{-18}\,\text{J}}{n_i^2} = -2.178 \times 10^{-18}\,\text{J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$\Delta E_{1 \to \infty} = -2.178 \times 10^{-18}\,\text{J} \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) \qquad \text{(Note: } \frac{1}{\infty^2} \approx 0 \text{)}$$

$$\Delta E_{1 \to \infty} = -2.178 \times 10^{-18}\,\text{J}\,(0 - 1)$$

$$\boxed{\Delta E_{1 \to \infty} = 2.178 \times 10^{-18}\,\text{J}} \qquad (\Delta E > 0 \text{ means energy is absorbed)}$$

$$\Delta E_{1 \to \infty} = 2.178 \times 10^{-18}\,\text{J} \times \frac{1\,\text{eV}}{1.6 \times 10^{-19}\,\text{J}} \qquad \boxed{\Delta E_{1 \to \infty} = 13.61\,\text{eV}}$$

Assignment
7.3 pg. 313−314 #23, 24 to 34 (even)

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)

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

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

| **Mass Equivalence of a Photon** |
| :---: |
| $m = \dfrac{h}{\lambda c}$ (**m** 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
$\lambda = \dfrac{h}{m\upsilon}$
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.
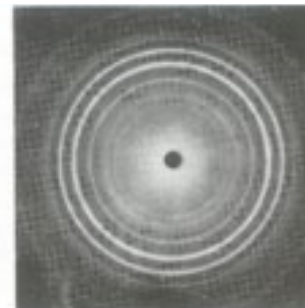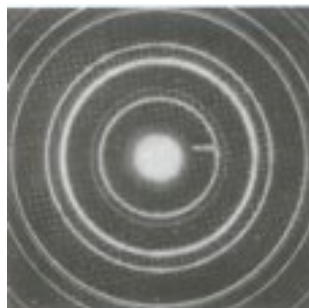
Example 1: Calculate the de Broglie wavelength of a proton with a mass of 1.67×10^{-27} kg moving at 25.0% of the speed of light.

$h = 6.63 \times 10^{-34}$ J s

$\upsilon = 0.250 \ (3.00 \times 10^8$ m/s$)$

    $= 7.50 \times 10^7$ m/s

$m = 1.67 \times 10^{-27}$ kg $\lambda = ?$

$$\lambda = \frac{h}{m\upsilon} = \frac{\left(6.63 \times 10^{-34} \text{ J s}\right)}{\left(1.67 \times 10^{-27} \text{ kg}\right)\left(7.50 \times 10^7 \text{ m/s}\right)}$$

$(1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2)$

$\lambda = 5.29 \times 10^{-15}$ m

Example 2: What is the velocity of an alpha particle (2 protons) that has a wavelength of 3.30×10^{-14} m as it is travelling towards a piece of gold foil in the Rutherford experiment?

$h = 6.63 \times 10^{-34}$ J s

$m = 2(1.67 \times 10^{-27}$ kg$)$

    $= 3.34 \times 10^{-27}$ kg

$\lambda = 3.30 \times 10^{-14}$ m

$\upsilon = ?$

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

$$\upsilon = \frac{h}{m\lambda} = \frac{\left(6.63 \times 10^{-34} \text{ J s}\right)}{\left(3.34 \times 10^{-27} \text{ kg}\right)\left(3.30 \times 10^{-14} \text{ m}\right)}$$

$(1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2)$

$\upsilon = 6.02 \times 10^6$ m/s   (about 2% of speed of light)

Assignment
7.4 pg. 314 #36 to 42 (even)

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 $\Delta x \bullet \Delta(m\upsilon) \geq \dfrac{h}{4\pi}$

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
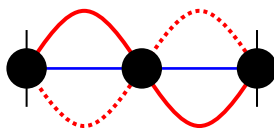5. Important People of Quantum Mechanics:
http://doctortang.com/AP%20Chemistry/Historical%20Development%20of%20Quantum%20Mechanics.pdf
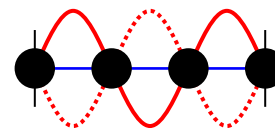
Schrödinger Wave Equation: - Schrödinger recognized that since electron can behave like waves (de Broglie), he proposed that electron could have quantized energy when it achieved a **standing wave** (wave that appears standing because it contains nodes which signifies exactly half a wavelength).
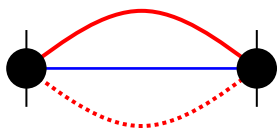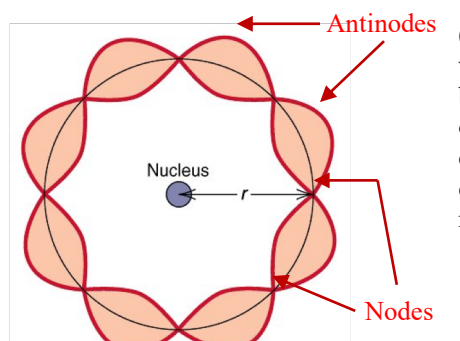
Standing Wave
(2 nodes – 1 half-λ)

Standing Wave
(3 nodes – 2 half-λ)

Standing Wave
(4 nodes – 3 half-λ)

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

Antinodes

Nucleus

Nodes

(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, …)

N = 5 4 3 2 1
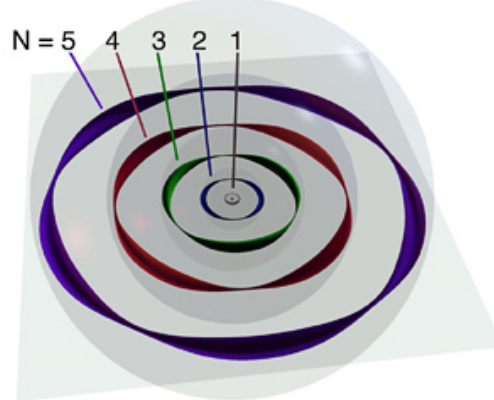
Bohr-de Broglie electron matterwave orbits
shells 1-5

Orbit

Standing electron wave

A

B
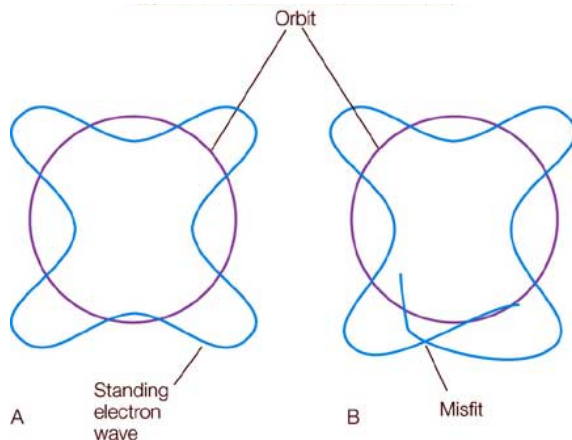
Misfit

(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.

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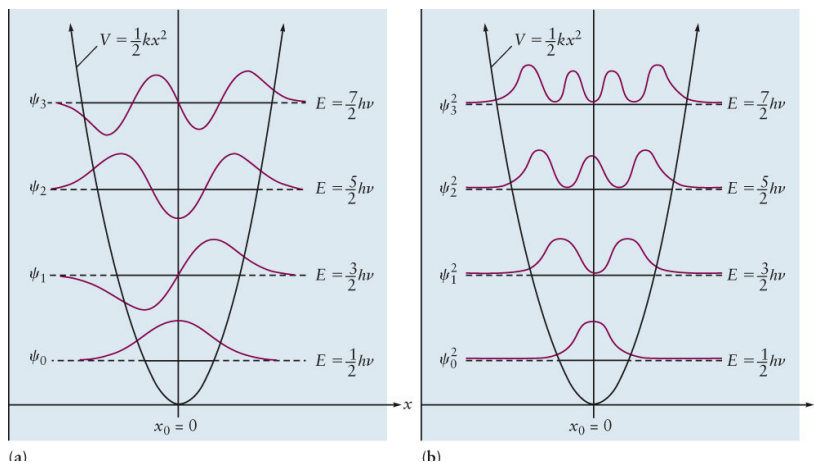
Probability Distribution (R^2): - the probability of the likely position of an electron around a nucleus.
- the probability distribution is equalled to the square of the wave function.
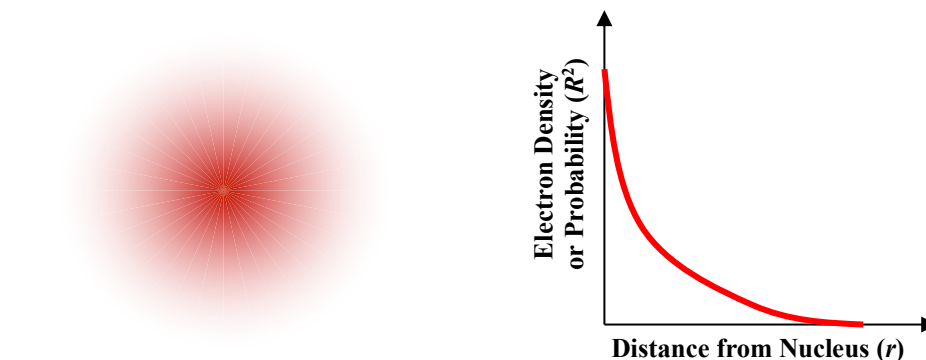
Probability Distribution

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

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

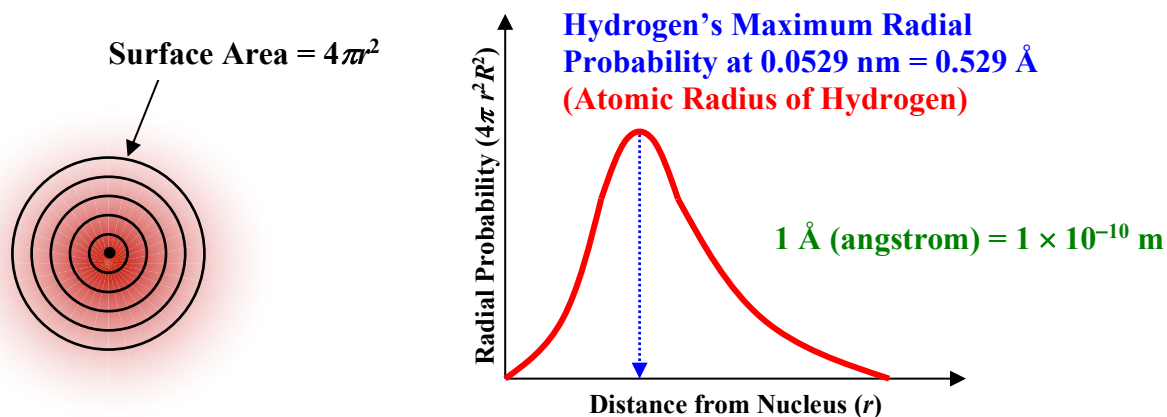(Right) (a) One Dimensional Schrödinger Wave Equations with their associated allowed energies. (b) Corresponding Probability Densities, $\psi_n{}^2(x)$.

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).

Surface Area = $4\pi r^2$

Hydrogen's Maximum Radial Probability at 0.0529 nm = 0.529 Å (Atomic Radius of Hydrogen)

1 Å (angstrom) = 1×10^{-10} m

Assignment
7.5 pg. 314 #43 to 47

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

2s orbit

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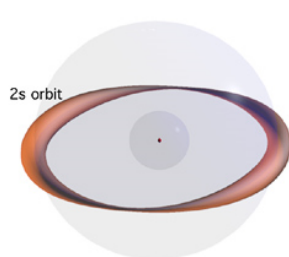
De Broglie 2nd energy level's original 2-wave orbit.
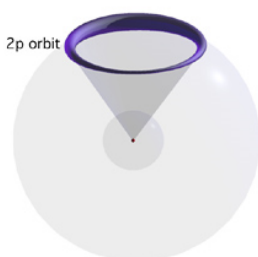
Snelson model's 2nd energy level 1-wave orbit with cone indicating its direction in space in relation to the nucleus.

1 wave orbit (3d)
2 wave orbit (3p)
3 wave orbit (3s)
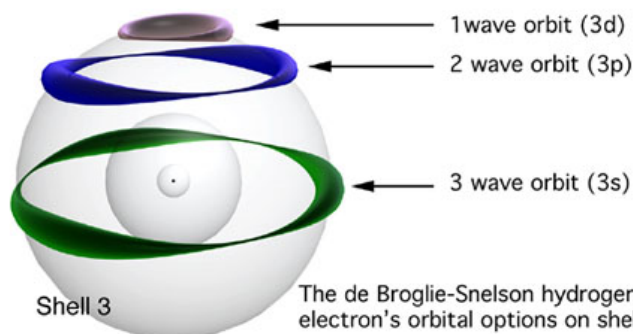
Shell 3

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

The hydrogen electron's orbital options for five energy levels

1s 2s 2p 3s 3p 3d 4s 4p 4d 4f 5s 5p 5d 5f 5g

Shell 1   Shell 2   Shell 3   Shell 4   Shell 5
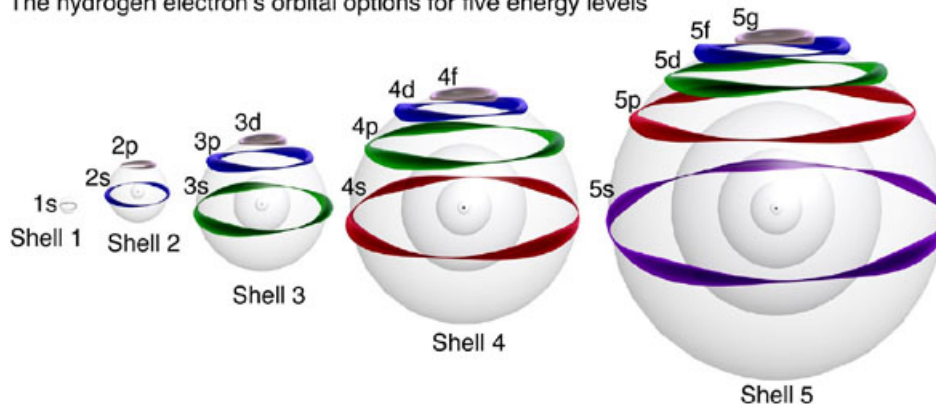
c. Magnetic Quantum Number (m_ℓ): - integral numbers $\{-\ell \leq m_\ell \leq \ell\}$ are used to show the orientation of the orbital in space relative to the other orbitals in the atom.
 - each m_ℓ value represents an atomic orbital.

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 $\pm\frac{1}{2}$ to denote the electron spin direction.
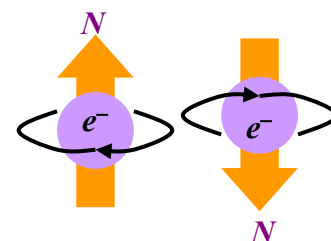
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Subshells: - are electron designations as indicated by the first two quantum numbers (Principal Quantum Number (n) and the letter used for Angular Momentum Quantum Number (ℓ)).

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	$1s$	0	1	1
2	0	$2s$	0	1	
	1	$2p$	$-1, 0, 1$ (p_y, p_z, p_x)	3	4
3	0	$3s$	0	1	
	1	$3p$	$-1, 0, 1$ (p_y, p_z, p_x)	3	9
	2	$3d$	$-2, -1, 0, 1, 2$ $(d_{x^2-y^2}, d_{yz}, d_{z^2}, d_{xz}, d_{xy})$	5	
4	0	$4s$	0	1	
	1	$4p$	$-1, 0, 1$ (p_y, p_z, p_x)	3	
	2	$4d$	$-2, -1, 0, 1, 2$ $(d_{x^2-y^2}, d_{yz}, d_{z^2}, d_{xz}, d_{xy})$	5	16
	3	$4f$	$-3, -2, -1, 0, 1, 2, 3$ $(f_{z(x^2-y^2)}, f_{y(z^2-x^2)}, f_{y^3}, f_{z^3}, f_{x^3}, f_{x(z^2-y^2)}, f_{xyz})$	7	
5	0	$5s$	0	1	
	1	$5p$	$-1, 0, 1$ (p_y, p_z, p_x)	3	
	2	$5d$	$-2, -1, 0, 1, 2$ $(d_{x^2-y^2}, d_{yz}, d_{z^2}, d_{xz}, d_{xy})$	5	
	3	$5f$	$-3, -2, -1, 0, 1, 2, 3$ $(f_{z(x^2-y^2)}, f_{y(z^2-x^2)}, f_{y^3}, f_{z^3}, f_{x^3}, f_{x(z^2-y^2)}, f_{xyz})$	7	25
	4	$5g$	$-4, -3, -2, -1, 0, 1, 2, 3, 4$ $(g_{xy(x^2-y^2)}, g_{zy^3}, g_{z^2(x^2-y^2)}, g_{z^3y}, g_{z^4}, g_{z^3x}, g_{z^2xy}, g_{zx^3}, g_{(x^4+y^4)})$	9	

Example 1: Explain why the following sets of quantum numbers combinations are incorrect.

a. $3f$

> $n = 3$ $\ell = 0, 1,$ or 2 ($s, p,$ or d subshells)
>
> Since $n = 3$, we cannot have a $3f$ subshell.

b. $n = 3, \ell = 3, m_\ell = -2$

> $n = 3$ $\ell = 0, 1,$ or 2 $m_\ell = -2, -1, 0, 1$ or 2
>
> Since $n = 3$, we cannot have $\ell = 3$.

c. $1d$

> $n = 1$ $\ell = 0$ (s subshell only)
>
> Since $n = 1$, we cannot have a $1d$ subshell.

d. $n = 5, \ell = 4, m_\ell = 5$

> $n = 5$ $\ell = 0, 1, 2, 3$ or 4
>
> $m_\ell = -4, -3, -2, -1, 0, 1, 2, 3$ or 4
>
> Since $n = 5$, and the maximum $\ell = 4$, we cannot have $m_\ell = 5$.

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.
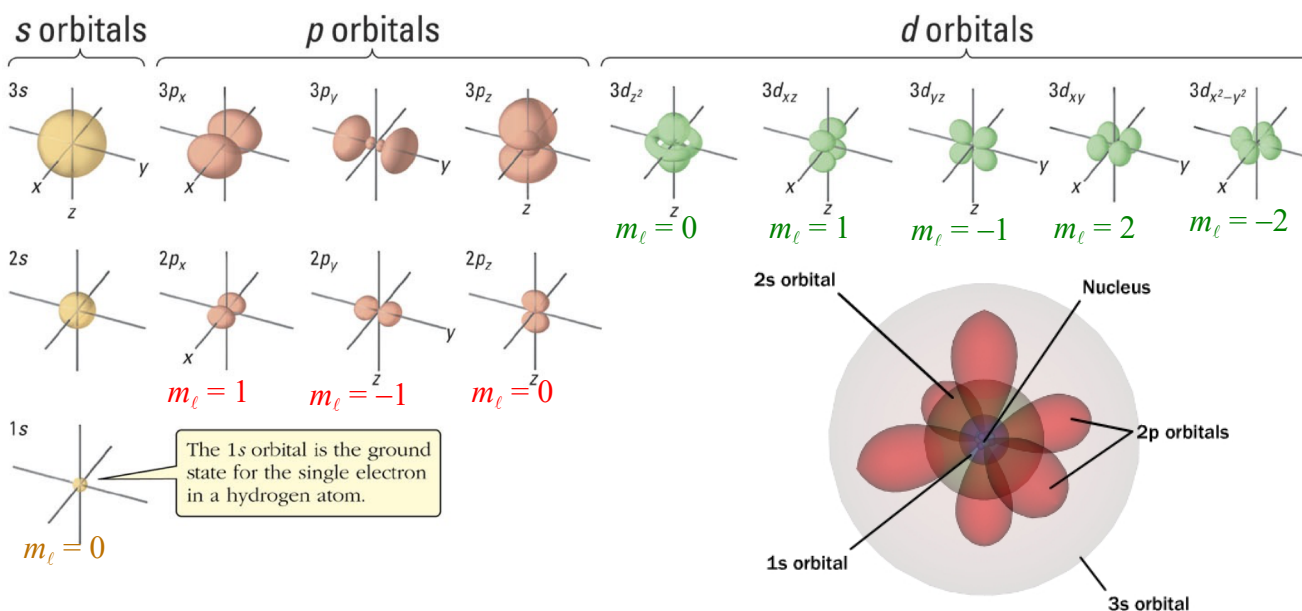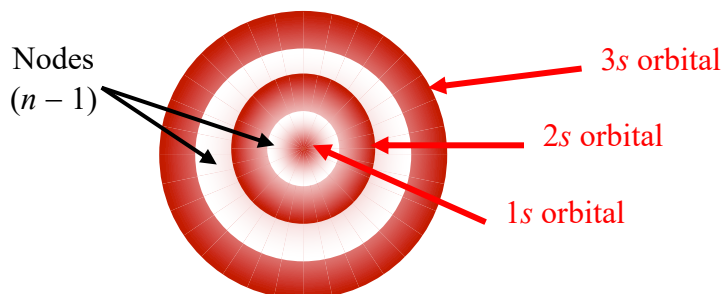
Energies of Orbitals:

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.

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

First four energy levels of a Hydrogen atom as proposed by Neils Bohr.
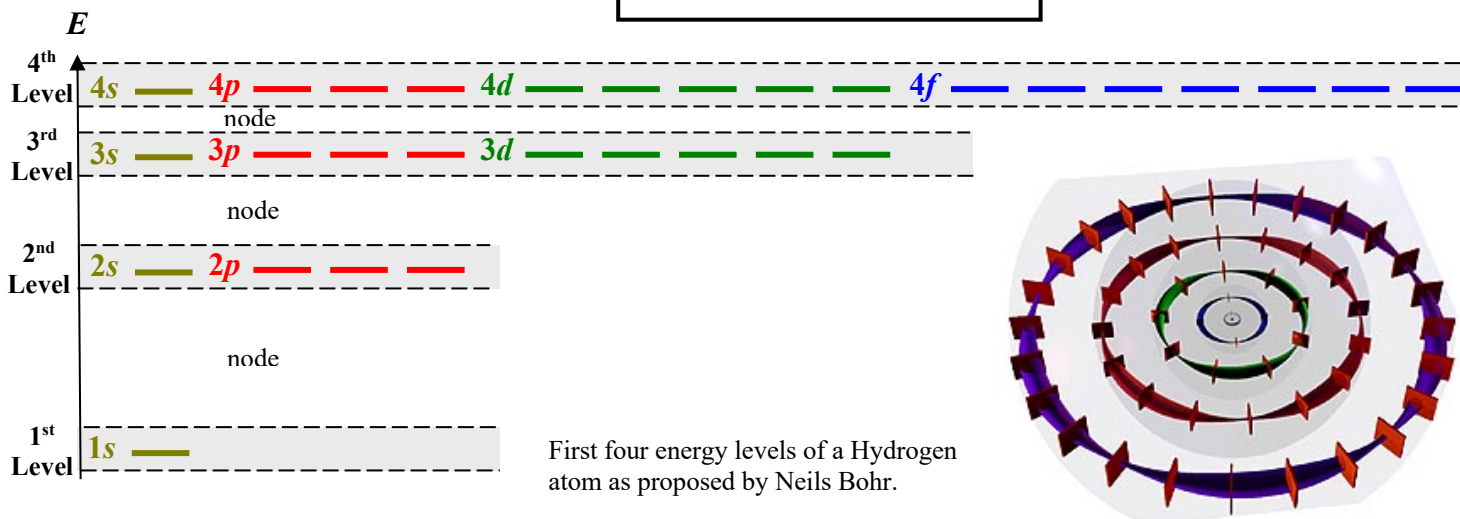
Polyelectronic Atoms: - atoms with more than one electron (all non-hydrogen atoms).

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** (more about shielding in section 7.8).

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

Note:

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

b. **The $3d$ 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**

***

Assignment
7.6 & 7.7 pg. 314–315 #48 to 70 (even)

***

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

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 $1s$ orbital, the four quantum numbers for the two electrons are:

$n = 1$ $n = 1$
$\ell = 0$ ⟶ $\ell = 0$
$m_\ell = 0$ $m_\ell = 0$
$m_s = ½$ **$1s$ orbital** $m_s = -½$
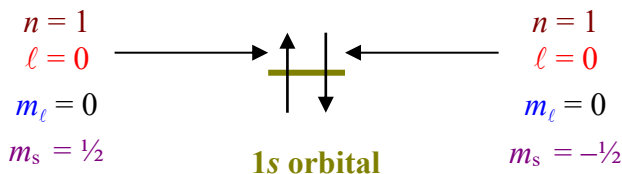
Penetration (Tunnelling) Effect:
    All **valence electrons** are "**shielded**" or "**blocked**" by the **inner or "core" electrons**. Hence, the
effective "hold" or attraction the protons in the nucleus on these valence electrons are minimized. (It
effectively reduces the electrostatic attraction between protons and electrons in the valence energy level.)
This being said, the s-electrons on average spend more time further away from the nucleus compared to the
p-electrons. Similarly, the p-electrons on average are farther away from the nucleus than the d-electrons
(see diagram below). However, these **electrons in s and p orbitals have other maximum radial
probabilities with closer proximity to the nucleus than d orbital at the same energy level** (see the small
peaks in the diagram below). Therefore, the **"penetrating" power decreases as the angular momentum
quantum number, ℓ, increase**.

Penetrating Power: $s > p > d > f$
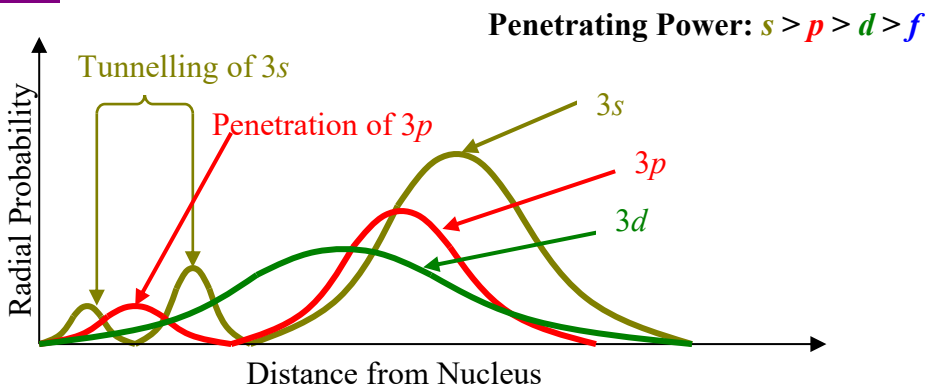
Aufbau (Building-Up) Principle: - "*Aufbau*" German for "building up"
                        - for each element, electrons are added up into the quantum orbitals
                        (after taken account with the electron correction problem and the
                        penetration effect) as protons 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.)

Increasing Energy (vertical arrow)

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s 7p

Order of appearance for Subshell ←
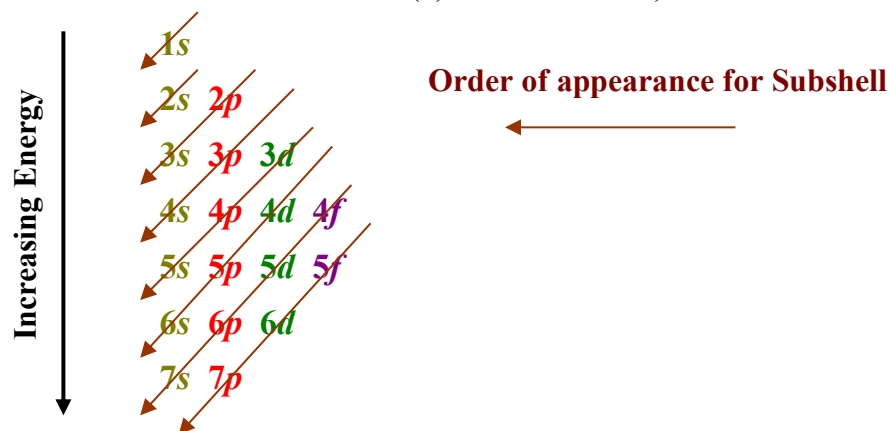
Example 1: Draw the quantum orbital diagrams and state the electron configurations for the following atoms.

Atomic #	Atom	Electron Configuration	Orbital Diagram 1s	2s	2p		
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 2: Draw the quantum orbital diagrams and state the electron configurations for the following atoms.

Atomic #	Atom	Electron Configuration	Orbital Diagram $4s$ — $3d$ — $4p$
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 $3d^{10}$.

Exceptions in Electron Configurations

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

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] $5s^1 4d^{10}$**
There are many more exceptions in the higher periods because the s, f and d orbitals are closer together when n increases.

6th Period:
Lanthanum ($_{57}$La): **[Xe] $6s^2 5d^1$**
Cerium ($_{58}$Ce):   **[Xe] $6s^2 4f^1 5d^1$** **(Lanthanide Series: 4f subshell begins)**
Gadolinium ($_{64}$Gd): **[Xe] $6s^2 4f^7 5d^1$**
Platinum ($_{78}$Pt):   **[Xe] $6s^1 4f^{14} 5d^9$**
Gold ($_{79}$Au):   **[Xe] $6s^1 4f^{14} 5d^{10}$**

7th Period:
Actinium ($_{89}$Ac):   **[Rn] $7s^2 6d^1$**
Thorium ($_{90}$Th):   **[Rn] $7s^2 6d^2$** **(Actinide Series: 5f subshell begins)**
Protactinium ($_{91}$Pa): **[Rn] $7s^2 5f^2 6d^1$**
Uranium ($_{92}$U):   **[Rn] $7s^2 5f^3 6d^1$**
Neptunium ($_{93}$Np):   **[Rn] $7s^2 5f^4 6d^1$**
Curium ($_{96}$Cm):   **[Rn] $7s^2 5f^7 6d^1$**

Electron Configurations in the Periodic Table of Elements

Representative Elements
(Main Groups)
s block

Transition Metals
d block

Representative Elements
(Main Groups)
p block

Lanthanide Series

Actinium Series

f block
Inner Transition Metals

Extended Periodic Table of Elements

| s | d | f | d | p |

Assignment
7.8 pg. 315 #72 to 78 (even)
7.9 pg. 315 #82 to 90 (even), 91, 92

Chapter 8: Periodic Relationships Among the Elements

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. [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 4p or higher orbitals than 4s and 3d.

b. [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 4p when the 3d 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]**
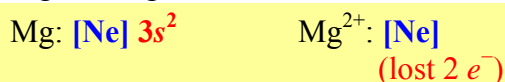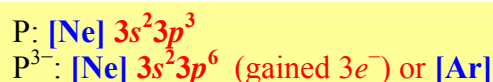
Electron Configurations of Ions from Transition Metals:

- 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. 356–357 #1 to 4
8.2 pg. 357−358 #11, 13, 15 to 20, 22, 23, 24 to 32 (even)

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.
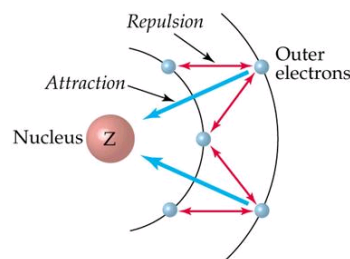
Effective Nuclear Charge (Z_{eff}): - the net nuclear charge actually experienced by an electron (the difference between the number of protons, Z, and the number of "shielded" core electrons).
- **the higher it is for Z_{eff}, the more effective for the protons to attract the valence electrons**.

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

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.

$2r$

Cl$_2$ Molecule
$2r = 132$ Å

Cl Atom
$r = 66$ Å

132 Å
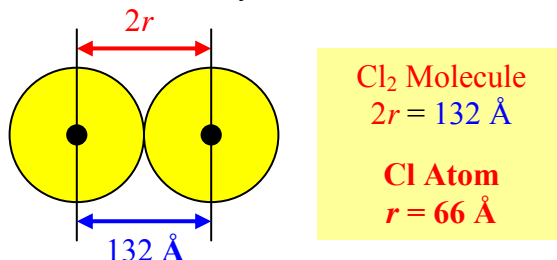
Several Notes on Trends in Atomic Radii

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 a stronger pull on the outer electrons), 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 located further away from the nucleus (shielding effect increases).

Relative Atomic Sizes of the Representative Elements

Sizes of atoms tend to increase down a group

Sizes of atoms tend to decrease across a period
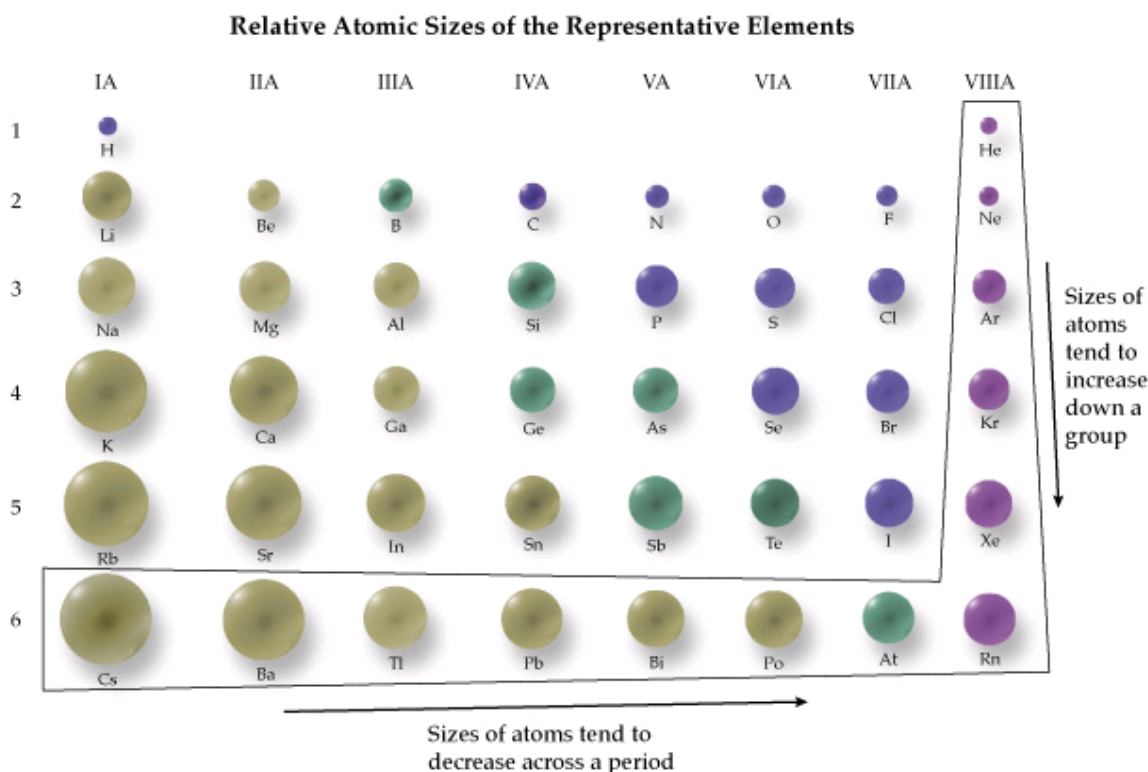
Example 1: Order the following atoms from the smallest to the largest.

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,

$$Cl < S < P < Mg < Na$$
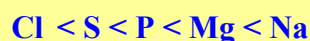
Ions Sizes: - the size of cations and anions.

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, they lose 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), thus drawing these outer electrons closer to the nucleus, decreasing in sizes as the result.

3. **Ionic Radii INCREASES 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 (increasing shielding effect).

4. When **Comparing Sizes of Isoelectronic Ions, the rule is that the Ion with the MOST PROTONS is the SMALLEST Ion**. More protons means stronger pull on the electrons, decreasing the ion size.
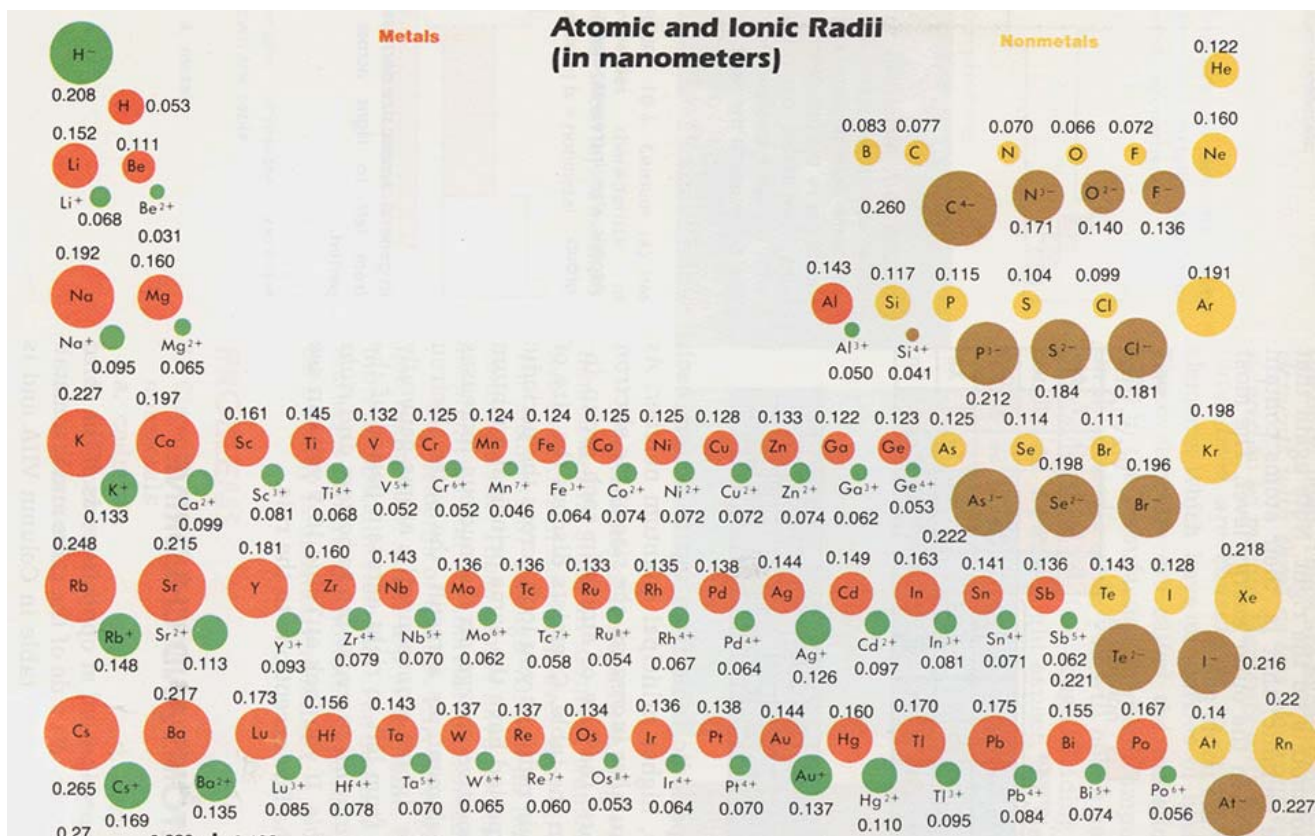
Example 2: Order the following ions from the smallest to the largest.

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

b. Na^+, Mg^{2+}, P^{3-}, S^{2-}, Cl^-
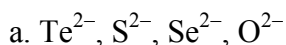
> **These anions are within the same Group (column). As we move down the column, ion size increases. Therefore,**
>
> $$O^{2-} < S^{2-} < Se^{2-} < Te^{2-}$$
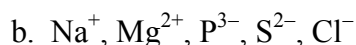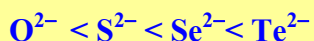
> **These ions are within the same Period (row). As we move to the right, ion size decreases within each of the metal and non-metal groups. Therefore,**
>
> $$Mg^{2+} < Na^+ < Cl^- < S^{2-} < P^{3-}$$

c. Ca^{2+}, K^+, Cl^-, S^{2-}, V^{5+}
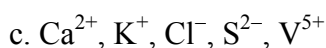
> **These ions are isoelectronic (all have $18e^-$). Since they have the same number of core and valence electrons in their various energy levels, the ions with the largest atomic number (number of protons) exerts more "pull" on these electrons. This in turn would make the size of the ion smaller.**
>
> $$V^{5+} \quad < \quad Ca^{2+} \quad < \quad K^+ \quad < \quad Cl^- \quad < \quad S^{2-}$$
> $$(23\,p^+) \quad (20\,p^+) \quad (19\,p^+) \quad (17\,p^+) \quad (16\,p^+)$$
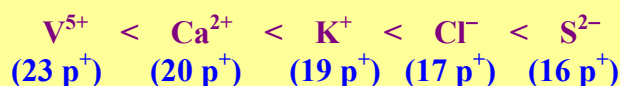
Assignment
8.3 pg. 358 #34 to 44 (even), 45 to 48

8.4 & 8.5: Ionization Energy & Electron Affinity

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

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

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

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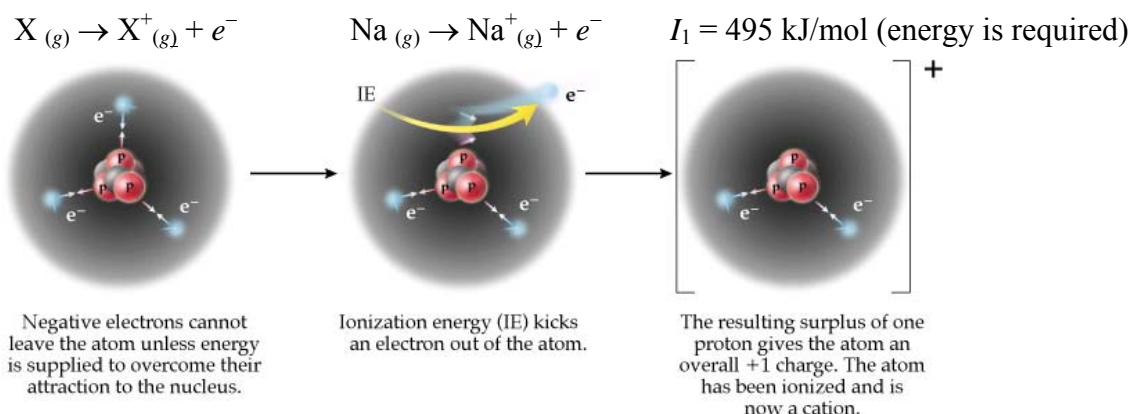
Second Ionization Energy: - the ionization energy required to remove the second highest-energy electron from the ion.

$$X^+_{(g)} \rightarrow X^{2+}_{(g)} + e^- \qquad Na^+_{(g)} \rightarrow Na^{2+}_{(g)} + e^- \qquad I_2 = 4560 \text{ kJ/mol}$$
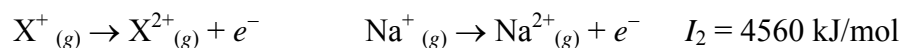
Successive Ionization Energies (kJ/mol) for Elements in Row 3 of the Periodic Table

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		Core Electrons		
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

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

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, shielding effect increases as 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 "holding on" to the electron.

3. In general, **Ionization Energies Increase as one move from Left to 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), thus requiring more energy to ionize them.

4. The notable exceptions to the above statement are 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).

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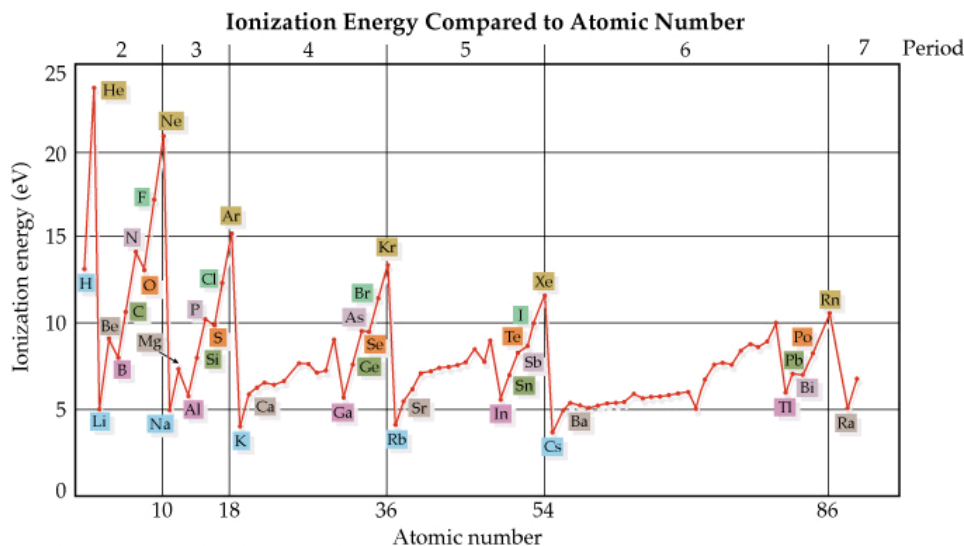
Electron Affinity: - the change in energy associates with an addition of an electron to a gaseous atom.
           - the larger negative electron affinity, the more stable the anion formed.

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

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \quad \Delta EA = -348.7 \text{ kJ/mol} \qquad (348.7 \text{ kJ/mol is released})$$
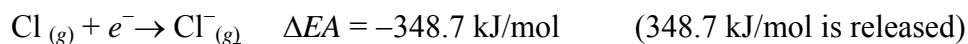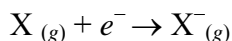
Several Notes on Trends in Electron Affinities

1. In general, **Electron Affinity DECREASES Down a Group (less energy is released)**. This is due to the fact there are more orbitals (and higher shielding effect) 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 2p orbitals. The Stronger Electron Repulsion between these orbitals in row 2 causes electron affinities in that row smaller than those in row 3.**

2. In most cases, **Electron affinity INCREASES (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.
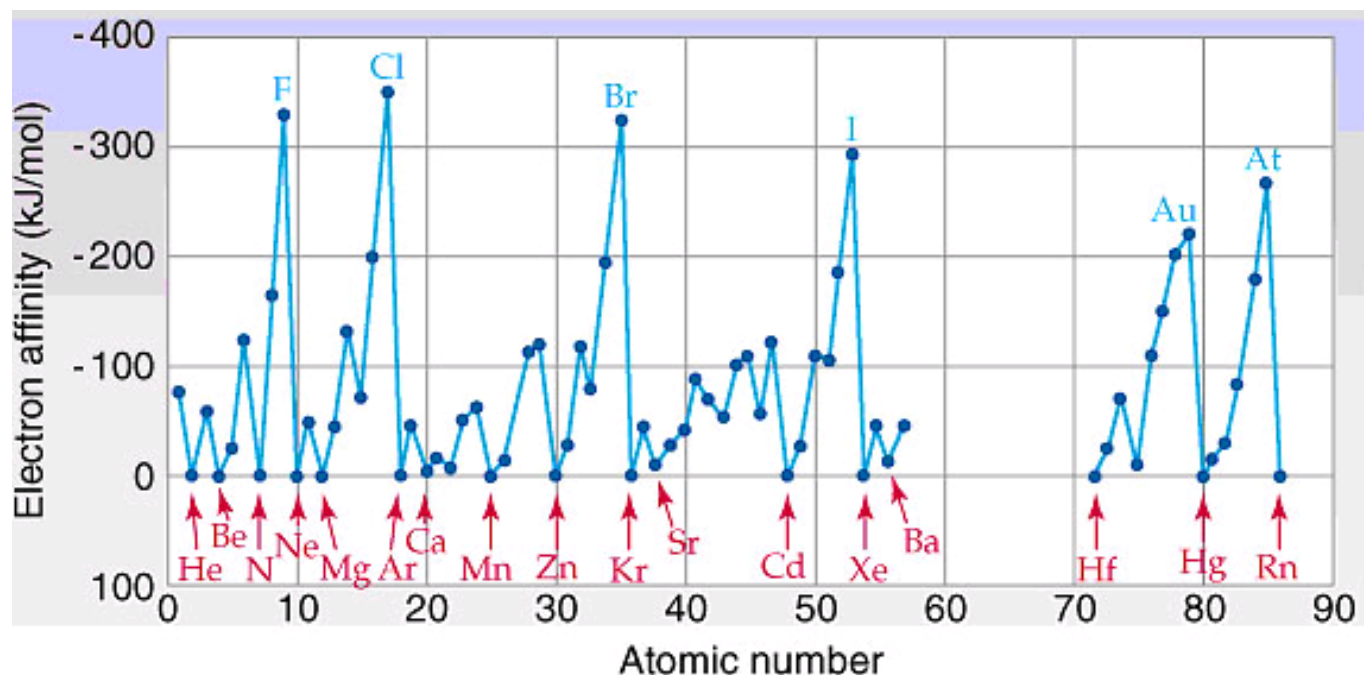
Assignment
8.4 pg. 358 #49 to 52, 54, 56
8.5 pg. 358−359 #59 to 64

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
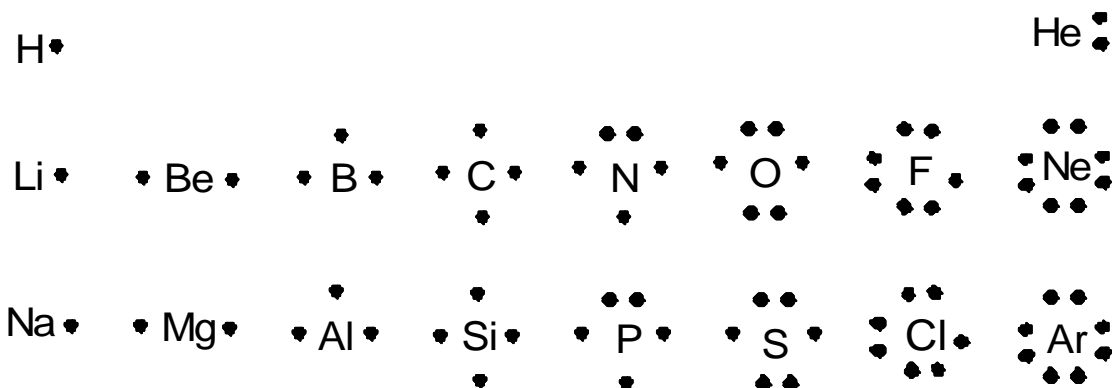
9.2: The Ionic Bond

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.

Pair of electrons on Cl;
not being shared with Na
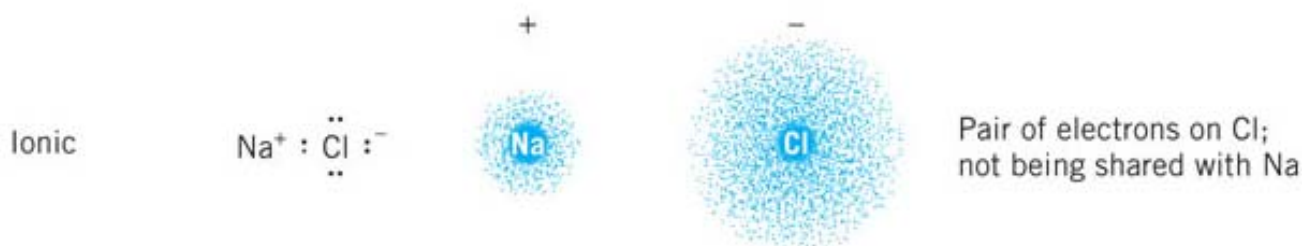
Example 1: For each ionic compound, draw the Lewis dot diagram for each atom and ion involved.

a. Mg and F
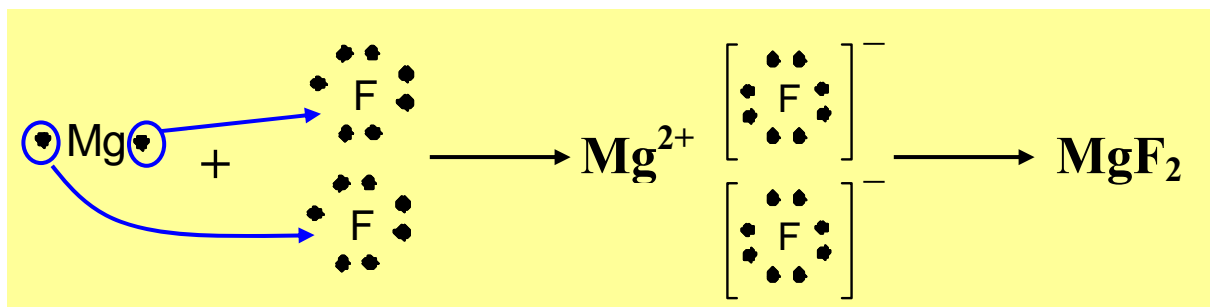
b. Al and S

<div style="border:1px solid black; text-align:center;">
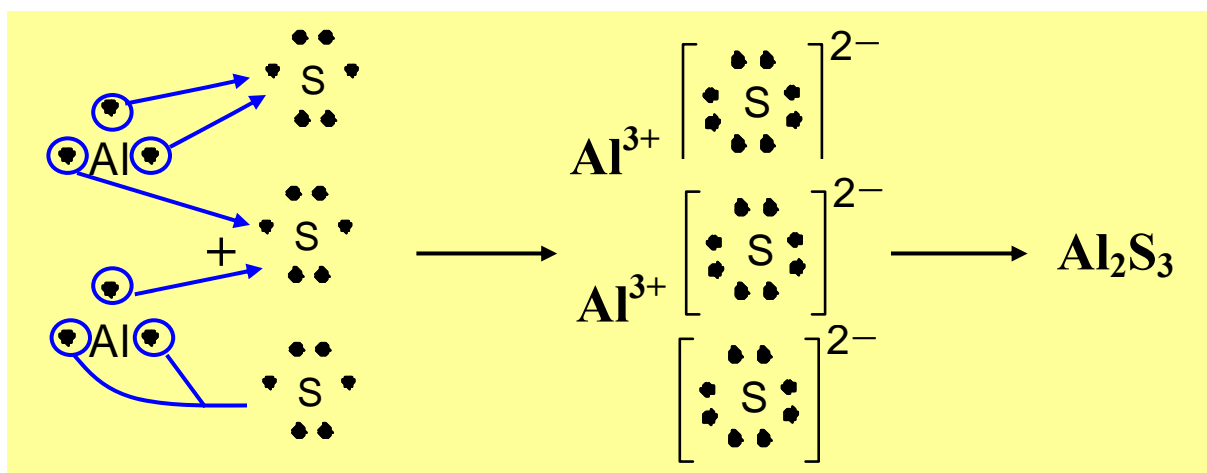
Assignment

9.1 pg. 400 #1 and 5

9.2 pg. 400 #7, 9, 10, 13, 15, 16, 18, 20

</div>

9.3: Lattice Energy of Ionic Compounds

Lattice Energy: - the energy involved when one mole of an ionic solid is formed from separated gaseous ions.
         - lattice energy is usually exothermic (energy is released).

$$M^+{}_{(g)} + X^-{}_{(g)} \rightarrow MX_{(s)} \qquad\qquad \Delta E_{lattice} < 0$$

(where M$^+$ = Metal Cation and X$^-$ = Non-Metal Anion)

Coulomb's Law: - the energy involved between the charges of two objects as well as the distance between them.
         - lattice energy between ions can be calculated from Coulomb's Law.
         - **since energy is released when ionic compounds are formed from ions, lattice energy is exothermic (negative value energy)**.
         - similarly, if ionic compounds are dissociated back into ions, the lattice energy will be endothermic (positive value energy).

<div style="border:1px solid black;">

$$\text{Lattice Energy} = -k\left(\frac{Q_1 Q_2}{r}\right) \qquad \textbf{(Coulomb's Law)}$$

r = distance between the two nuclei (m)   **k = Electric Constant (8.99×10^9 N • m^2/C^2)**
Q_1 = Charge of Cation (C)   **Q_2 = Charge of Anion (C) – ignoring negative sign**

</div>

1. **The higher the charge for the cation and / or anion, the more exothermic is the lattice energy.**

2. **The bigger the ions, the more distance it is between the nuclei. Hence, decreasing the lattice energy.**

3. **In general, the higher the lattice energy, the higher the melting point of the ionic compound. This is because higher lattice energy (more negative) equate to more stability. Hence, it is more difficult to break the ionic bonds, which is what melting an ionic compound involves.**

Ionic Bonding: - a chemical bond (attraction) that is characterized by the **transfer of electrons** to form
                ions between metals and non-metals.
                - the amount of energy involved in is calculate using Coulomb's Law

$$E = (2.31 \times 10^{-19} \text{ J} \bullet \text{nm}) \left(\frac{Q_1 Q_2}{r} \right) \text{ s(where } Q_1 \text{ and } Q_2 \text{ are ion charges and } r \text{ is the}$$

distance between the two nuclei).

Example 1: The ionic bond of LiF has a distance of 0.196 nm. Calculate the lattice energy of the LiF ionic
                bond.

0.196 nm

Li$^+$ F$^-$
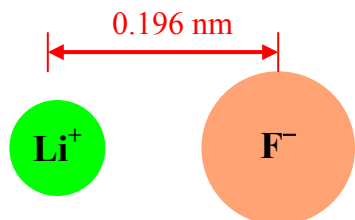
$$E = (2.31 \times 10^{-19} \text{ J} \bullet \text{nm}) \left(\frac{Q_1 Q_2}{r} \right)$$

$$E = (2.31 \times 10^{-19} \text{ J} \bullet \text{nm}) \left(\frac{(+1)(-1)}{0.196 \text{ nm}} \right)$$

$E = -1.17 \times 10^{-18}$ J (lower energy than ions that are separated)

Example 2: Explain the lattice energies of NaF, NaCl, MgF$_2$, and MgCl$_2$ being −923 kJ/mol, −786 kJ/mol,
                −2957 kJ/mol, and −2526 kJ/mol respectively.

**$| E_{lat} \text{(NaF)} | > | E_{lat} \text{(NaCl)} |$ and $| E_{lat} \text{(MgF}_2) | > | E_{lat} \text{(MgCl}_2) |$ because $r_F < r_{Cl}$. As r decreases,
E_{lat} increases ($E_{lat} = -k\left(\frac{Q_1 Q_2}{r} \right)$).**

**$| E_{lat} \text{(MgF}_2) | > | E_{lat} \text{(NaF)} |$ and $| E_{lat} \text{(MgCl}_2) | > | E_{lat} \text{(NaCl)} |$ because $Q_{Mg} > Q_{Na}$ (2+ > 1+). As
Q_1 increases, $|E_{lat}|$ increases ($E_{lat} = -k\left(\frac{Q_1 Q_2}{r} \right)$).**

Molar Heat of Formation (ΔH_f): - the amount of heat involved when 1 mole of compound is formed from
                its elements.

Haber-Born Cycle: - a procedure where the energy of every step of the process are accounted for to find
                the overall energy of the entire process.
                - in the formation of ionic compound, the Haber-Born cycle involves sublimation of
                metal, ionization of metal into gaseous cation, bond energy of non-metal molecules
                (if any), electron affinity of non-metal anions, and the lattice energy.

Determining the Molar Heat of Formation of Ionic Compounds

1. **Enthalpy (Heat) Sublimation of Solid Metal into Gaseous Metal (ΔE_{sub}).**   M$_{(s)}$ → M$_{(g)}$
2. **Ionization of Gaseous Metal into Gaseous Cation (I_n).**   M$_{(g)}$ → M$^+_{(g)} + e^-$
3. **Dissociation of Non-Metal Molecules into Atoms (E_{bond} = Bond Energy).**   ½ X$_{2 (g)}$ → X$_{(g)}$
4. **Formation of Anion from Non-Metal Atom ($E_{affinity}$ = Electron Affinity).**   X$_{(g)} + e^-$ → X$^-_{(g)}$
5. **Formation of Solid Ionic Compound from Gaseous Ions ($\Delta E_{lattice}$).**   M$^+_{(g)}$ + X$^-_{(g)}$ → MX$_{(s)}$
6. **Summation of all Energies involved for ΔH_f**   M$_{(s)}$ + ½ X$_{(g)}$ → MX$_{(s)}$
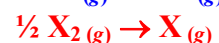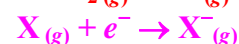
Potential Energy Diagram: - diagram that shows the energy changes of various stages of a reaction.
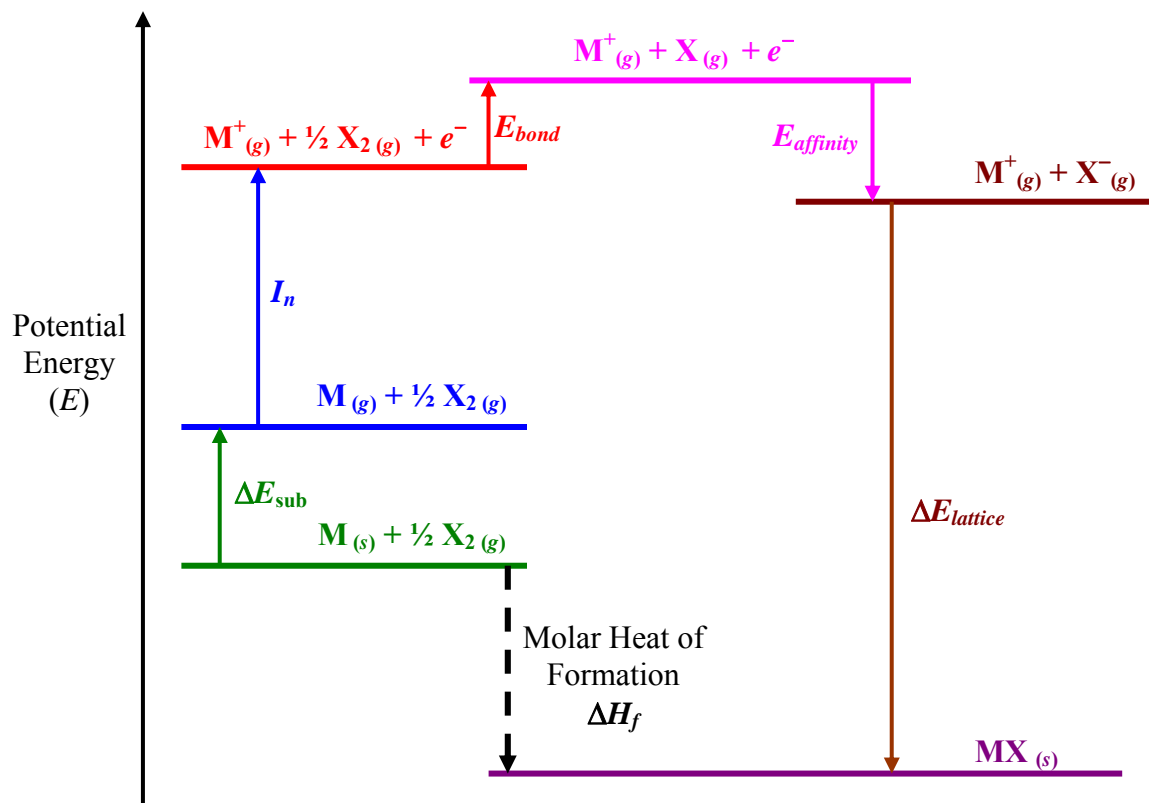
Example 3: Given the following information, calculate the molar heat of formation of MgF_2. Draw a potential energy diagram to illustrate the steps involved.

Bond Energy of F_2	154 kJ/mol	Lattice Energy (per mole of MgF_2)	−3916 kJ/mol
Electron Affinity of F	−328 kJ/mol	First Ionization Energy of Mg	735 kJ/mol
Enthalpy of Sublimation of Mg	150. kJ/mol	Second Ionization Energy of Mg	1445 kJ/mol

Molar Heat of Formation of MgF_2:

ΔH_f = 150. kJ + 735 kJ + 1445 kJ + 154 kJ + 2(−328 kJ) + (−3916 kJ)

ΔH_f = −2088 kJ/mol
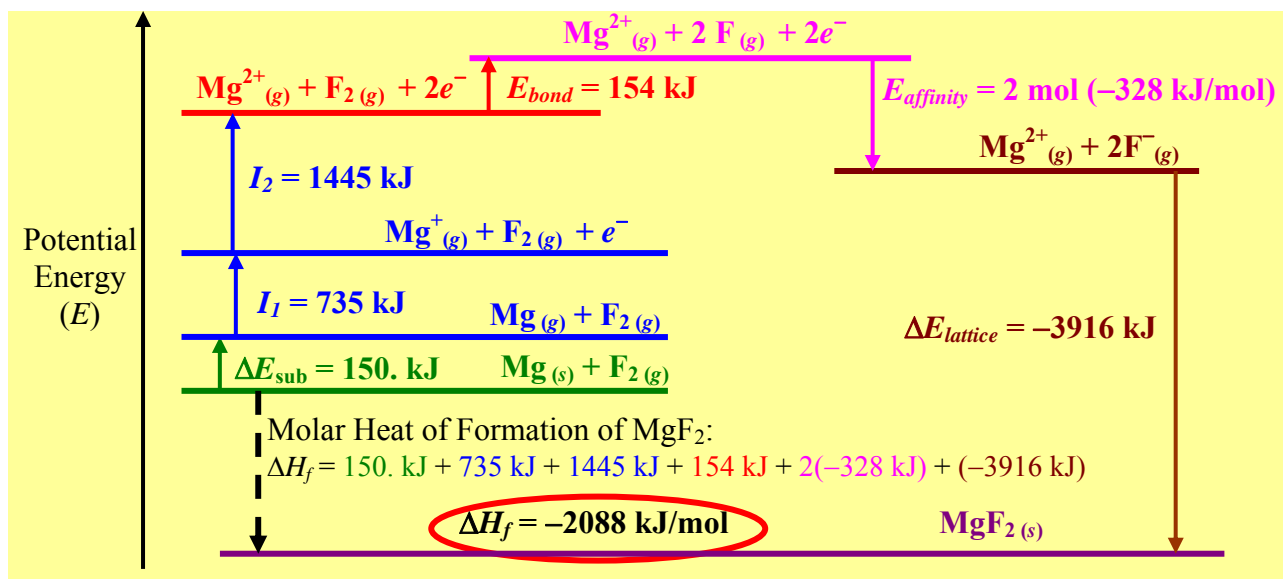
Assignment
9.3 pg. 400−401 #21, 22, 24 to 26

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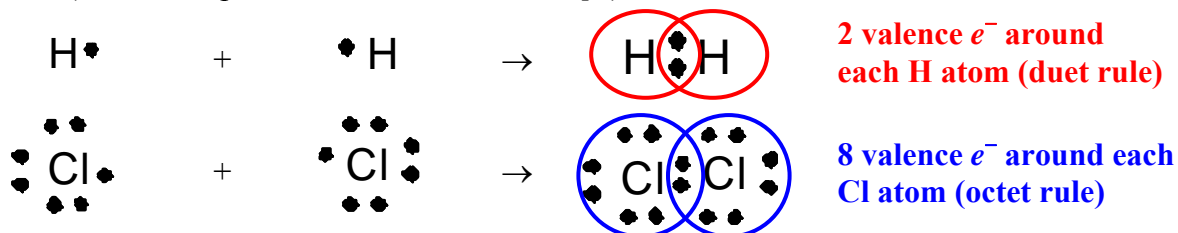
Covalent Compound: - a compound that consists of only covalent bonds.
- sometimes refers to as **molecular compound**.

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)
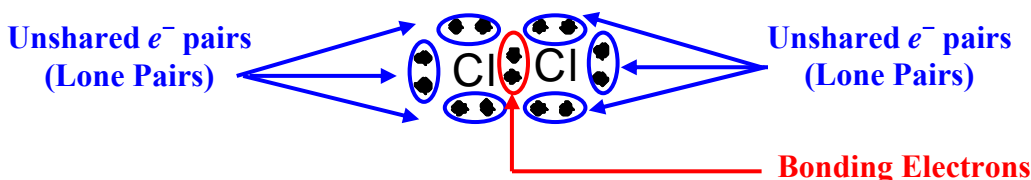
Bonding Electrons

Structural Formula: - a Lewis dot diagram of a molecule where the bonding electrons are replaced
by a short line.
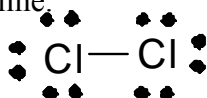
2. **Double Covalent Bond**: - covalent bond where there are only **four valence electrons** being shared
between two atoms.
- denotes by a double line in the structural formula.

only 7 e^- around
each O atom

2 unshared e^- become
another bonding pair

double bond results and
$8e^-$ around each O atom
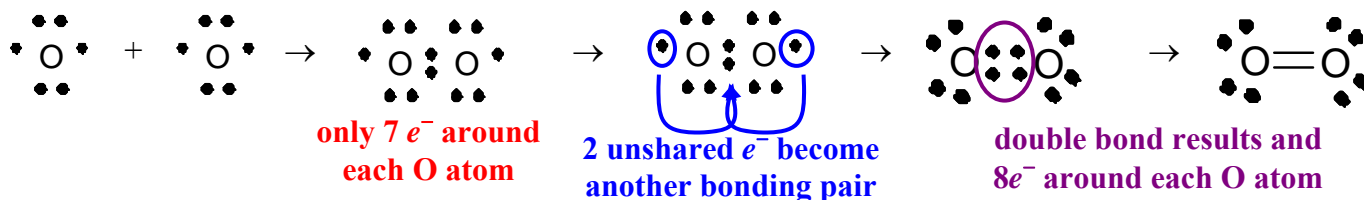
3. **Triple Covalent Bond**: - covalent bond where there are only **six valence electrons** being shared
between two atoms.
- denotes by a triple line in the structural formula.

only 6 e^- around
each N atom

4 unshared e^- become
2 other bonding pairs

triple bond results and
$8e^-$ around each N atom
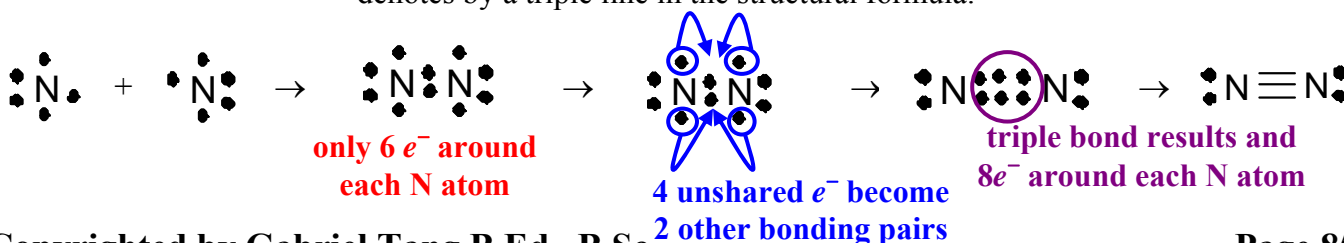
Coordinate Covalent Bond: - where an atom contributes an unshared electron pair (lone pair) to form double or triple bonds to achieve a stable octet around both atoms.
- sometimes refer to as **multiple bond**.

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.

$2\delta -$

O

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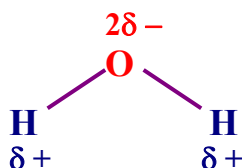
Electronegativity: - first determined by **Linus Pauling**, it is a measure of the **capability of an atom within a molecule to attract shared electrons around itself**.
- the better the atom is able to attract electrons, the higher the electronegativity value.
- electronegativity of noble gases is 0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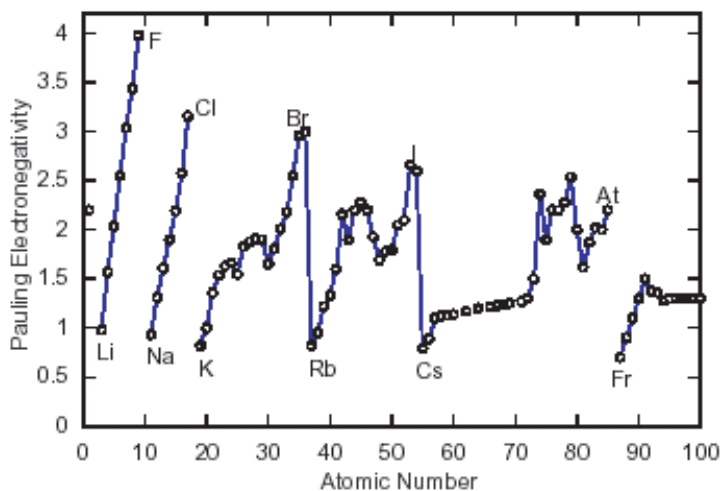
Several Notes on Trends in Electronegativity

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   **Difference in Electronegativity = 0 (Non-Polar Covalent Bonds – No Bond Polarity)**
3.2   3.2

H —— Cl   **Difference in Electronegativity = 1 (Polar Covalent Bonds – Some Bond Polarity)**
2.2   3.2

Li —— Cl   **Difference in Electronegativity = 2.2 (Ionic Bonds – High Bond Polarity)**
1.0   3.2

Assignment
9.4 pg. 401 #30 to 32
9.5 pg. 401 #34, 36, 37, 39, 40

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

$\underline{\quad 2e^- \text{ (2 H atoms)}\quad}$
$2e^-$ Total
$\underline{- 2e^- \text{ (1 bond)}\quad}$
$0e^-$

H   H

H – H
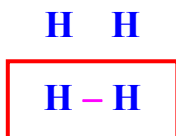
b. Cl_2

$\underline{\quad 14e^- \text{ (2 Cl atoms)}\quad}$
$14e^-$ Total
$\underline{- \quad 2e^- \text{ (1 bond)}\quad}$
$12e^-$ Left
$- \quad 12e^- \text{ (6 lone pairs on}$
$\underline{\qquad\qquad \text{Cl's for octets)}\quad}$
$0e^-$

Cl   Cl

Cl – Cl

c. O_2

$\underline{\;\;12e^- \;(2 \text{ O atoms})}$
$12e^-$ Total
$\underline{-\;\;2e^- \;(1 \text{ bond})}$
$10e^-$ Left
$-\;\;6e^- \;(3 \text{ lone pairs on}$
      one O for octet)
$-\;\;4e^- \;(2 \text{ lone pair}$
$\underline{\qquad\quad \text{on other O})}$
$0e^-$

O O

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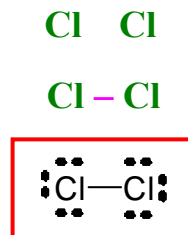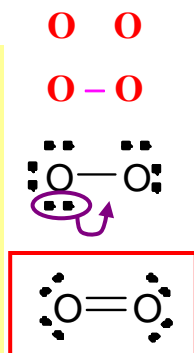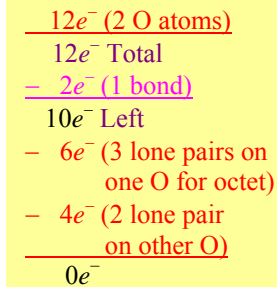
Need to move a lone pair between the atoms because the oxygen to the right does not have enough e^- for an octet.

d. N_2

$\underline{\;\;10e^- \;(2 \text{ N atoms})}$
$10e^-$ Total
$\underline{-\;\;2e^- \;(1 \text{ bond})}$
$8e^-$ Left
$-\;\;6e^- \;(3 \text{ lone pairs on}$
      one N for octet)
$\underline{-\;2e^- \;(\text{lone pair on other N})}$
$0e^-$

N N

N – N

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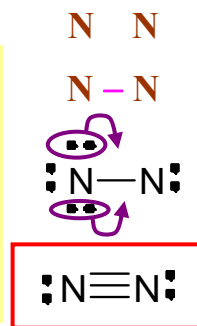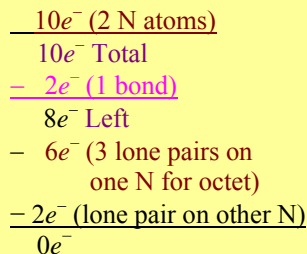
Need to move two lone pairs between the atoms because the nitrogen to the right does not have enough e^- for an octet.

e. H_2O

$\;\;2e^- \;(2 \text{ H atoms})$
$\underline{+\;6e^- \;(1 \text{ O atom})}$
$8e^-$ Total
$\underline{-\;4e^- \;(2 \text{ bonds})}$
$4e^-$ Left
$-\;4e^- \;(2 \text{ lone-pairs}$
$\underline{\qquad \text{on O for octet})}$
$0e^-$

H O H

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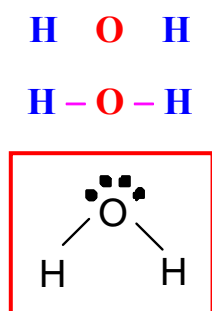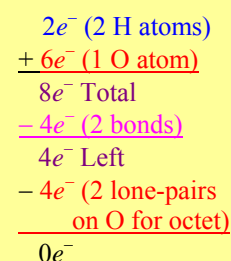
Reason for why the H_2O structure is bent will be explained in section 10.2

f. H_2O_2

$\;\;2e^- \;(2 \text{ H atoms})$
$\underline{+\;12e^- \;(2 \text{ O atoms})}$
$14e^-$ Total
$\underline{-\;\;6e^- \;(3 \text{ bonds})}$
$8e^-$ Left
$-\;\;8e^- \;(4 \text{ lone-pairs on}$
$\underline{\qquad\quad \text{O's for octets})}$
$0e^-$

H O O H

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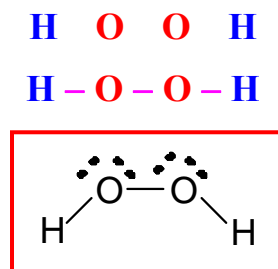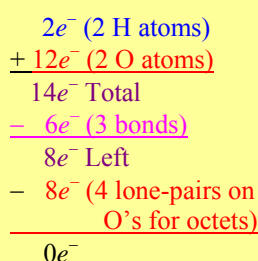
Since H can only form 1 bond each, both oxygen atoms are the central atoms

g. NH_4^+

$\;\;5e^- \;(1 \text{ N atom})$
$+\;\;4e^- \;(4 \text{ H atoms})$
$\underline{-\;\;1e^- \;(+1 \text{ charge of } NH_4^+)}$
$8e^-$ Total
$\underline{-\;\;8e^- \;(4 \text{ bonds})}$
$0e^-$

h. CN^-

$\;\;5e^- \;(1 \text{ N atom})$
$+\;\;4e^- \;(1 \text{ C atom})$
$\underline{+\;\;1e^- \;(-1 \text{ charge of } CN^-)}$
$10e^-$ Total
$\underline{-\;\;2e^- \;(1 \text{ bond})}$
$8e^-$ Left
$-\;\;6e^- \;(3 \text{ lone pairs}$
      on N for octet)
$\underline{-\;2e^- \;(\text{last lone pair on C})}$
$0e^-$

$[C \quad N]^-$
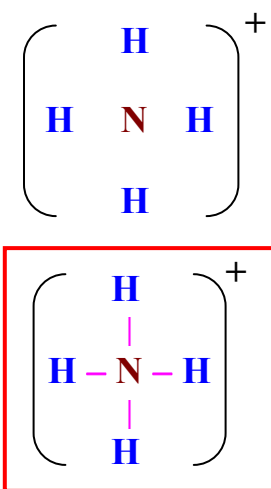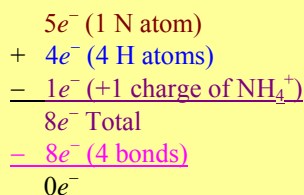
$[C – N]^-$
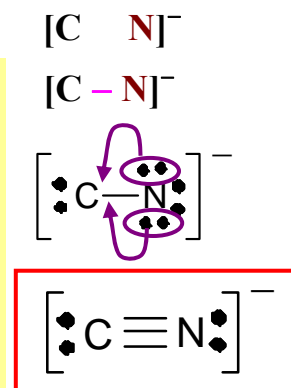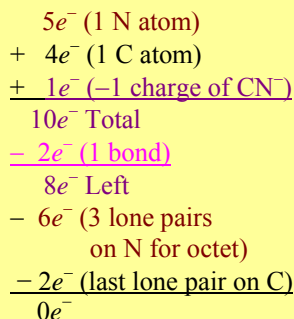
There are only 4 e^- around C. **Nitrogen atoms need to contribute 2 lone pairs to form a triple bond.**

Assignment
9.6 pg. 401 #43 to 48

9.9: Exceptions to the Octet Rule

1. **In the second row, due to the $2s$ and the $2p$ 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 <u>Incomplete Octet</u>.**

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 $3d$ orbitals to exceed the 8 electrons limit. (Examples: P can have $10e^-$ rule; S and Cl can have $10e^-$ or $12e^-$ rule) – <u>Expanded Octet</u>**

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 $12e^-$) – <u>Expanded Octet</u>**

Note: <u>**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**</u>. This will be discussed in following section.
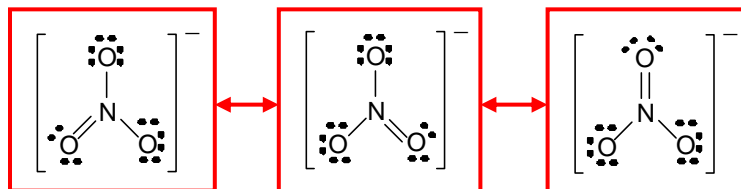
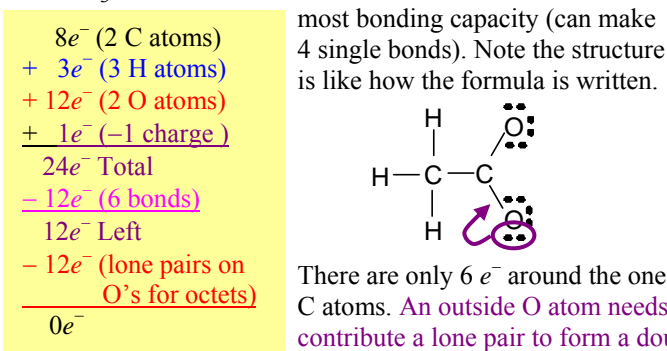**Example 1**: Draw the Lewis structure for the following molecules and polyatomic ions.

a. BCl_3

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

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.
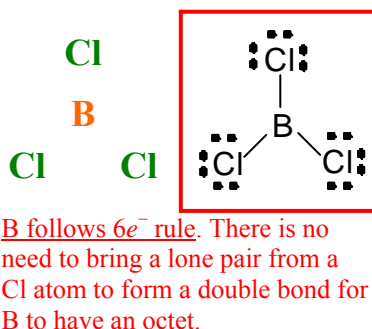
b. BeI_2

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

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.
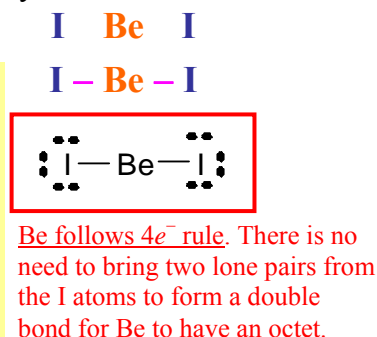
c. ICl_4^-

$7e^-$ (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 octets)
$- 4e^-$ (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.
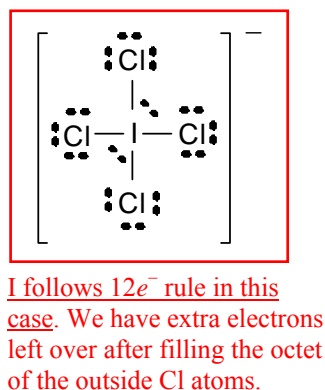
d. SCl_6

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

S follows $12e^-$ rule in this case. (There are 6 bonds from the central S atom.)
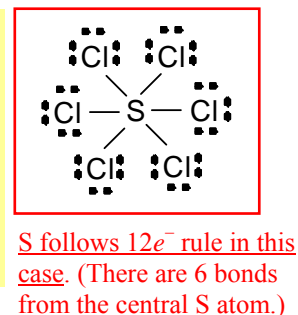
e. PF_5

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

P follows $10e^-$ rule in this case. (There are 5 bonds from the central P atom.)
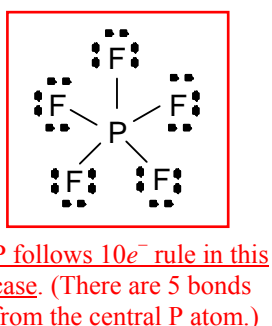
f. ClF_3

$7e^-$ (Cl atom)
$+ 21e^-$ (3 F atoms)
$28e^-$ Total
$- 6e^-$ (3 bonds)
$22e^-$ Left
$- 18e^-$ (lone-pairs on F's for octets)
$- 4e^-$ (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.
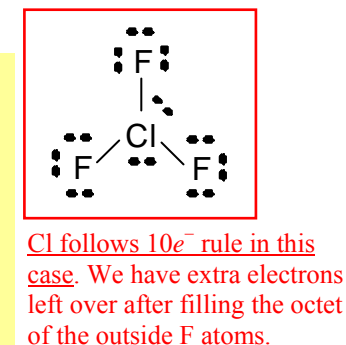
g. XeF_4

$8e^-$ (Xe atom)
$+ 28e^-$ (4 F atoms)
$36e^-$ Total
$- 8e^-$ (4 bonds)
$28e^-$ Left
$- 24e^-$ (lone-pairs on F's for octets)
$- 4e^-$ (lone pairs on Xe)
$0e^-$
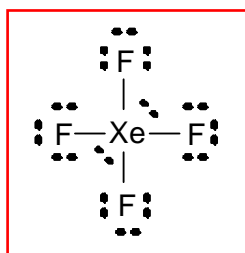
Xe follows $12e^-$ rule. We have extra electrons left over after filling the octet of the outside F atoms.

h. IF_5

$7e^-$ (I atom)
$+ 35e^-$ (5 F atoms)
$42e^-$ Total
$- 10e^-$ (5 bonds)
$32e^-$ Left
$- 30e^-$ (lone-pairs on F's for octets)
$- 2e^-$ (lone pair on I)
$0e^-$
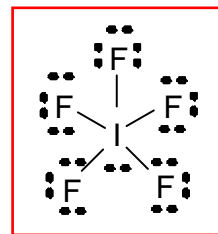
I follows $12e^-$ rule. We have extra electrons left over after filling the octet of the outside F atoms.

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)
$0e^-$
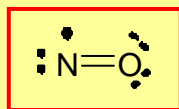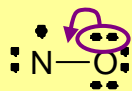
Need to move a lone pair from oxygen to between the atoms because the nitrogen does not have enough e^- for an octet.

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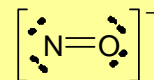
Remedy #2: Bond with another NO molecule to form a dimer – dinitrogen dioxide (N_2O_2)

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 octets)
$- 1e^-$ (a radical e^- on N)
$0e^-$
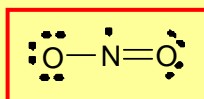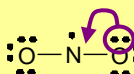
Need to move a lone pair from oxygen to between the atoms because the nitrogen does not have enough e^- for an octet.

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: Lose an electron and form a polyatomic ion (NO_2^+)

Remedy #3: Bond with another NO_2 molecule to form a dimer – dinitrogen tetraoxide (N_2O_4)
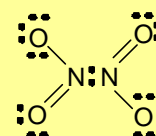
Assignment
9.9 pg. 402 #57, 59, 63 to 66

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 octets)	
$-$ $2e^-$ (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.
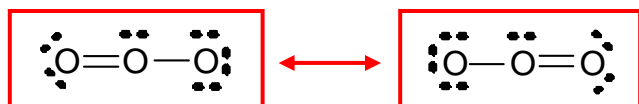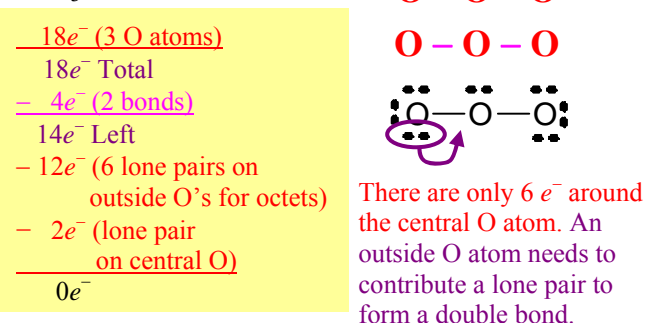
The double bond can be on either the left or right side
of the central oxygen atom (resonance).

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 octets)	
$0e^-$	

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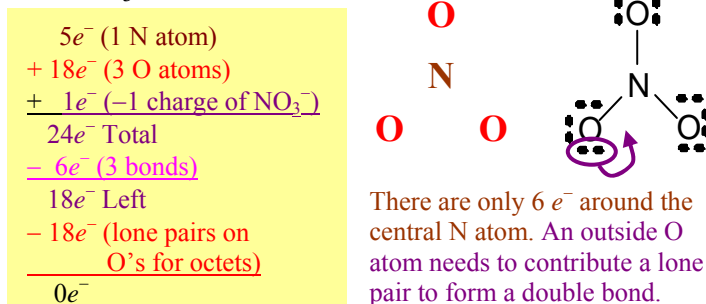
The double bond can come from any one of the O atoms (resonance).

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 octets)	
$0e^-$	

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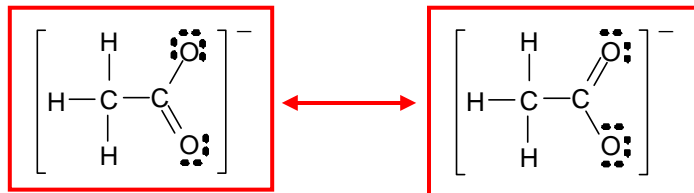
The double bond can be on either the top or bottom side of
the second carbon atom (resonance).

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

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 octets)
$0e^-$
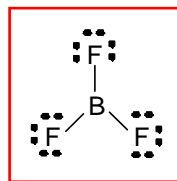
Formal Charge (B)
$= 3e^- - 0e^- - ½(6e^-)$
(val.) (lone pair) (bonding)
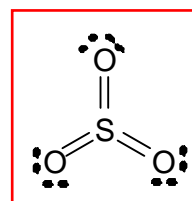**Formal Charge (B) = 0**
(Correct Structure)
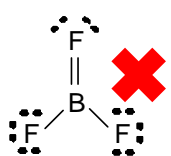
Formal Charge (B)
$= 3e^- - 0e^- - ½(8e^-)$
(val.) (lone pair) (bonding)
Formal Charge (B) = −1
(incorrect structure)

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 octets)
$0e^-$
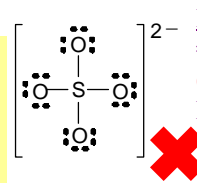
Formal Charge (S)
$= 6e^- - 0e^- - ½(8e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 2
(incorrect structure)
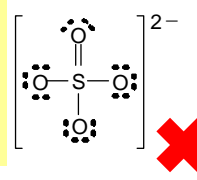
Formal Charge (S)
$= 6e^- - 0e^- - ½(10e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 1
(incorrect structure)
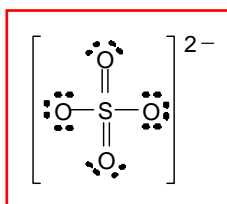
Formal Charge (S)
$= 6e^- - 0e^- - ½(12e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 0
(Correct structure)

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 octets)
$- 2e^-$ (lone pair on central S)
$0e^-$
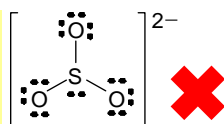
Formal Charge (S)
$= 6e^- - 2e^- - ½(6e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 1
(incorrect structure)
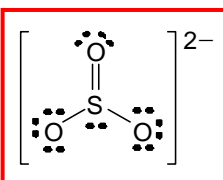
Formal Charge (S)
$= 6e^- - 2e^- - ½(8e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 0
(Correct structure)

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 octets)
$0e^-$
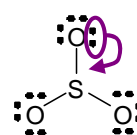
There are only $6\ e^-$ around the central S atom. An outside O atom needs to contribute a lone pair to form a double bond.
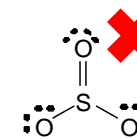
Formal Charge (S)
$= 6e^- - 0e^- - ½(8e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 2
(incorrect structure)
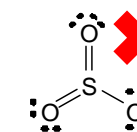
Formal Charge (S)
$= 6e^- - 0e^- - ½(10e^-)$
(val.) (lone pair) (bonding)
Formal Charge (S) = 1
(incorrect structure)

Formal Charge (S)
$= 6e^- - 0e^- - ½(12e^-)$
(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 pg. 401 #42
9.8 pg. 401−402 #51 to 56

9.10: Bond Enthalpy

Model: - an attempt to explain how nature works on a small level based in empirical observation in a larger level.

Chemical Bond Model: - chemical bonds are the result when atoms are arranged to achieve a lower energy state.

Molar Bond Energy (Enthalpy): - the energy to required breaking or released from forming one mole of a particular chemical bond.
- in general, $\Delta E_{bond} > 0$ **(endothermic) when breaking a bond**; $\Delta E_{bond} < 0$ **(exothermic) when forming a bond**.

Average Molar Bond Energy: - the average of an individual molar bond energy from all similar type bonds in a mole of molecule.

Example: Elimination of H from CH_4 (435 kJ/mol); Elimination of H from CH_3 (453 kJ/mol); Elimination of H from CH_2 (425 kJ/mol); Elimination of H from CH (339 kJ/mol)

- actual bond energy for molecules with different kinds of bonds are different than average bond energy calculated from molecules with identical bonds.

Example 1: Calculate the average bond energy of C−H bond if CH_4 has total bond energy of 1652 kJ/mol.

There are four C−H bonds in CH_4. Therefore,   Average $\Delta E_{\text{C−H bond}} = \dfrac{1652 \, \text{kJ/mol}}{4}$

$$\text{Average } \Delta E_{\text{C−H bond}} = 413 \text{ kJ/mol}$$

Example 2: Using the answer from the previous example, determine the bond energy of C−F bond if CH_3F has total bond energy of 1724 kJ/mol.

There are three C−H bonds and one C−F bond in CH_3F.
Total $\Delta E_{bond} = 3 \, (\Delta E_{\text{C−H bond}}) + \Delta E_{\text{C−F bond}}$
$\Delta E_{\text{C−F bond}} = \text{Total } \Delta E_{bond} - 3 \, (\Delta E_{\text{C−H bond}})$
$\Delta E_{\text{C−F bond}} = 1724 \text{ kJ/mol} - 3 \, (413 \text{ kJ/mol})$ $\Delta E_{\text{C−F bond}} = 485 \text{ kJ/mol}$

Bond Enthalpies of Multiple Bonds: - in general, bond energy increases with multiple bonds because their lengths are shorter than single bonds**.**

Bond and Bond Type	Bond Length (pm)	Bond Energy (kJ/mol)
C − C (single bond)	154	247
C = C (double bond)	134	614
C ≡ C (triple Bond)	120	839

> **Determining the Molar Heat of Formation / Reaction of Covalent Compounds:**
>
> $$\Delta H = \Sigma BE \text{ (breaking old bonds)} + \Sigma BE \text{ (forming new bonds)}$$
>
> (ΣBE mean Sum of Bond Energy = $n\Delta E_{bond}$)
>
> $\Delta E_{bond} > 0$ (endothermic) when breaking a bond (positive)
> $\Delta E_{bond} < 0$ (exothermic) when forming a bond (negative)

Example 3: Ethene is burned as described in the following equation.

$$C_2H_{4\,(g)} + 3\,O_{2\,(g)} \rightarrow 2\,CO_{2\,(g)} + 2\,H_2O_{(g)}$$
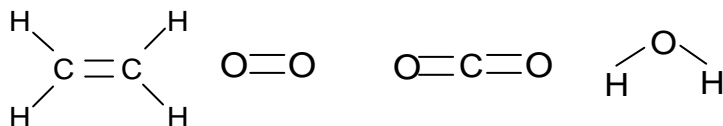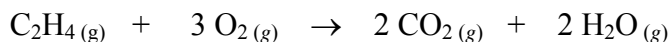
C = C	614 kJ/mol	O = O	495 kJ/mol	O – H	467 kJ/mol
C – H	413 kJ/mol	C = O	745 kJ/mol	C = O	795 kJ/mol (CO_2)

  a. Using the bond energy data above, determine the heat of reaction for the combustion of ethene.
  b. The actual ΔH for the reaction is -1323 kJ/mol. Explain the difference between the two results.

a. **ΣBE (breaking bonds):**   **ΣBE (forming bonds):**

   1 C = C bond   (1 mol)(614 kJ/mol)   4 C = O bond   (4 mol)(-795 kJ/mol)
   4 C – H bonds   (4 mol)(413 kJ/mol)   4 O – H bonds   + (4 mol)(-467 kJ/mol)
   3 O = O bonds   + (3 mol)(495 kJ/mol)   **ΣBE (forming bonds) = -5048 kJ**
   ΣBE (breaking bonds) = +3751 kJ

    $\Delta H = \Sigma BE$ (breaking bonds) + ΣBE (forming bonds)
    $\Delta H = (3751$ kJ$) + (-5048$ kJ$)$ **$\Delta H = -1297$ kJ**
          $C_2H_{4\,(g)} + 3\,O_{2\,(g)} \rightarrow 2\,CO_{2\,(g)} + 2\,H_2O_{(g)} + 1304$ kJ

  b. The calculation result from part a. is a theoretical value. The bond energy data used are average bond enthalpies. In reality, the bond enthalpies are different when molecules break or form bonds at different stages of the reaction. Hence, we often see a difference between the theoretical and actual ΔH values.

> ### Assignment
> **9.10 pg. 402 #69 to 72**

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*.
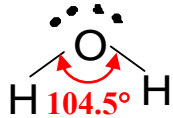> - most often used to predict molecular structures involving non-metals.
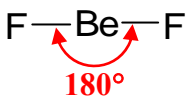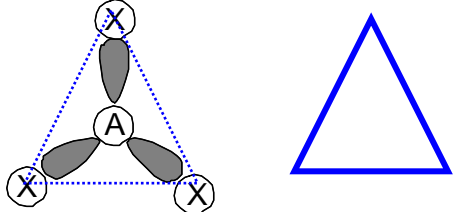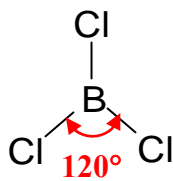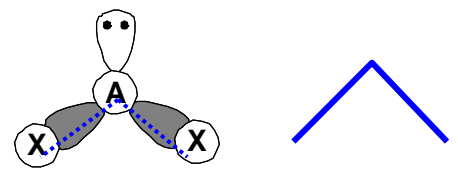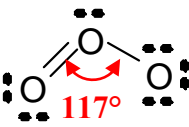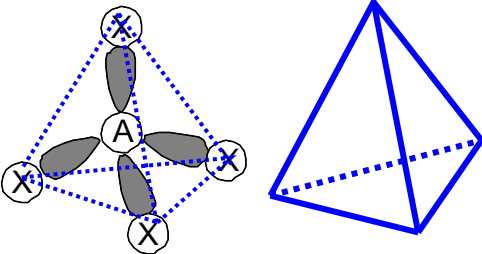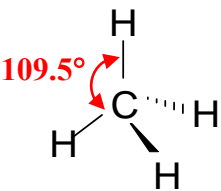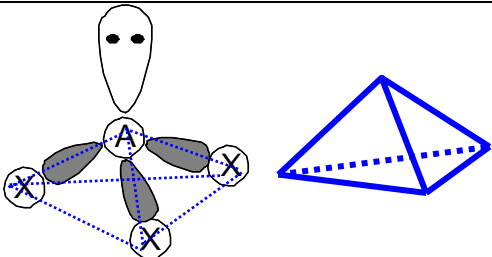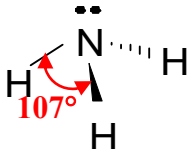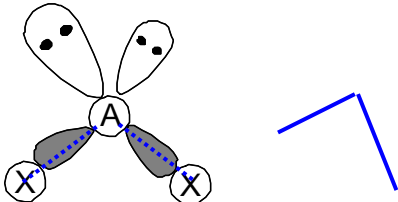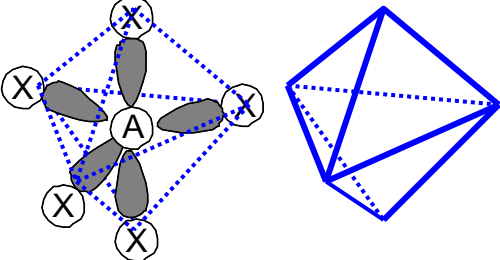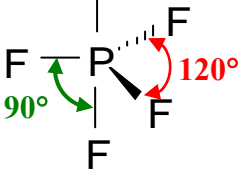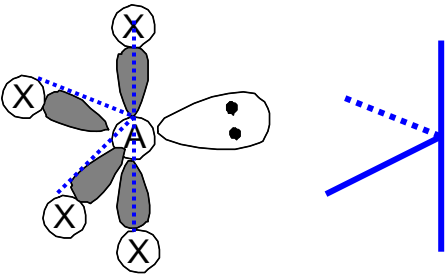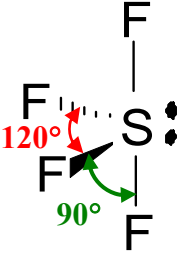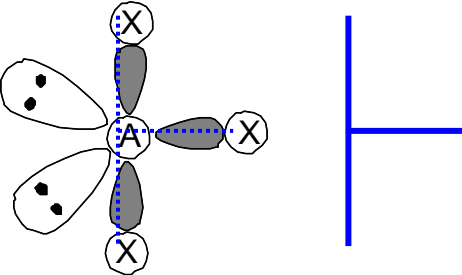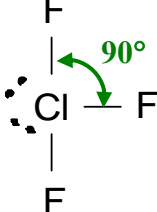
Example: For molecules with a total of 4 e^- pairs, the bond angles decreases from 109.5° as more lone
pairs added. (Repulsion of Lone Pair(s) with bond electrons pushed the angle down.)

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 F—Be—F **180°**
3	0		Trigonal planar	BCl_3 Cl—B Cl **120°** Cl
3	1		V-Shape (Bent)	O_3 O O **117°** O
4	0		Tetrahedral	CH_4 H **109.5°** C····H H H

Around Central Atom		Molecular Structures	Geometrical Shape	Example and Bond Angles
Total # of Eff. e^- Pairs	# of Lone Pairs			
4	1		Trigonal pyramid	NH_3 107°
4	2		V-Shape (Bent)	H_2O 104.5°
5	0		Trigonal bipyramid	PF_5 120° 90°
5	1		See-saw	SF_4 120° 90°
5	2		T-Shape	ClF_3 90°

Around Central Atom		Molecular Structures	Geometrical Shape	Example and Bond Angles
Total # of Eff. e^- Pairs	# of Lone Pairs			
5	3		Linear	Br_3^- 180°
6	0		Octahedral	SCl_6 90° 90°
6	1		Square pyramid	ICl_5 90° 90°
6	2		Square planar	XeF_4 90°

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)

107°

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)
$+ \quad 6e^-$ (6 H atoms)
$+ \quad 6e^-$ (1 O atom)
$\quad 20e^-$ Total
$- 16e^-$ (8 bonds)
$\quad 4e^-$ Left
$- \quad 4e^-$ (lone-pairs
$\qquad$ on O for octet)
$\quad 0e^-$

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).

$\delta-$
Negative Pole
(More Electronegative)

$\delta+$
Positive Pole
(Less Electronegative)
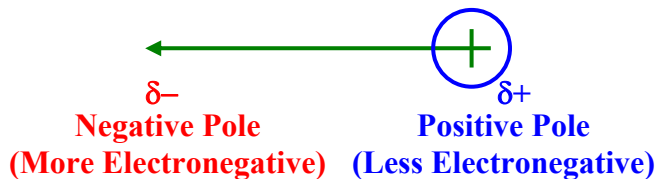
Example 1: Draw the molecular structures. Determine the dipole moments (if any) and their overall polarity of the following molecules.

a. CO_2

3.4   2.6   3.4

Electronegativities
C = 2.6   O = 3.4

Dipole Moment
C=O Bond = 3.4 − 2.6
C=O Bond = 0.8
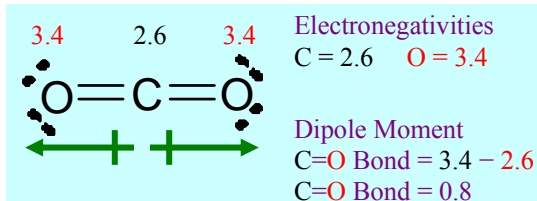
Overall, CO_2 is Non-Polar. Both dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.

b. SO_3

3.4
3.4   2.6   3.4

Electronegativities
S = 2.6   O = 3.4

Dipole Moment
S=O Bond = 3.4 − 2.6
S=O Bond = 0.8
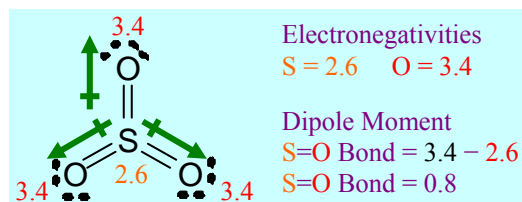
Overall, SO_3 is Non-Polar. All dipole moments are equivalent **and** the central atom has no lone pair. Hence, the dipole moments cancel out.

c. H_2O

Electronegativities
H = 2.2   O = 3.4

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

Overall Polarity

3.4
2.2 H   H 2.2

Net Vector

Vectors (arrows) are added by "head to tail".
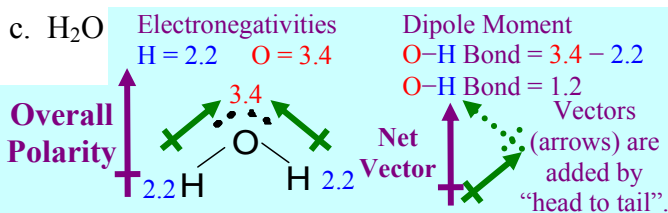
Overall, H_2O is Polar. Both dipole moments are the same, **but** there are two lone pairs on the central atom. The dipole moments do **NOT** cancel out due to the **bent** geometry of the molecule. The overall polarity of H_2O points towards the oxygen atom.
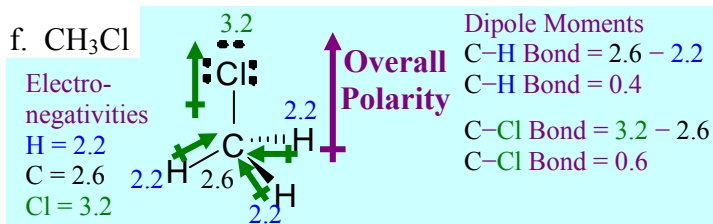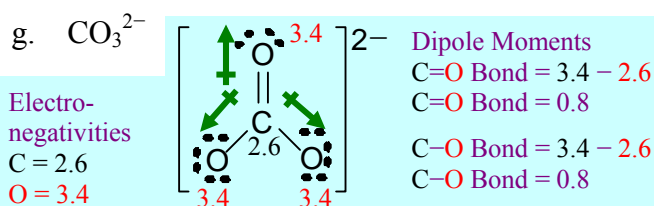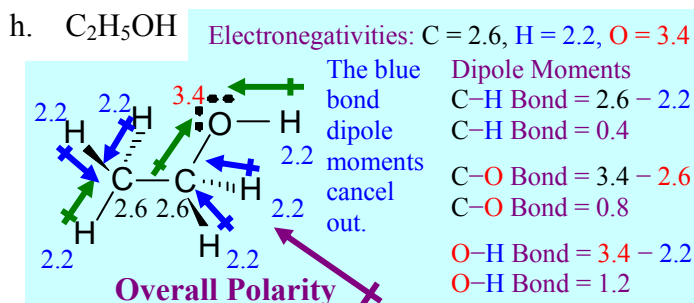
d. NH_3

Overall Polarity

3.0
2.2
H   H
2.2   H   2.2

Electronegativities
H = 2.2   N = 3.0

Dipole Moment
N−H Bond = 3.0 − 2.2
N−H Bond = 0.8
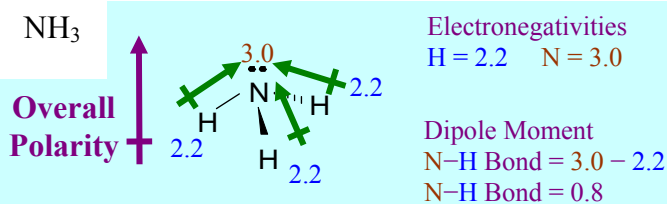
Overall, NH_3 is Polar. All dipole moments are the same, **but** there is a lone pair on the central atom. The dipole moments do **NOT** cancel out due to the **trigonal pyramid** geometry of the molecule. The overall polarity of NH_3 points towards the nitrogen atom.

e. CH_4

Electronegativities
H = 2.2   C = 2.6

Dipole Moment
C−H Bond = 2.6 − 2.2
C−H Bond = 0.4
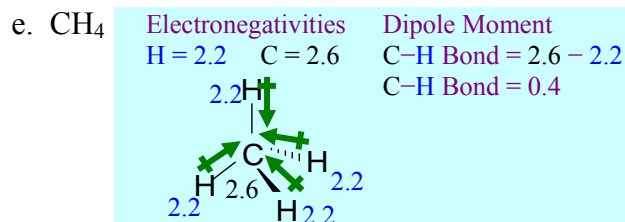
Overall, CH₄ is Non-Polar. All dipole moments are the same **and** the central atom has no lone pair. Hence, the dipole moments cancel out.

f. CH_3Cl

Overall Polarity

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, CH₃Cl 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, CO₃²⁻ 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. 453 #2, 4, 5, 8 to 14** │
│ **10.2 pg. 453−454 #16, 17, 20 to 24** │
└─────────────────────────────┘

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 Polarity

Overall, C₂H₅OH 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.

10.3: Valence Bond Theory

Bond Energy: - a measure of the strength of the chemical bond or energy needed to break the same bond.

Bond Length: - the length of a chemical bond as measured by the **lowest energy level**.

Nuclei are too close causing High Electronic Repulsion

HH

H .... H

Nuclei are too far apart to have any interaction

H H

E_{min}
−458

Energy (kJ/mol)

0

Actual Bond Length that has Minimum Energy Level with Ideal Amount of **Orbital Overlapping**

0.74 Å   Intermolecular Distance (Å)
Hydrogen Bond Length
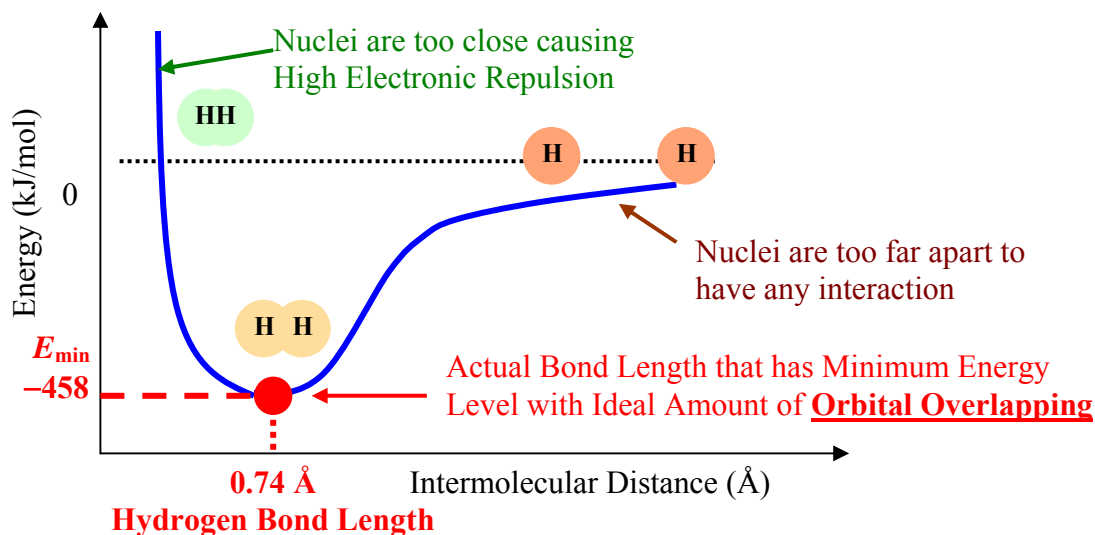
10.4 & 10.5: Hybridization of Atomic Orbitals & Molecules Containing Multiple Bonds

Hybridization: - the combining of orbitals of different atomic subshells into new orbitals.
                  - the new hybridized orbitals tend to have minimized energy levels.

Effective Electron Pairs: - the number of pairs of electrons including lone pairs and bonding pairs
                             (however, multiple bonds are counted as one bonding pair).

Sigma (σ) Bond: - a bonding electron pair localized in the area centred along a line between the two
                  nuclei.

Pi (π) Bond: - a bonding pair that utilizes a p orbital that is not involved in the hybridization process.
                - it exists away from the centred line between the two nuclei.

3 Steps to Describe using the Valence Bond Theory

1. Write the Lewis Structures and Account for Minimization of Formal Charges.
2. Using the VSEPR model, determine the electron pairs arrangement.
3. State the type of hybrid atomic orbital for all bonding and lone pairs.

Different Types of Hybridization

(Check out this website: http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/hybrv18.swf)

1. sp^3 **Hybridization**: - characterized by **4 effective electron pairs** where one s and three p orbitals are mixed.
                         - possible orbital shapes around the atom involved are tetrahedral, trigono pyramid,
                          V-shape, and linear.
                         - all bonding electron pairs form σ bonds.
                          - bond angles can be 109.5°, 107°, 104.5° and 180°.
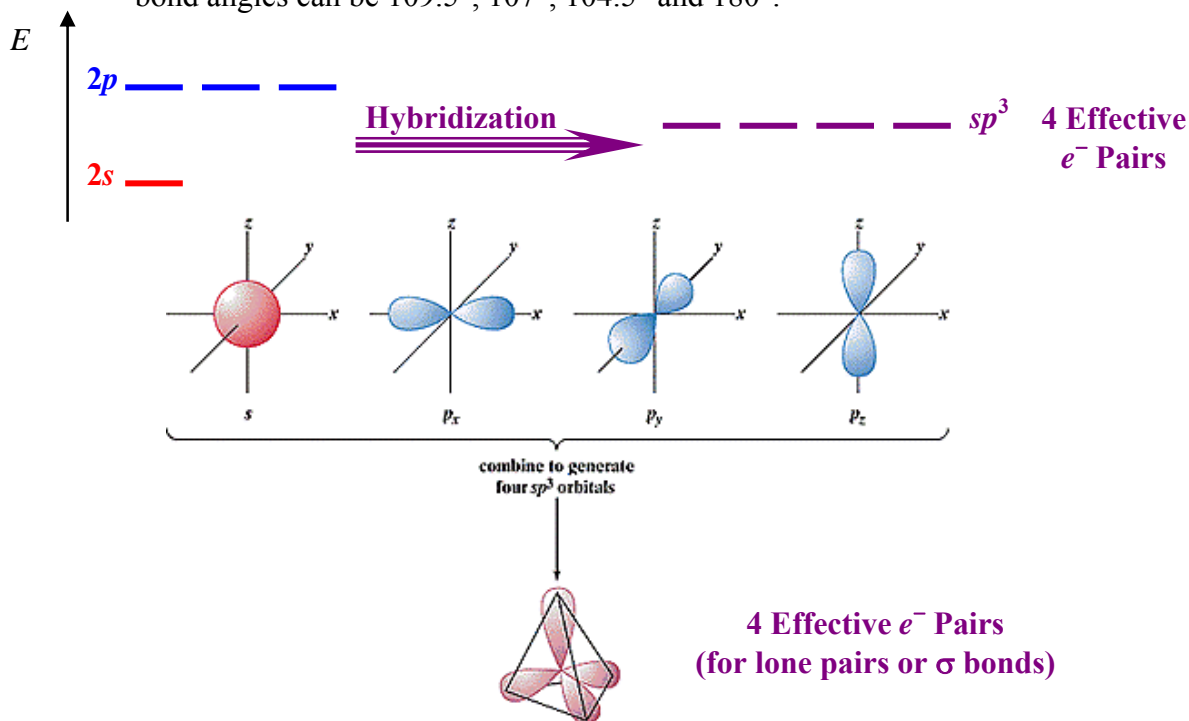
Example 1: Describe the bonding of H_2O using the Valence Bond Theory.

a. Lewis Structure and Formal Charges: c. State the type hybrid orbitals
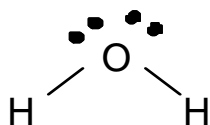
Minimize Formal Charges
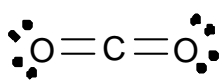$O = 6 - 4 - \frac{1}{2}(4) = 0$
$H = 1 - 0 - \frac{1}{2}(2) = 0$

b. VSEPR model:

H_2O is **V-shape** because of 4 effective e^- pairs around oxygen with two lone pairs and 2 bonding pair. Due to two lone pair repulsions, **bond angle is 105°**.

$2sp^3$

$1s$

Two σ bonds

$2sp^3$

$1s$
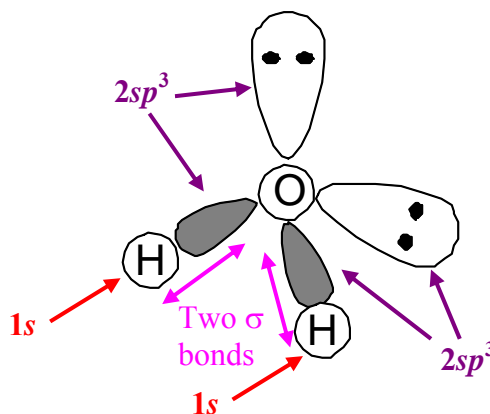
All e^- pairs around the oxygen atom have $2sp^3$ orbitals. Both hydrogen atoms have $1s$ orbitals.

2. sp^2 **Hybridization**: - characterized by **3 effective electron pairs** where one s and two p orbitals are mixed. One set of p orbital remains unmixed and becomes the π bond.
   - orbital shapes around the atom involved are trigono planar and linear.
   - there is at least one bonding electron pair that is a σ bond, one other bonding pair is a π bond. (together they make a double bond)
   - the notable exception is boron compounds. Boron has 3 valance electrons. Even with sp^2 hybridization (due to the trigono planar geometry), there are no electrons in the unmixed p orbital. Thus, no π bond and no double bond.
   - bond angles can be 120° and 180°.

E

$2p$ ——— ——— ———

Hybridization

$2p$ ———   **1 π bond**
sp^2 —— —— ——   **3 Effective**
                  e^- **Pairs**

$2s$ ———

Hybridization

Empty p_z **orbital for π bond**

3 Effective e^- **Pairs (for lone pairs or σ bonds)**
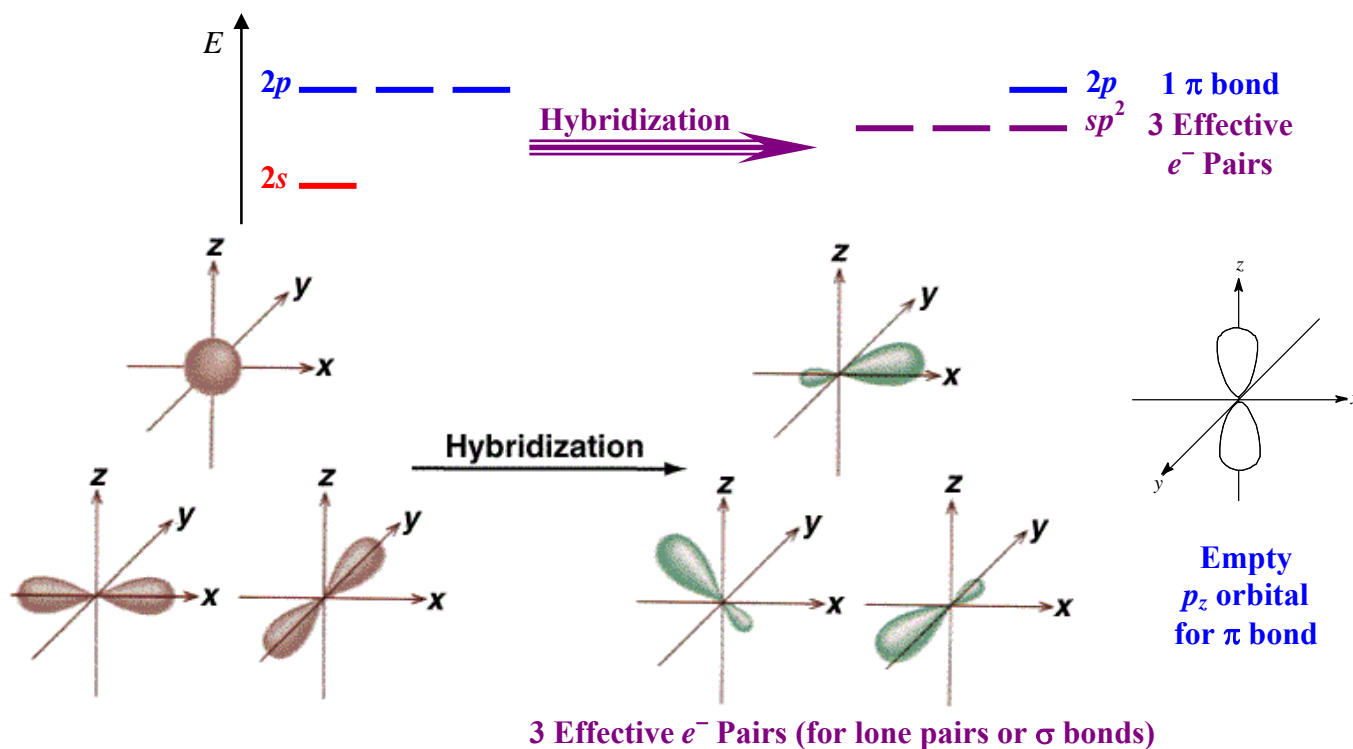
Example 2: Describe the bonding of O_2 using the Valence Bond Theory.

a. Lewis Structure and Formal Charge: c. State the type hybrid orbitals
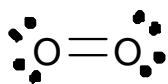
Minimizes Formal Charge
$O = 6 – 4 – \frac{1}{2}(4) = 0$

b. VSEPR model:

O_2 is **linear** because of 3 effective e^- pairs around oxygen with 2 lone pairs and 1 bonding pair. Due to the single bonding pair (σ and π bonds) between two nuclei, the **bond angle is 180°**.

All lone pairs and the σ bond around both oxygen atoms are $2sp^2$ orbitals. The $2p_z$ orbitals situate above and below the axis of the σ bond become the π bond. Together, they form a double bond as predicted in the Lewis structure.
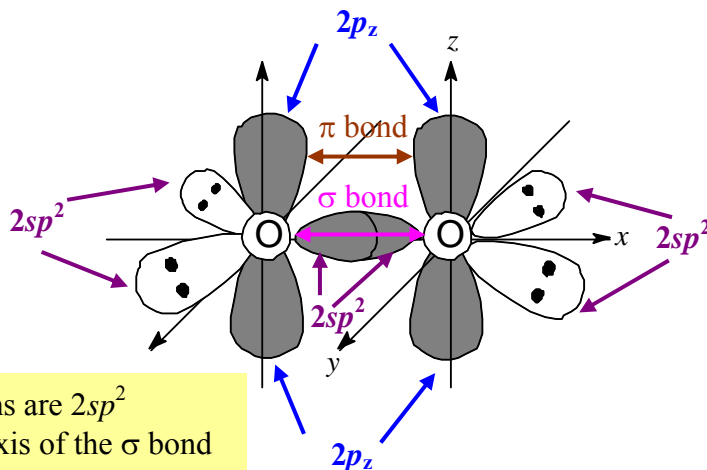
3. **_sp_ Hybridization**: - characterized by **2 effective electron pairs** where one _s_ and one _p_ orbitals are mixed. Two sets of _p_ orbitals remain unmixed and become two π bonds.
   - orbital shape around the atom involved is linear.
   - at least one bonding electron pair is a σ bond, two other bonding pairs are π bonds. (together they make a triple bond or two double bonds)
   - the notable exception is beryllium compounds. Be has 2 valance electrons. Even with _sp_ hybridization (due to the linear geometry), there is no electrons in the two unmixed _p_ orbitals. Thus, no π bonds and no triple bond.
   - bond angles are 180°.
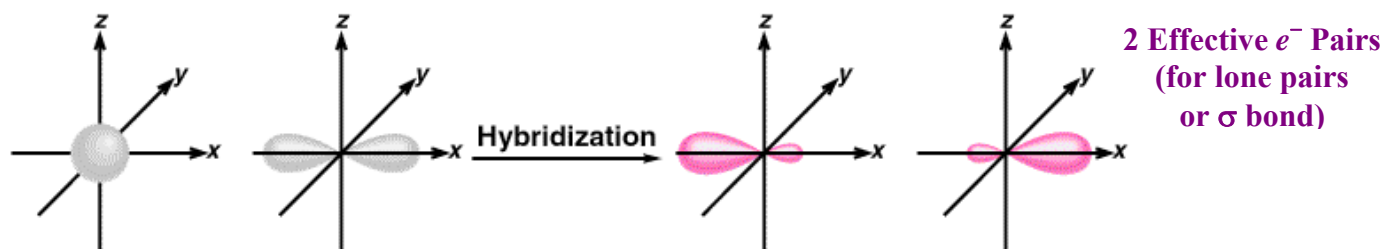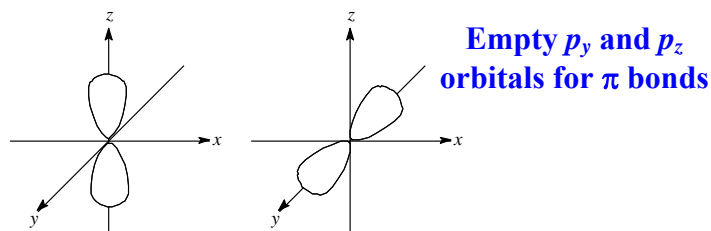
Example 3: Describe the bonding of CO_2 using the Valence Bond Theory.

a. Lewis Structure and Formal Charge:

$\ddot{O}=C=\ddot{O}$

Minimize Formal Charges
$C = 4 - 0 - \frac{1}{2}(8) = 0$
$O = 6 - 4 - \frac{1}{2}(4) = 0$

b. VSEPR model:

CO_2 is **linear** because of 2 effective e^- pairs around the central carbon with no lone pairs and 2 bonding pair. Due to the two double bonds between the three nuclei, the **bond angle is 180°**.

c. State the type hybrid orbitals
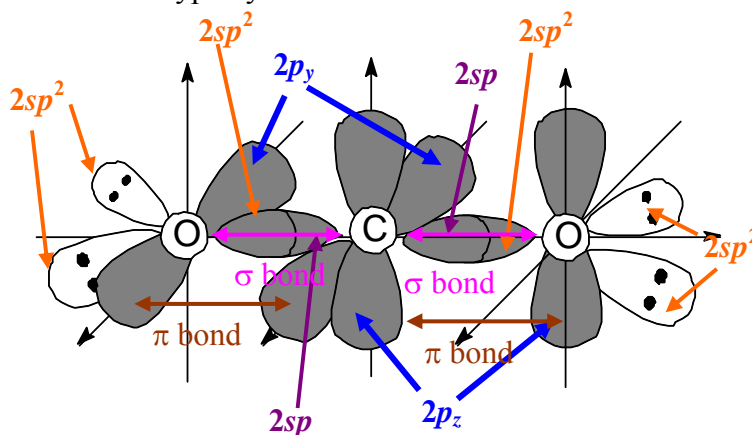
The $2sp$ orbital form the bonds on the left and right side of the carbon atom form the two σ bonds. All lone pairs and the σ bond around both oxygen atoms are $2sp^2$ orbitals. The $2p_z$ orbitals situate above and below the axis of the σ bond become the one of the two π bonds. The other π bond comes from the $2p_y$ orbital into and out of the page. Together, they form two double bonds as predicted in the Lewis structure.

4. **dsp^3 Hybridization**: - characterized by **5 effective electron pairs** where one s, three p and one d orbitals are mixed.
   - possible orbital shapes around the atom involved are trigono bipyramid, see-saw, T-shape, and linear.
   - all bonding electron pairs are σ bonds.
   - bond angles can be 120° and 90°, or 180°.

Example 4: Describe the bonding of PF_5 using the Valence Bond Theory.

a. Lewis Structure and Formal Charge:

c. State the type hybrid orbitals
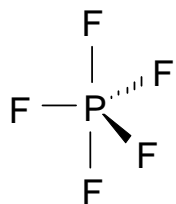
Minimize Formal Charges
$P = 5 - 0 - \frac{1}{2}(10) = 0$
$F = 7 - 6 - \frac{1}{2}(2) = 0$

b. VSEPR model:

PF$_5$ is **trigono bipyramid** because of 5 effective e^- pairs around the central phosphorus atom with no lone pairs and 5 bonding pair. Due to these five bonding pairs, the **bond angles are 120° and 90°**.
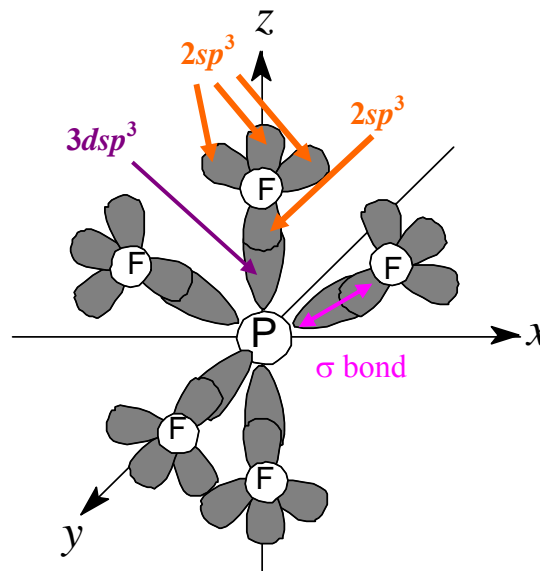
All e^- pairs around the phosphorus atom have $3dsp^3$ orbitals, and all five fluorine atoms have $2sp^3$ orbitals. There are a total of 5 sigma bonds. Each composes of an overlapping between these $3dsp^3$ and $2sp^3$ orbitals.

5. d^2sp^3 Hybridization: - characterized by **6 effective electron pairs** where one s and two p orbitals are mixed.
- possible orbital shapes around the atom involved are octahedral, square pyramid and square planar.
- all bonding electron pairs are σ bonds.
- bond angles are 90°.

Example 5: Describe the bonding of XeF_4 using the Valence Bond Theory.

a. Lewis Structure and Formal Charge:
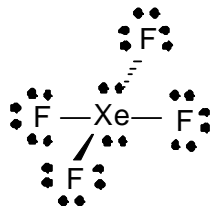
Minimize Formal Charges
Xe = 8 − 4 − ½(8) = 0
F = 7 − 6 − ½(2) = 0

c. State the type hybrid orbitals

b. VSEPR model:

XeF_5 is **square planar** because of 6 effective e^- pairs around the central xenon atom with two lone pairs and 4 bonding pair. Due to these four bonding pairs bonding pairs, the **bond angles are 90°**.
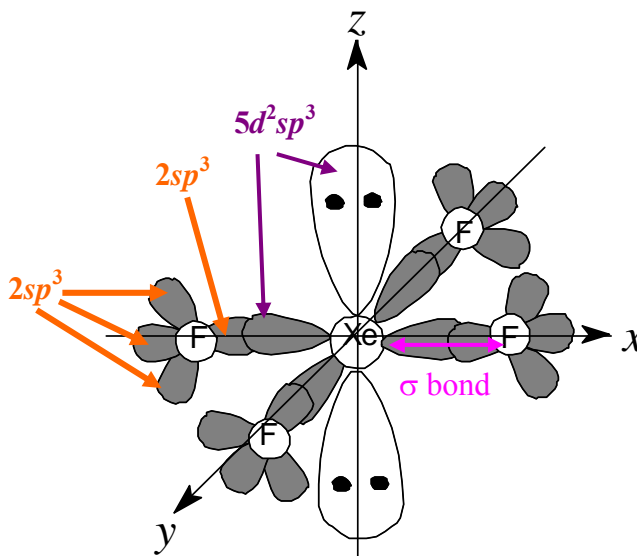
All e^- pairs around the xenon atom have $5d^2sp^3$ orbitals, and all four fluorine atoms have $2sp^3$ orbitals. There are a total of 4 σ bonds and 2 lone pairs. Each sigma bond composes of an overlapping between these $5d^2sp^3$ and $2sp^3$ orbitals.

Assignment
10.3 pg. 454 #26
10.4 & 10.5 pg. 454−455 #29, 30, 32, 34, 36 to 42

Chapter 24: Organic Chemistry

24.1: Classes of Organic Compounds

Organic Chemistry: - the branch of chemistry the studies hydrocarbon compounds.

Hydrocarbons: - compounds that contains hydrogen and carbon atoms that are bonded to each other.
- it may contain oxygen, nitrogen and other halogen atoms. In complex organic compound, it may even contain transition metals.

Examples: CH_4 (Methane), C_3H_8 (Propane), $C_6H_{12}O_6$ (Glucose), CH_3OH (Methanol) are hydrocarbons.
CO_2 (Carbon dioxide) and CO (Carbon monoxide) are not hydrocarbons (no hydrogen atoms).

Functional Group: - the part of an organic molecule that is responsible for the physical and chemical behaviour of the overall molecule.

Aliphatic Hydrocarbons: - alkanes, alkenes and alkynes that show distinct reactivity based on their σ or π bonds.   (more explanation in section 24.2)

Aromatic Hydrocarbons: - a class of cyclic hydrocarbons characterize by alternating double bonds (delocalised π bonds – having resonance structures). (more in section 24.3)

24.2: Aliphatic Hydrocarbons

Saturated Bonds: - bonds in hydrocarbons that are single bonds only (mainly $2sp^3$ orbitals for carbon and oxygen and $1s$ orbital for hydrogen).

Unsaturated Bonds: - bonds in hydrocarbons that are double or triple bonds ($2sp^2$ orbitals for C=C and C=O bonds; $2sp$ orbitals for C≡C and C≡N bonds).

Lewis Structure of Hydrocarbons: - each carbon has 4 valence electrons; therefore it has a maximum of 4 bonding sites.
- all lone pairs must be drawn in.

Example: C_2H_5COOH (Propanoic Acid)
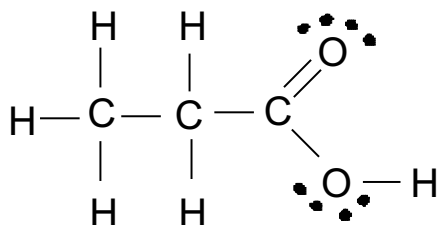
Note that there are 4 bonds around each carbon atom.

Structural Formulas: - a Lewis structure without any lone pairs notations.
- there are many forms to write the structural formulas

Example: $C_5H_{11}OH$ (1-Pentanol)

$CH_3CH_2CH_2CH_2CH_2OH$

or

$CH_3(CH_2)_4OH$

(Truncated Structural Formulas)

Complete Extended Structural Formula
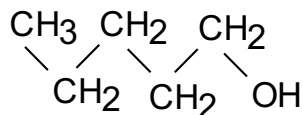
or
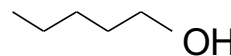
Skeletal Forms
(Each endpoint of the zigzag represents a carbon atom)
(Notice the two lone pairs around the oxygen atom are not drawn)

Prefixes of Organic Compounds Nomenclature (You are responsible for the first 10 prefixes)

1 carbon – Meth~	6 carbons – Hex~	11 carbons – Undec~	20 carbons – Icos~
2 carbons – Eth~	7 carbons – Hept~	12 carbons – Dodec~	21 carbons – Henicos~
3 carbons – Prop~	8 carbons – Oct~	13 carbons – Tridec~	22 carbons – Docos~
4 carbons – But~	9 carbons – Non~	14 carbons – tetradec~	30 carbons – Triacont~
5 carbons – Pent~	10 carbons – Dec~	15 carbons – pentadec~	40 carbons – Tetracont~

Alkane: - a group of hydrocarbons that has a molecular formula C_nH_{2n+2}.
         - nomenclature of alkane involves the use of the suffix ~*ane* (like in Alk ~**ane**).

Normal Hydrocarbons: - also refer to as Straight Chained or Unbranched Hydrocarbons.
                - hydrocarbons that do NOT branched out.

Example 1: Name the following organic compounds or give the molecular formula. Provide a structural
             formula for these compounds.

a. C_2H_6

    Alkane: $C_2H_{2(2)+2}$ **Ethane**
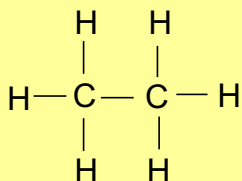
b. C_5H_{12}

    Alkane: $C_5H_{2(5)+2}$ **Pentane**
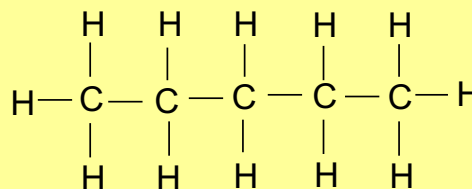
c. Octane

    Alkane: $C_8H_{2(8)+2}$ C_8H_{18}

    $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
        or $CH_3(CH_2)_6CH_3$

d. Decane

    Alkane: $C_{10}H_{2(10)+2}$ **$C_{10}H_{22}$**
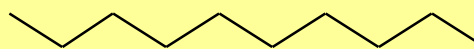
Isomers: - hydrocarbons with the same molecular formula that can have other structural formulas.
     - *Iso~* means the same. Sometimes refer to as **Structural Isomers**.

Example: C_4H_{10} has two structural formulas.

Substituent

Unbranched (Straight Chain)   **Branched (the branched group is called a substituent)**
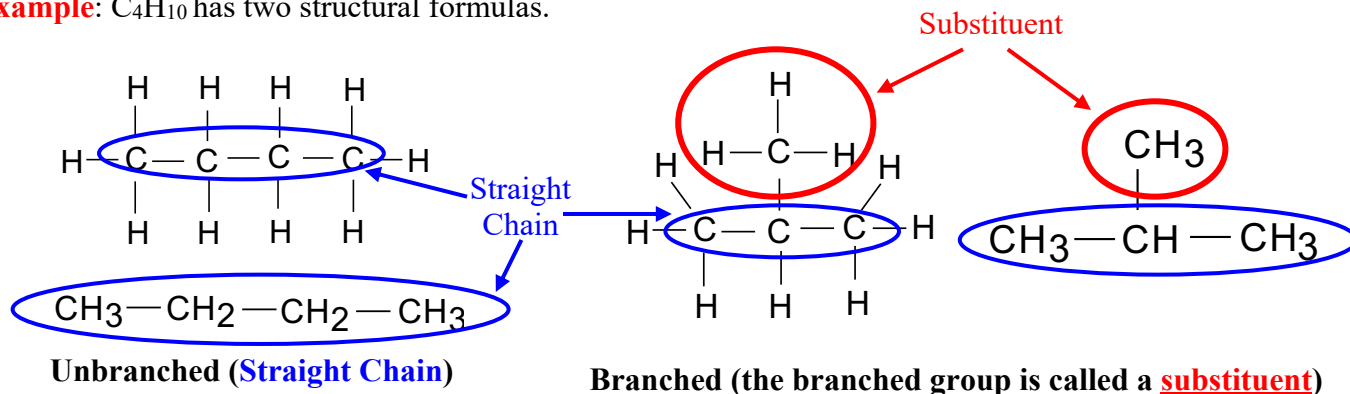
Alkyl Group: - the substituent component of a branched hydrocarbon. C_nH_{2n+1}
     - nomenclature of alkyl group involves the use of the suffix *~yl* (like in Alk ~**yl**). This is
       followed by the longest main chain of the hydrocarbons.

Nomenclature of Alkanes

1. Identify the number of carbons in the longest chain. (It is not always the straight one. It can be bent).

Example:

7 Carbons: root name is heptane

Only 6 Carbons: Not the Longest Chain
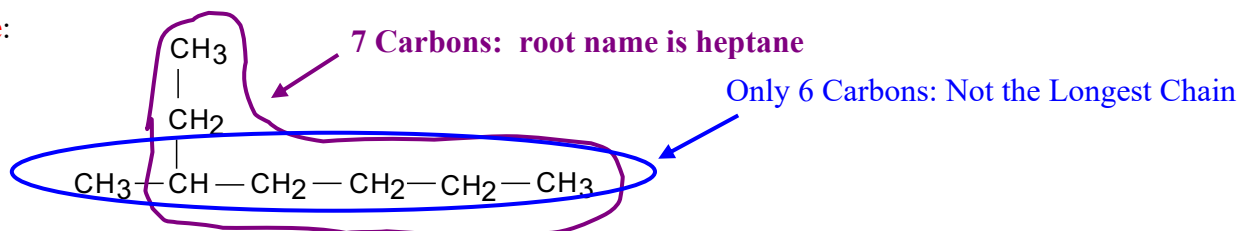
2. Number the carbons of the longest chain with the first alkyl group at the lowest carbon position possible.

Example:

Alkyl Group:
1 Carbon
(methyl)
at Position 3

methyl at Position 5
(Not the Lowest
Carbon Position)
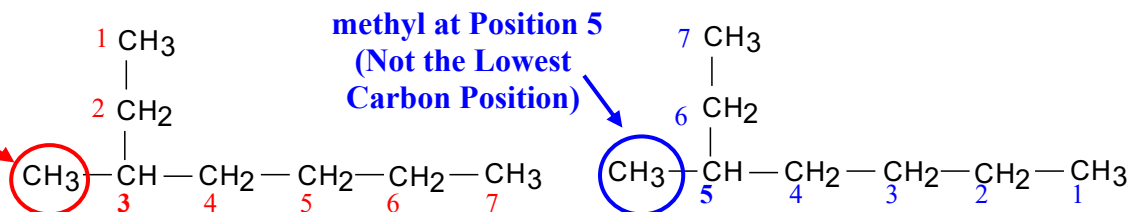
3. Start with the position of the alkyl group, then the name of the alkyl group. Finally the name of the main chain (root name).

Example:

3-methylheptane
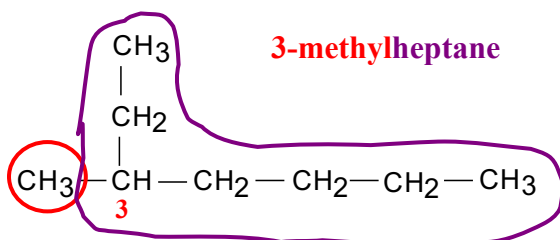
Hyphen should be added
between number and alphabet.

There is no space between the
alkyl group and the root name.

4. If there are more than one alkyl groups, and they are at the different carbon positions, the alkyl groups shall be name by their positions but their appearance in the final name has to follow alphabetical order.

Example:

**5-ethyl-2-methylheptane
(Correct Name)**

**methyl
at Position 2**

2-methyl-5-ethylheptane
**(Incorrect Name – substituent groups
are not in alphabetical order)**

**Alkyl Group:
2 Carbon (ethyl)
at Position 5**

**3-ethyl-6-methylheptane
(Incorrect Name – position
combination is larger)**

methyl at Position 6

ethyl at Position 3
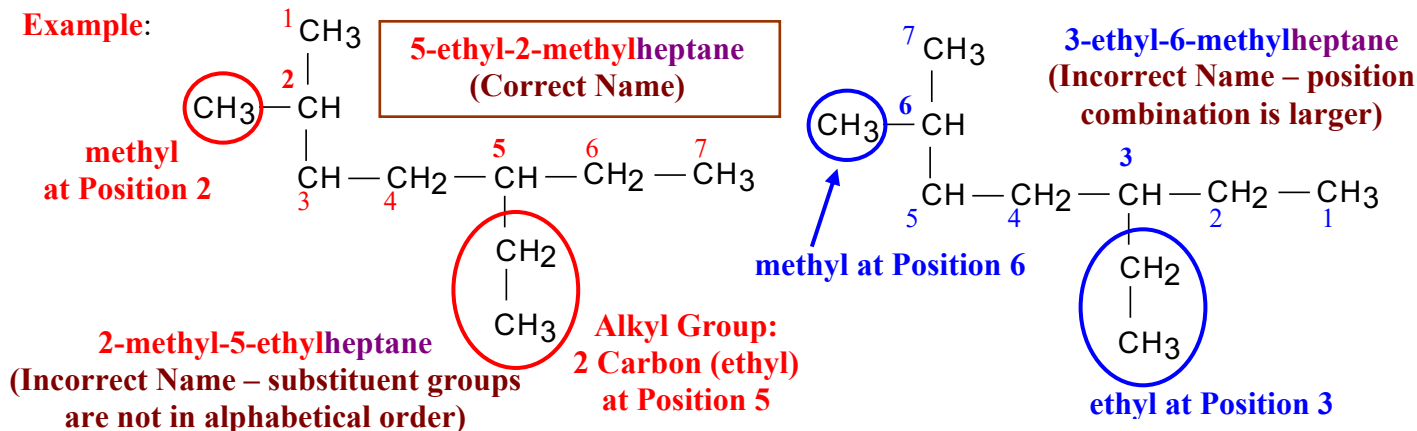
5. If there are more than one alkyl groups, and they are at the same carbon position, then we can name the position as a **repeated number separated by a comma**. In any case, we have to name all positions. If the alkyl groups have the same name, then we can use **prefixes** with the alkyl groups. **(These prefixed are the same as the ones for molecular formulas.)**

Example:

**3,5-diethyl-2,2-dimethylheptane
(Correct Name)**

Two methyl groups and
both at position 2
(2,2-dimethyl)

Two ethyl groups at
positions 3 and 5
(3,5-diethyl)
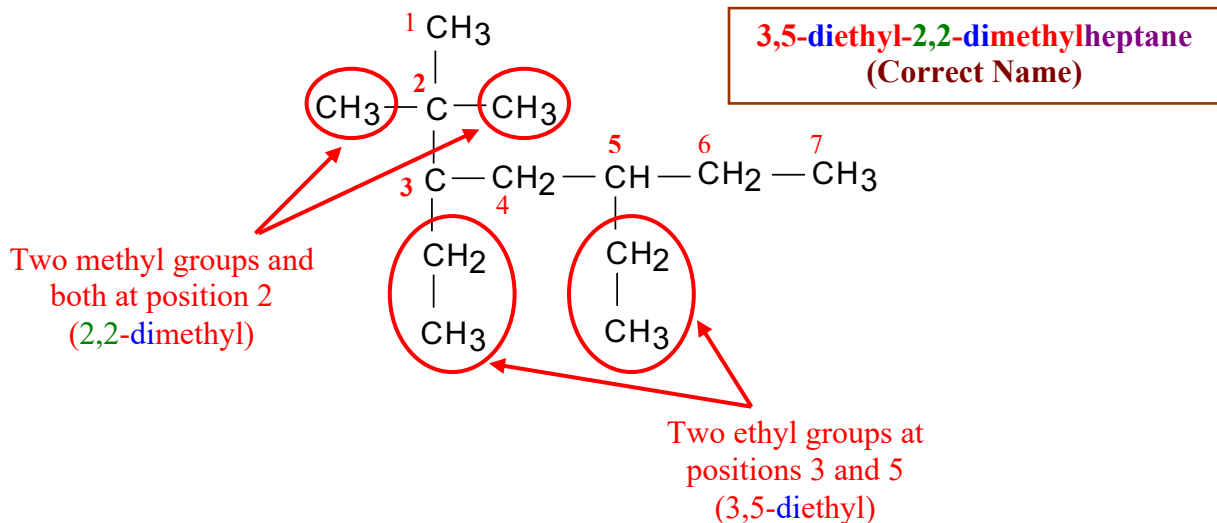
Example 2: Provide the names and structural formulas for all the isomers of heptane.
(Hint: there are 9 isomers)
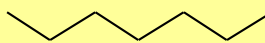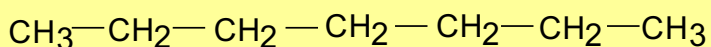
heptane
$CH_3(CH_2)_5CH_3$
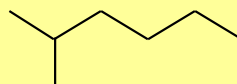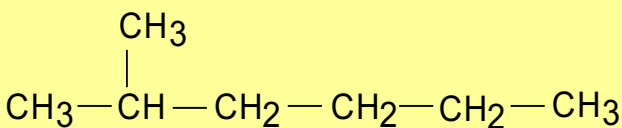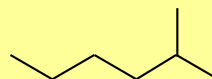
2-methylhexane
$CH_3CHCH_3(CH_2)_3CH_3$

or

CH_3
$CH_3-CH_2-CH-CH_2-CH_2-CH_3$ or   **3-methylhexane**
$CH_3CH_2CHCH_3(CH_2)_2CH_3$

CH_3
$CH_3-C-CH_2-CH_2-CH_3$ or   **2,2-dimethylpentane**
CH_3 $CH_3C(CH_3)_2(CH_2)_2CH_3$

CH_3
$CH_3-CH_2-C-CH_2-CH_3$ **3,3-dimethylpentane**
CH_3 $CH_3CH_2C(CH_3)_2CH_2CH_3$

CH_3
$CH_3-CH-CH-CH_2-CH_3$ or   **2,3-dimethylpentane**
CH_3 $CH_3CHCH_3CHCH_3CH_2CH_3$

CH_3
$CH_3-CH-CH_2-CH-CH_3$ **2,4-dimethylpentane**
CH_3 $CH_3CHCH_3CH_2CHCH_3CH_3$

$CH_3-CH_2-CH-CH_2-CH_3$
CH_2 **ethylpentane**
CH_3 $CH_3CH_2CH(C_2H_5)CH_2CH_3$

CH_3
$CH_3-C-CH-CH_3$ or   **trimethylbutane**
CH_3 CH_3 $CH_3C(CH_3)_2CHCH_3CH_3$

Halogen Derivatives: - hydrocarbons that contain halogen substituent(s).
                 - uses the same rules as naming branched alkanes.
                 - F (fluro), Cl (chloro), Br (bromo), I (iodo).

Example 3: Name the following halogen derivatives or give the molecular formula. Provide a structural
                formula for these compounds.

a. CH_3CH_2Cl b. $CH_2FCH_2CHBr_2$
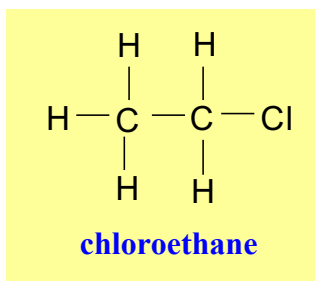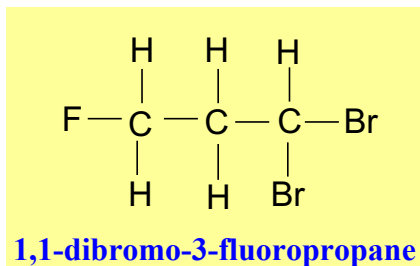
chloroethane

3,3-dibromo-1-fluoropropane
(Incorrect Naming – number
sequence could be better)

1,1-dibromo-3-fluoropropane
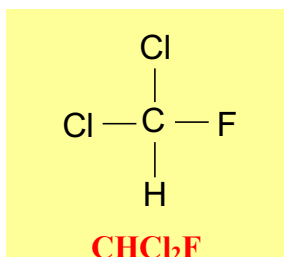
c. dichlorofluromethane   d. 1,1,2-trichloro-1,3-diiodo-2-methylbutane

CHCl₂F

CCl₂ICCH₃ClCHICH₃
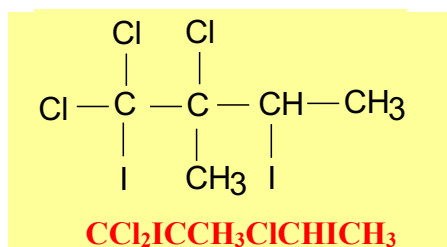
Cyclic Alkane: - where the ends of an alkane chain are connected to each other in a cyclical shape.
                - the molecular formula has a form of C_nH_{2n}.
                - naming contains the prefix *cyclo*~ before the root name.
                - substituents are named the same way as branched alkanes (pick any corner as carbon 1).
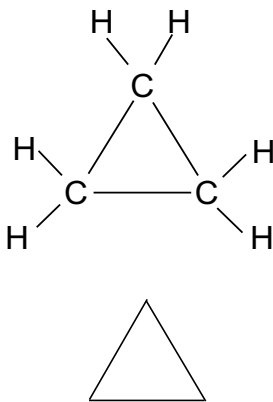
Cyclopropane (C_3H_6)
(bond angle 60°)
(Too tight – unstable)
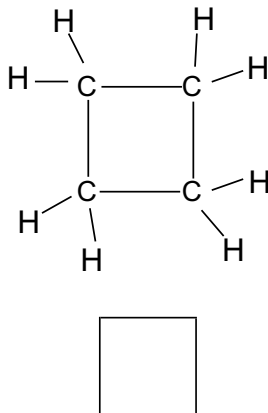
Cyclobutane (C_4H_8)
(bond angle 90°)
(still tight – unstable)
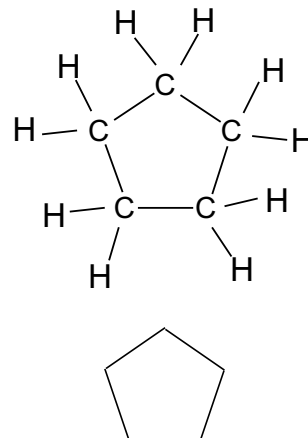
Cyclopentane (C_5H_{10})
**(bond angle 108° - close
to tetrahedral - stable)**

3-D (use molecular model to demonstrate)

"Chair" Conformation

"Boat" Conformation
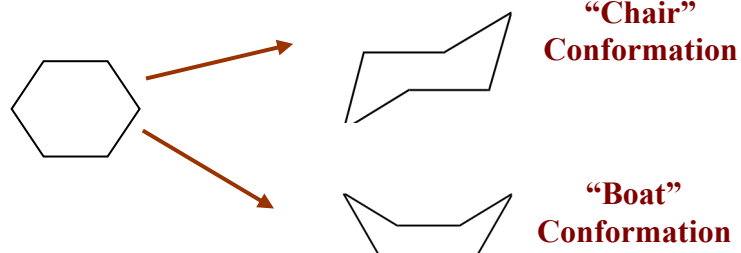
Cyclohexane (C₆H₁₂)
(bond angle 109.5° - same as tetrahedral)
(very stable)
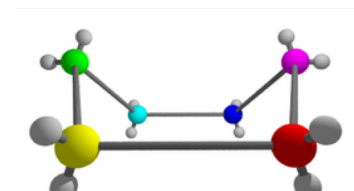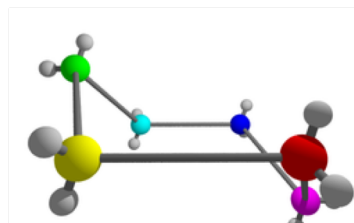
The Chair formation is slightly more stable

Example 4: Provide a structural formula for these organic compounds below.
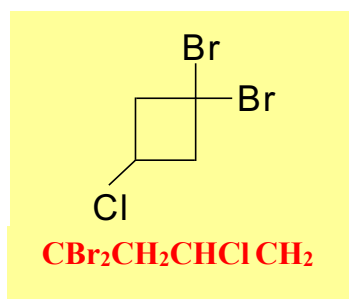
a. methylcyclopentane
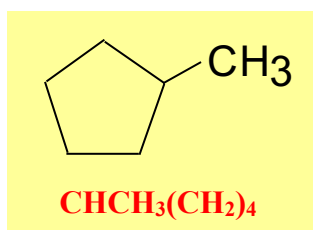
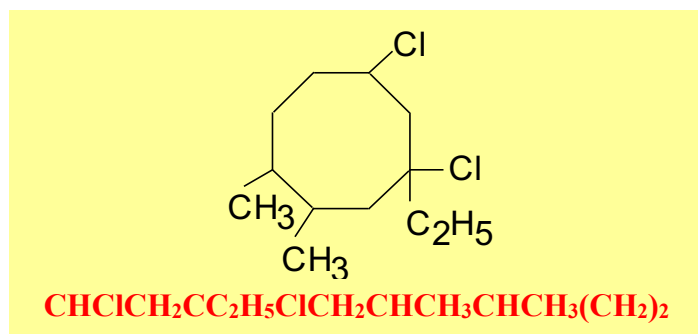Whenever the position of the substituent is not stated, it is always assume as position 1.

CHCH₃(CH₂)₄

b. 1,2-dimethylcyclohexane

CHCH₃CHCH₃(CH₂)₄
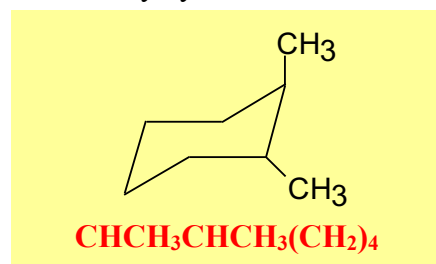
c. 1,1-dibromo-3-chlorocyclobutane

CBr₂CH₂CHCl CH₂

d. 1,3-dichloro-3-ethyl-5,6-dimethylcycloctane

CHClCH₂CC₂H₅ClCH₂CHCH₃CHCH₃(CH₂)₂

Reactions of Alkanes

1. Combustion: **Alkane + Oxygen → Carbon Dioxide + Water Vapour**

Example: Propane   +   Oxygen   →   Carbon Dioxide   +   Water Vapour
                        $C_3H_{8\,(g)}$ + $5\,O_{2\,(g)}$ → $3\,CO_{2\,(g)}$ + $4\,H_2O_{\,(g)}$

                        $CH_3 - CH_2 - CH_3$ + $5\,O = O$ → $3\,\,O = C = O$ +   4
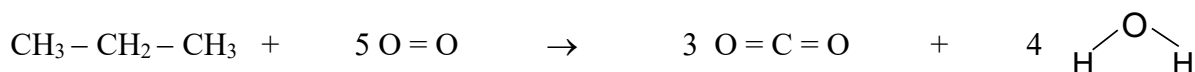
2. **Substitution:** Alkane + Halogen (X₂) $\xrightarrow{h\nu}$ Halogen Derivate + HX $\quad$ **$h\nu$= light energy**

(Check out animation at **https://www.youtube.com/watch?v=t6fTDStG35c**)

Example: Propane $\quad$ + $\quad$ Chlorine $\quad \xrightarrow{h\nu}$ $\quad$ 1-chloropropane $\quad$ + $\quad$ Hydrogen Chloride

$C_3H_{8\ (g)}$ $\quad$ + $\quad$ $Cl_{2\ (g)}$ $\quad \xrightarrow{h\nu}$ $\quad$ $CH_3CH_2CH_2Cl_{(g)}$ $\quad$ + $\quad$ $HCl_{(g)}$

$CH_3 - CH_2 - CH_3$ + $Cl - Cl$ $\quad \xrightarrow{h\nu}$

$$CH_3 \!-\! CH_2 \!-\! \overset{\displaystyle Cl}{\underset{|}{CH_2}} \quad + \quad H - Cl$$
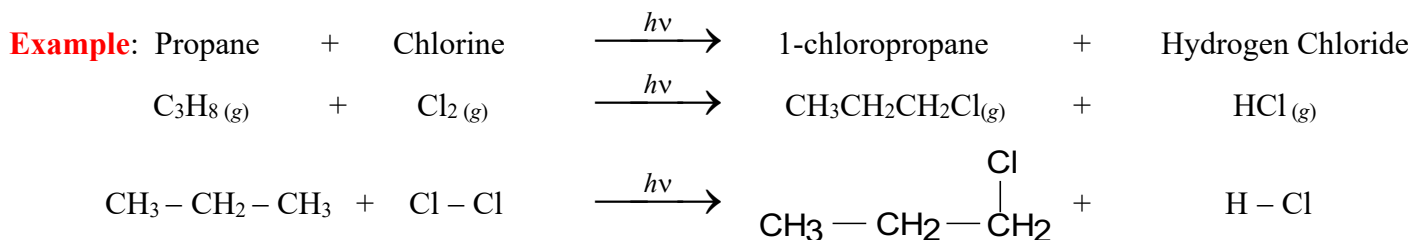
3. **Dehydrogenation:** $\quad$ Alkane $\xrightarrow{Pt}$ **Alkene (double bond) + Hydrogen**

Example: $\quad$ Ethane $\quad \xrightarrow{Pt}$ $\quad$ Ethene $\quad$ + $\quad$ Hydrogen

$C_2H_{6\ (g)}$ $\quad \xrightarrow{Pt}$ $\quad$ $C_2H_{4\ (g)}$ $\quad$ + $\quad$ $H_{2\ (g)}$

$CH_3 - CH_3$ $\quad \xrightarrow{Pt}$ $\quad$ $CH_2 = CH_2$ $\quad$ + $\quad$ $H - H$
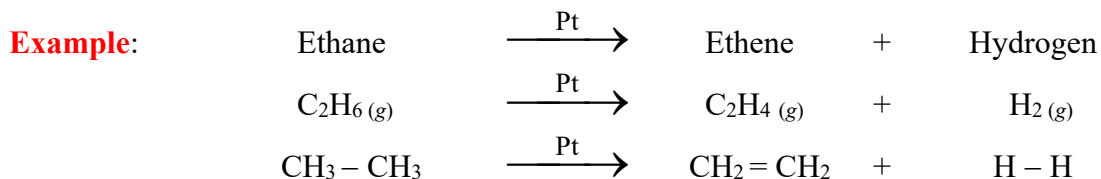
Alkenes: - hydrocarbons that contain a C = C (double bond)
- nomenclature of alkane involves the use of the suffix ~*ene* (like in Alk ~**ene**).
- hydrocarbons with two double bonds are named with the suffix ~*diene* (~**di ene** as in two double bonds).
- hydrocarbons with three double bonds are named with the suffix ~*triene* (~**tri ene** as in three double bonds).
- unless it is understood, all double bond locations along the longest carbon chain must be identified.
- prefixes to indicate the number of carbon atoms in the longest chain along with the naming of any alkyl group remains the same as alkane compounds with the lowest numerical combination given to the double bonds. *Note: The alkene group takes precedent in the root naming over any substituents.*
- **for one double bond alkenes, the molecular formula C_nH_{2n}.** *Note:* It is the same as cycloalkanes. Therefore, *one double bond alkenes are isomers to cycloalkanes.*

Example 5: Name the following alkenes or give the molecular formula or vice-versa. Provide a structural formula for these compounds.
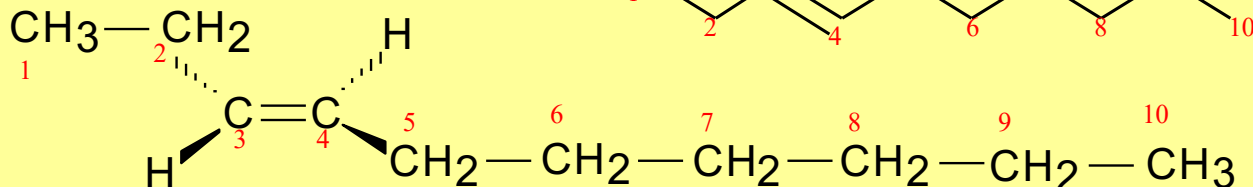
a. C_2H_4 $\qquad\qquad\qquad\qquad$ b. 1-octene

Alkene: $C_2H_{2(2)}$ $\quad$ **Ethene** $\qquad$ Alkene: $C_8H_{2(8)}$ $\qquad\qquad$ **C_8H_{16}** $\qquad$ **The double bond starts at carbon-1.**

$$\text{CH}_2\text{=CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$
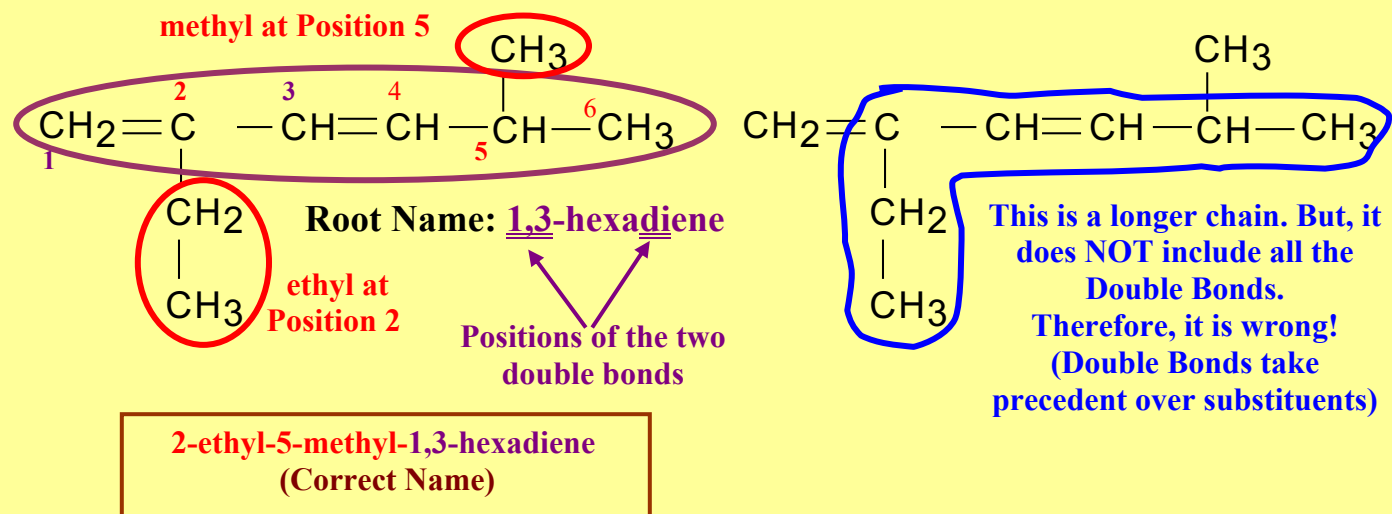$$\text{or } \text{CH}_2\text{CH(CH}_2\text{)}_5\text{CH}_3$$
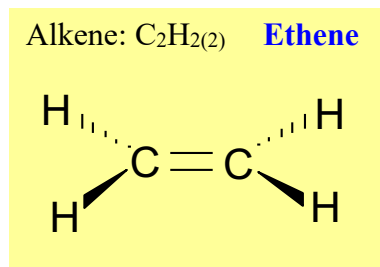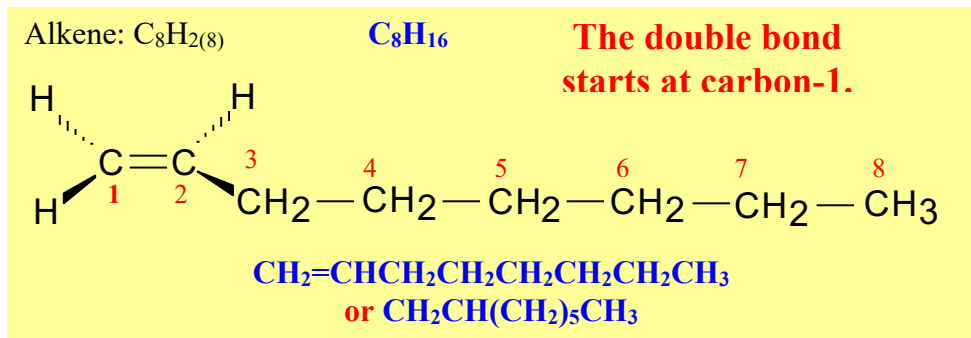
c. 3-decene

Alkene: $C_{10}H_{2(10)}$ $C_{10}H_{20}$

$CH_3 — CH_2$ H

$C = C$

H $CH_2 — CH_2 — CH_2 — CH_2 — CH_2 — CH_3$

**The double bond
starts at carbon-3.**

$CH_3CH_2CH=CHCH_2CH_2CH_2CH_2CH_2CH_3$
or $CH_3CH_2CHCH(CH_2)_5CH_3$

d. $CH_2=C(C_2H_5)CH=CH–CH(CH_3)CH_3$

First, we draw the structural formula.

methyl at Position 5

CH_3

$CH_2=C — CH=CH—CH—CH_3$

CH_2 **Root Name: 1,3-hexadiene**

CH_3 **ethyl at Position 2**

**Positions of the two
double bonds**

**2-ethyl-5-methyl-1,3-hexadiene
(Correct Name)**

CH_3

$CH_2=C — CH=CH—CH—CH_3$

CH_2 This is a longer chain. But, it
does NOT include all the
Double Bonds.
CH_3 Therefore, it is wrong!
(Double Bonds take
precedent over substituents)

Example 6: Provide the names and structural formulas for all the isomers of C_5H_{10}.

There are 10 isomers to C_5H_{10}.
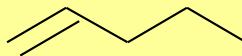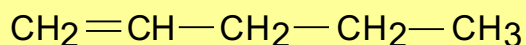
$CH_2=CH—CH_2—CH_2—CH_3$

1-pentene
$CH_2CHCH_2CH_2CH_3$
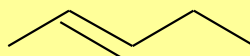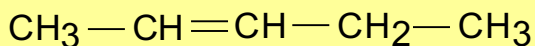
$CH_3—CH=CH—CH_2—CH_3$

2-pentene
$CH_3CHCHCH_2CH_3$

CH_3
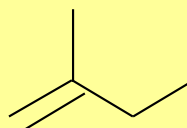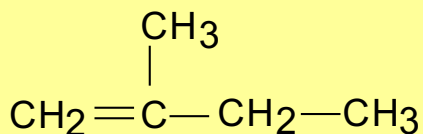
$CH_2=C—CH_2—CH_3$

2-methyl-1-butene
$CH_2C(CH_3)CH_2CH_3$

CH_3
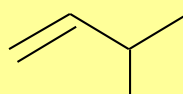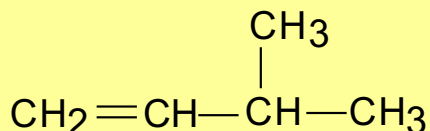
$CH_2=CH—CH—CH_3$

3-methyl-1-butene
$CH_2CHCH(CH_3)CH_3$

CH3

CH3—C=CH—CH3   or

2-methyl-2-butene
CH₃C(CH₃)CHCH₃

cyclopentane
(CH₂)₅

methylcyclobutane
CH(CH₃)CH₂CH₂CH₂

1,2- dimethylcyclopropane
CH(CH₃)CH(CH₃)CH₂

1,1- dimethylcyclopropane
C(CH₃)₂CH₂CH₂

ethylcyclopropane
CH(C₂H₅)CH₂CH₂
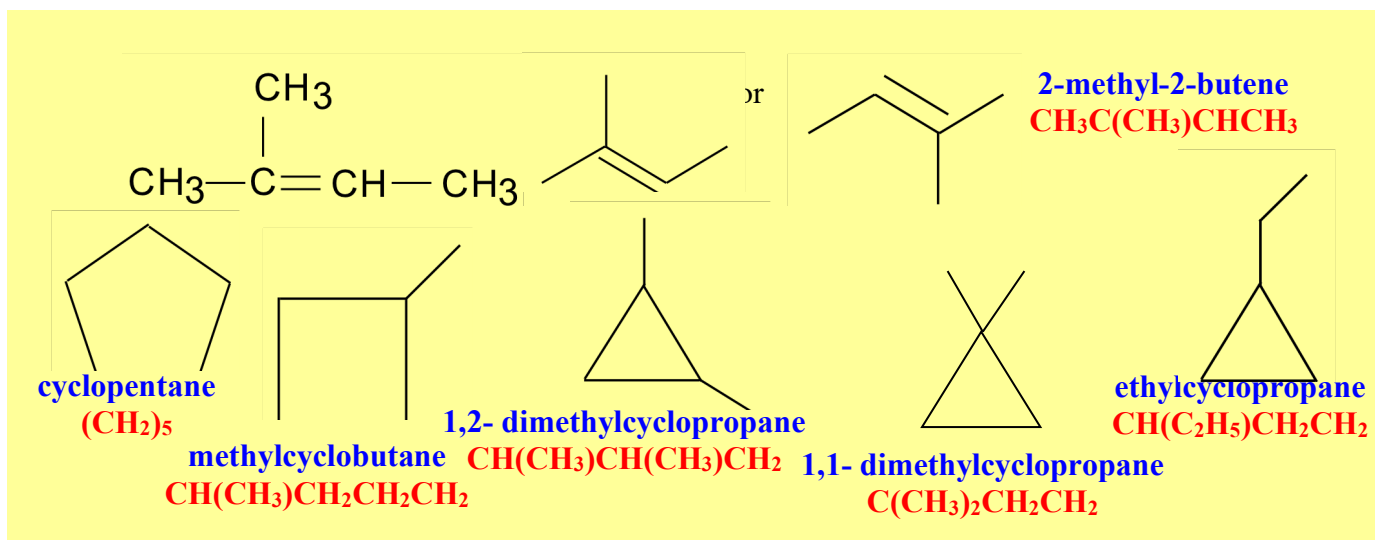
cis-trans <u>isomerism</u>: - **geometrical isomers** of hydrocarbons or cycloalkanes which differ in the positions
            of atoms (or groups) relative to a reference plane
        - in the ***cis*-isomer** the atoms are **on the same side**.
        - in the ***trans*-isomer** they **are on opposite sides**.

Examples:

***cis*-1-fluoro-2-chloroethene**

***trans*-1-fluoro-2-chloroethene**

***cis*-1-fluoro-2-chlorocyclobutane**

***trans*-1-fluoro-2-chlorocyclobutane**
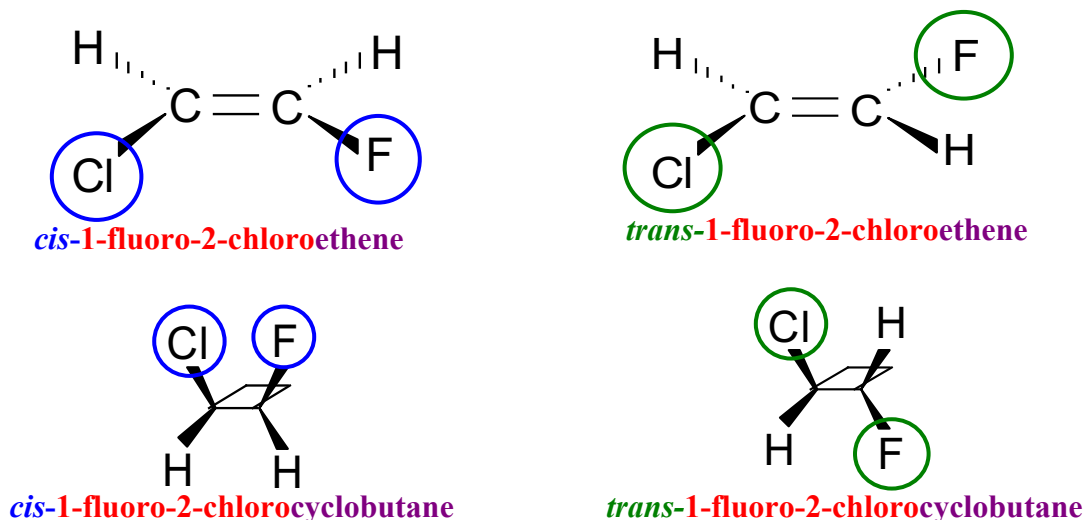
Example 7: Draw the structural formula and state the name for the following organic compounds.

a. *cis*-2-pentene
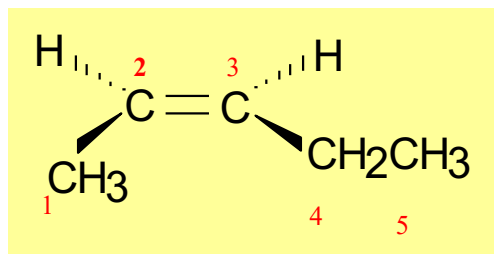
b. *trans*-1-ethyl-2-methylcyclohexane

c.

trans-3,4-dimethyl-2-pentene

(**trans** are on the main chain)
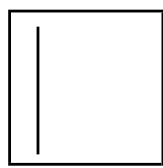
d.
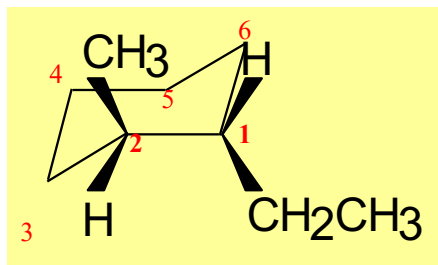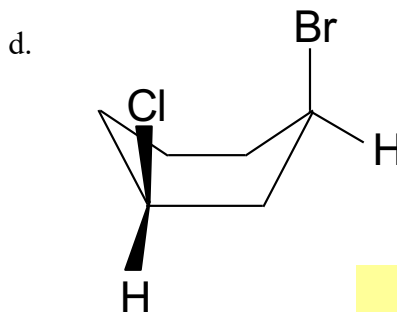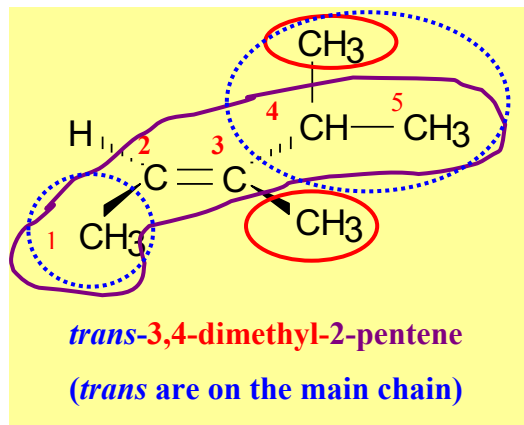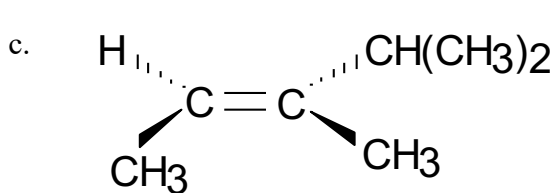
cis-1-bromo-3-chlorocyclohexane
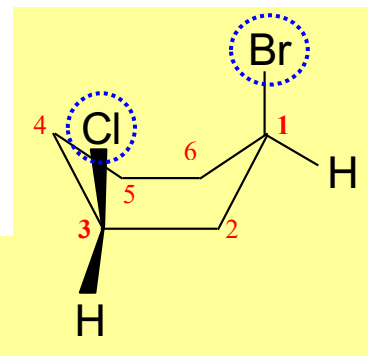
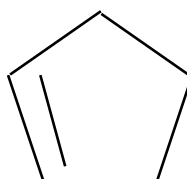**Cyclic Alkene**: - where the ends of an alkene chain are connected to each other in a cyclical shape.
- the molecular formula has a form of C_nH_{2n-2}.
- naming contains the prefix *cyclo~* before the root name.
- substituents are named the same way as branched alkenes (pick any corner as carbon 1).
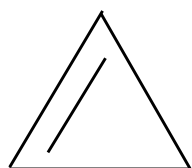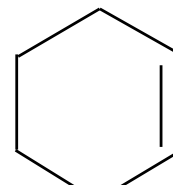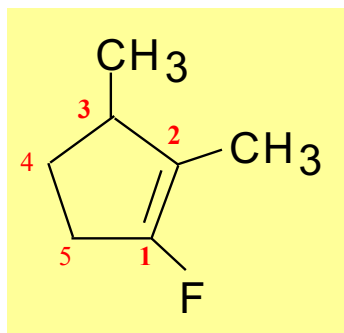

Cyclopropene
(C_3H_4)

Cyclobutene
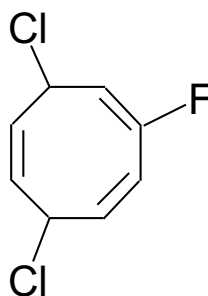**(C_4H_6)**

Cyclopentene
(C_5H_8)

Cyclohexene
(C_6H_{10})

Example 8: Draw the structural formula and state the name for the following organic compounds.

a. 1-fluoro-2,3-dimethylcyclopentene

b.

**5,8-dichloro-2-fluoro-1,3,6-cycloctatriene**
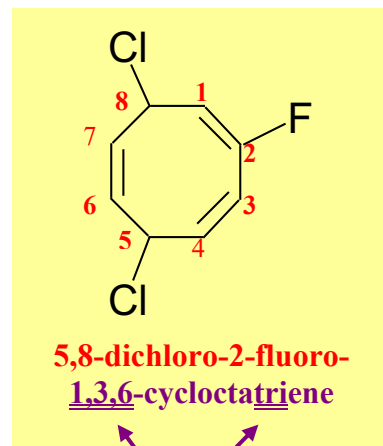
Positions of the three double bonds

Alkynes: - hydrocarbons that contain a C ≡ C (triple bond)
- nomenclature of alkane involves the use of the suffix ~*yne* (like in Alk ~**yne**).
- hydrocarbons with two triple bonds are named with the suffix ~*diyne* (~**di yne** as in two triple bonds).
- hydrocarbons with three triple bonds are named with the suffix ~*triyne* (~**tri yne** as in three triple bonds).
- unless it is understood, all triple bond locations along the longest carbon chain must be identified.
- prefixes to indicate the number of carbon atoms in the longest chain along with the naming of any alkyl group remains the same as alkane compounds with the lowest numerical combination given to the triple bonds. *Note: The alkyne group takes precedent in the root naming over any substituents.*
- **for one triple bond alkenes, the molecular formula C_nH_{2n-2}.** *Note:* It is the same as cycloalkenes. Therefore, *one triple bond alkynes are isomers to cycloalkenes*.

Example 9: Name the following alkynes or give the molecular formula or vice-versa. Provide a structural formula for these compounds.

a. C_3H_4
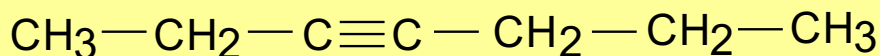
Alkyne: $C_3H_{2(3)-2}$ **Propyne**
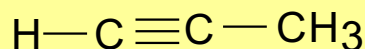
$$H—C≡C—CH_3$$

b. 3-heptyne

Alkene: $C_7H_{2(7)-2}$ **C_7H_{12}**   **The triple bond starts at carbon-3.**

$$CH_3—CH_2—C≡C—CH_2—CH_2—CH_3$$

$CH_3CH_2CCCH_2CH_2CH_3$
or $CH_3CH_2CC(CH_2)_2CH_3$
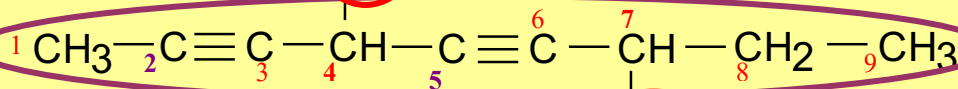
c. $CH_3C≡CCH(C_2H_5)C≡CCH(CH_3)CH_2CH_3$

First, we draw the structural formula.

Root Name: 2, 5-nonadiyne

ethyl at Position 4

$$CH_3$$
$$|$$
$$CH_2$$

Positions of the two triple bonds

$$^1CH_3—_2C≡C_3—^4CH—_5C≡^6C—^7CH—^8CH_2—_9CH_3$$

methyl at Position 7 $$CH_3$$

4-ethyl-7-methyl-2,5-nonadiyne (Correct Name)

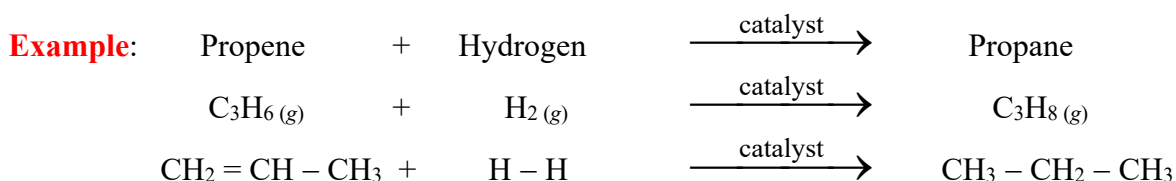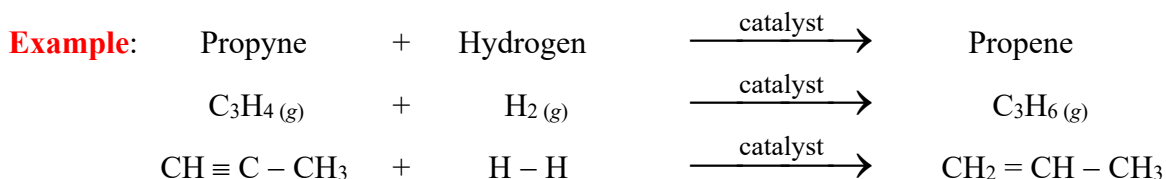**Properties of Aliphatic Hydrocarbons**:
1. All branched and unbranched aliphatic hydrocarbons (with the exception of halogen derivatives) are non-polar. They are not soluble in water. The more carbons it has, the higher the boiling point.
2. Most halogen derivates are polar. This is especially true for cis- isomers. Hence, they are fairly soluble in water. If there are equivalent substituents in the trans- configuration, the halogen derivative might be non-polar.

Reactions of Alkenes and Alkynes

1. **Hydrogenation: -** when hydrogen is added across a double bond or triple bond (π bond) to form single bond (σ bond).
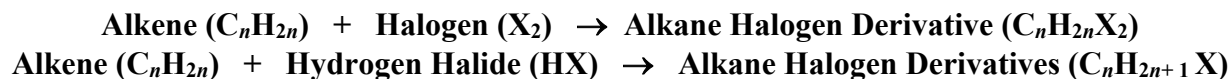
Alkyne + Hydrogen $\xrightarrow{\text{catalyst}}$ **Alkene**   **Alkene + Hydrogen** $\xrightarrow{\text{catalyst}}$ **Alkane**

(Check out the animation at https://www.youtube.com/watch?v=R27PkAWqSTc)

Example: Propyne   +   Hydrogen $\xrightarrow{\text{catalyst}}$ Propene

   $C_3H_{4\,(g)}$ + $H_{2\,(g)}$ $\xrightarrow{\text{catalyst}}$ $C_3H_{6\,(g)}$

   $CH \equiv C - CH_3$ + $H - H$ $\xrightarrow{\text{catalyst}}$ $CH_2 = CH - CH_3$

Example: Propene   +   Hydrogen $\xrightarrow{\text{catalyst}}$ Propane

   $C_3H_{6\,(g)}$ + $H_{2\,(g)}$ $\xrightarrow{\text{catalyst}}$ $C_3H_{8\,(g)}$

   $CH_2 = CH - CH_3$ + $H - H$ $\xrightarrow{\text{catalyst}}$ $CH_3 - CH_2 - CH_3$

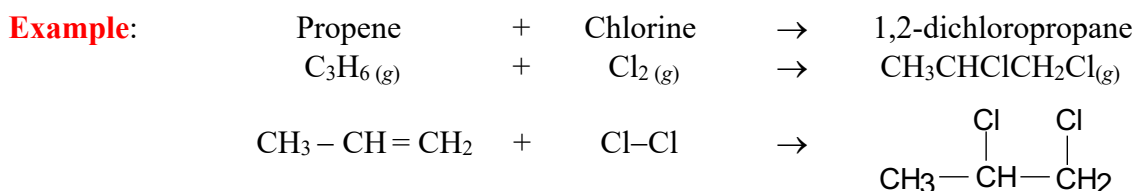**(*Note*: From Propyne to Propane Hydrogenation, it is stepwise.)**
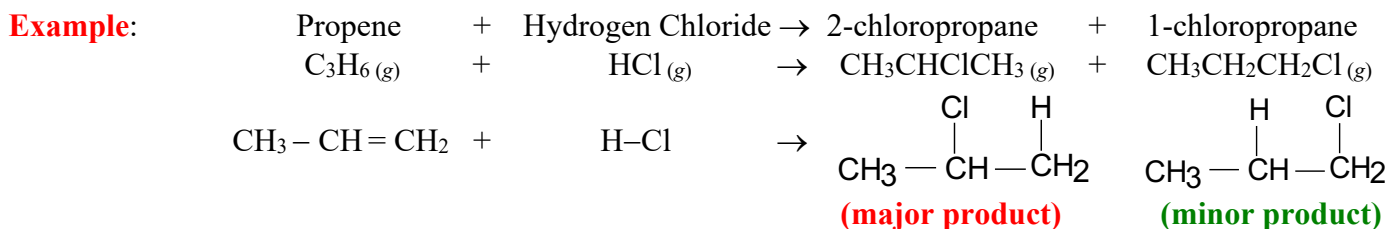
2. **Halogenations (Addition): -** when halogens (X_2) or hydrogen halide (HX) is added across a double bond or triple bond to form halogen derivatives.

Alkene (C_nH_{2n}) + Halogen (X_2) → Alkane Halogen Derivative ($C_nH_{2n}X_2$)
Alkene (C_nH_{2n}) + Hydrogen Halide (HX) → Alkane Halogen Derivatives ($C_nH_{2n+1}X$)

(Check out the animation at https://www.youtube.com/watch?v=Cuf7TA_OnN0)

Example: Propene   +   Chlorine   →   1,2-dichloropropane
        $C_3H_{6\,(g)}$ + $Cl_{2\,(g)}$ → $CH_3CHClCH_2Cl_{(g)}$

   $CH_3 - CH = CH_2$ +   Cl–Cl   →
$$\begin{array}{ccc} & Cl & Cl \\ & | & | \\ CH_3 - & CH - & CH_2 \end{array}$$

(Check out the animation at https://www.youtube.com/watch?v=X-VCk3WrGlM)

Example: Propene   + Hydrogen Chloride → 2-chloropropane   +   1-chloropropane
        $C_3H_{6\,(g)}$ + $HCl_{(g)}$ → $CH_3CHClCH_{3\,(g)}$ + $CH_3CH_2CH_2Cl_{(g)}$

   $CH_3 - CH = CH_2$ +   H–Cl   →
$$\begin{array}{ccc} Cl & H \\ | & | \\ CH_3 - CH - CH_2 \end{array} \qquad \begin{array}{ccc} H & Cl \\ | & | \\ CH_3 - CH - CH_2 \end{array}$$
        (major product)   **(minor product)**

According to Markovnikov's rule, halogen atom tends to bond with the carbon with the least number of hydrogen atoms.

Assignment
24.1 pg. 1052 #1 and 2
24.2 pg. 1052 − 1053 #3 to 8, 11 to 18, 20, 23, 24, 26 to 28

24.3: Aromatic Hydrocarbons

Aromatic Hydrocarbons: - a class of cyclic hydrocarbons characterize by alternating double bonds (delocalised π bonds).

**Example: C_6H_6 (Benzene): a very stable compound due to the delocalized double bonds to form a ring.**

Resonance structures for benzene

The π bonding framework for benzene
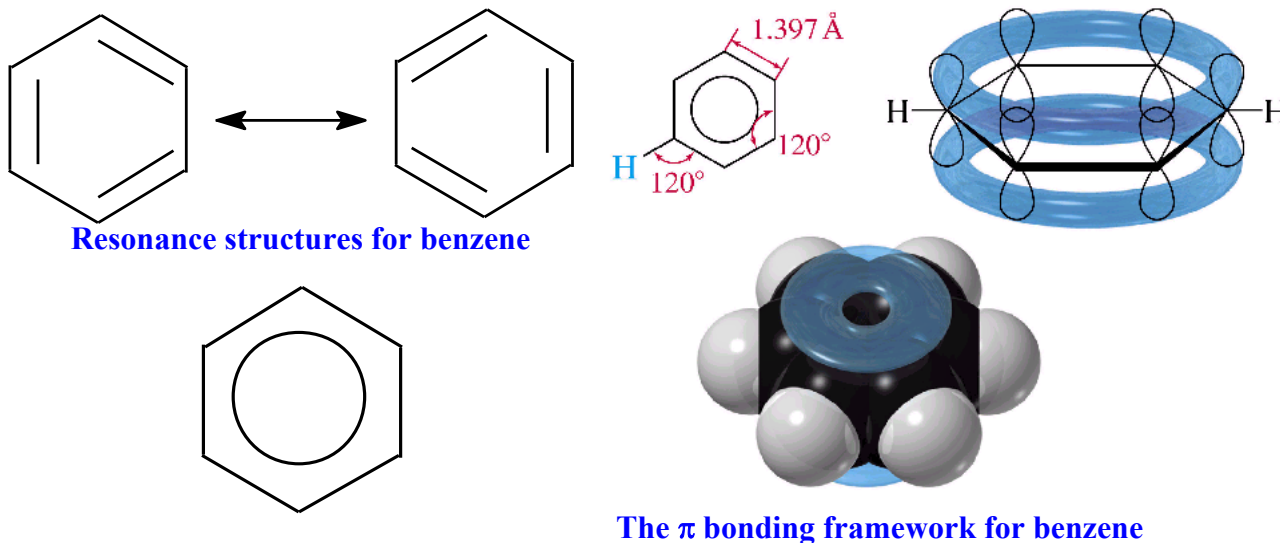
<u>**Naming Aromatic Compounds:**</u>

1. If benzene is used as the main group then the word "benzene" becomes the root name.
2. If benzene is used as a substituent as C_6H_5 – (like CH_3 – methyl from CH_4), then the substituent name becomes **phenyl**.
3. The positions of substituents on the benzene ring is like those on the cyclo-aliphatic hydrocarbons. We pick a substituent corner and call it carbon position 1. Then, we go around the benzene ring such that the final combinations of the positions are the lowest.

Example 1: Name the following aromatic compounds

a.
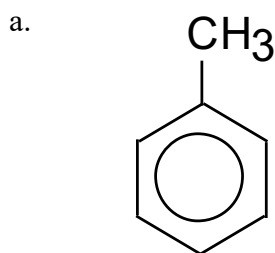
methylbenzene
Common name: Toluene

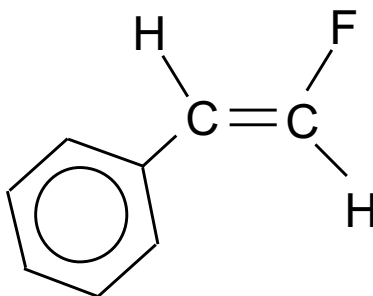b.
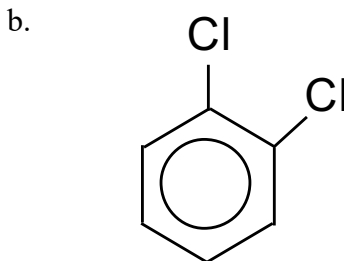
1,2-dichlorobenzene
(ortho-dichlorobenzene)

c.
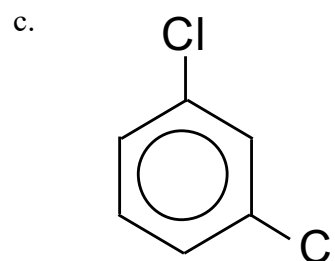
1,3-dichlorobenzene
(meta-dichlorobenzene)

d.

Cl
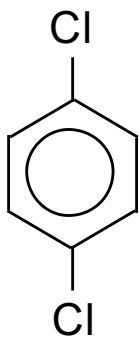
1,4-dichlorobenzene
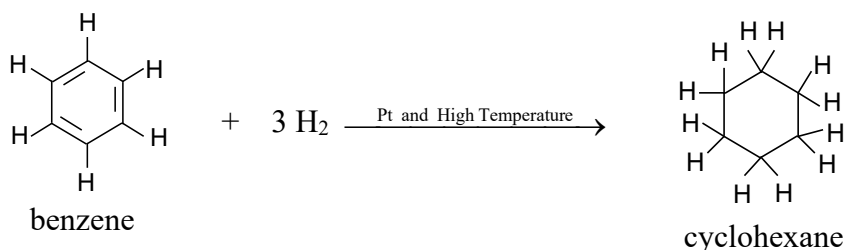(***para*-dicholrobenzene**)

e.
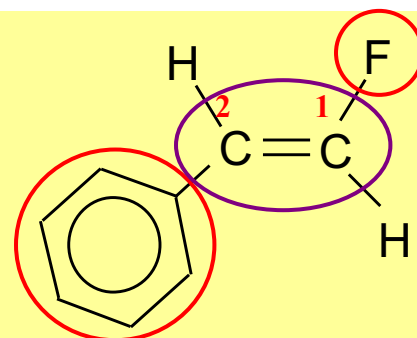
trans-**1-fluoro-2-phenylethene**
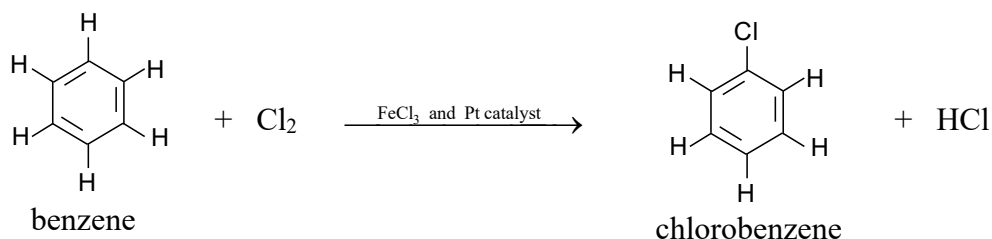
Properties of Aromatic Compounds:

1. Due to the delocalized double bonds around the benzene ring, it is a very stable and inert compound.
2. Because of this stability, benzene tends to undergo substitution reactions in room temperature.
3. The only addition reaction benzene will experience is the addition of hydrogen with a catalyst and high temperature to form cyclohexane.
4. It is non-polar and it does not dissolve in water well (unless it has a halogen substituent).

Reactions of Aromatic Compounds:

1. **Addition of Hydrogen**:

benzene $+$ $3 H_2$ $\xrightarrow{\text{Pt and High Temperature}}$ cyclohexane

2. **Halogen Substitution**:

benzene $+$ Cl_2 $\xrightarrow{\text{FeCl}_3 \text{ and Pt catalyst}}$ chlorobenzene $+$ HCl

3. **Alkyl Substitution**:

benzene $+$ CH_3Br $\xrightarrow{\text{AlBr}_3 \text{ and Pt catalyst}}$ methylbenzene $+$ HBr
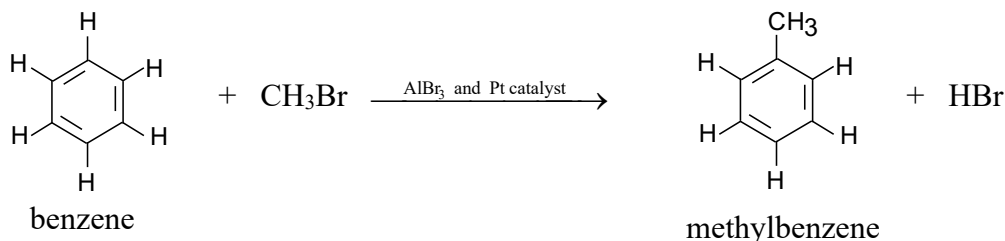
┌─────────────────────────────┐
│   **Assignment**   │
│   **24.3 pg. 1053 #29 to 32**   │
└─────────────────────────────┘

24.4: Chemistry of the Functional Groups

Hydrocarbon Derivatives: - an almost unlimited number of carbon compounds that can be formed by
addition of other elements like halogen (halogen derivatives-organic halides)
and/or **functional groups** to a hydrocarbon.

Functional Group: - a reactive portion of a molecule that gives the resulting hydrocarbon derivatives their
special chemical and physical properties.

Alcohols: - organic compounds containing a **hydroxyl functional group**, (**R-OH**), substituted for a
hydrogen atom. (**R – represent the rest of the carbon main chain.**)
  - **polar molecules** (due to oxygen's two lone pairs); **very soluble in water** (*R*-OH compares to
    H–OH)
  - naming of alcohols starts with the prefix of the number of carbon in the longest chain including
    the –OH group but end with the suffix ~*ol* (like in Alcoh ~**ol**).
  - hydrocarbons with two –OH groups are named with the suffix ~*diol* (~**di ol** as in two –OH
    groups).
  - hydrocarbons with three –OH groups are named with the suffix ~*triol* (~**tri ol** as in 3 –OH
    groups).
  - unless it is understood, all –OH locations along the longest carbon chain must be identified.
  - prefixes to indicate the number of carbon atoms in the longest chain along with the naming of
    any alkyl group remains the same as alkane compounds with the lowest numerical combination
    given to the –OH group. *Note: The alcohol group takes precedent in the root naming over any
    substituents (alkyl and halogen substituents).* **If –OH is a substituent because of higher
    precedent functional group, it is called –*hydroxy.***

  a. **Primary Alcohol**: - **–OH group attaches to a carbon with <u>one alkyl group</u>.**
   - can react to form functional group like **aldehydes** (will explain later).
       - higher boiling point than secondary and tertiary alcohols because of the strong
         hydrogen bonding between molecules (–OH group is at a carbon site that is least
         crowded; making strong O----H intermolecular bonds possible).

  b. **Secondary Alcohol**: - **–OH group attaches to a carbon with <u>two alkyl groups</u>.**
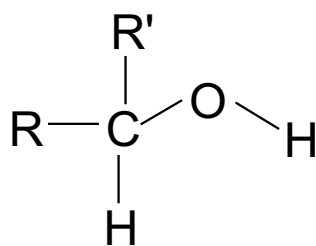   - can react to form functional group like **ketones** (will explain later).
       - lower boiling point than primary but higher than tertiary alcohols. This is
         because of the somewhat weaker hydrogen bonding between molecules
         compared to primary alcohol (–OH group is at a carbon site that is more
         crowded; making O----H intermolecular bonds weaker).

  c. **Tertiary Alcohol**: - **–OH group attaches to a carbon with <u>three alkyl groups</u>.**
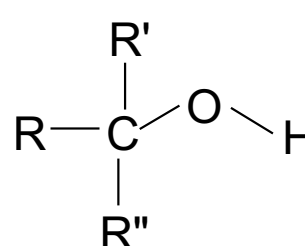   - do not usually react to form other functional groups (**chemically stable**).
       - lower boiling point compared to primary and secondary alcohols (**physically
         volatile**). This is because of the weakest hydrogen bonding between molecules
         compared to primary and secondary alcohols (–OH group is at a carbon site that
         is most crowded; making O----H intermolecular bonds weakest).
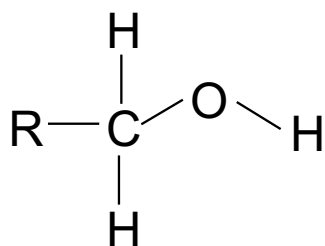
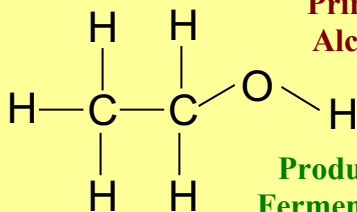| **Primary Alcohol**	**Secondary Alcohol**	**Tertiary Alcohol**
(one alkyl group R attached to C which attached to –OH group)	(two alkyl groups R and R' attached to C which attached to –OH group)	(three alkyl groups R, R', and R" attached to C which attached to –OH group)

Example 1: Name the following alcohols or give the molecular formula or vice-versa. Provide a structural formula for these compounds. Indicate whether the alcohol is primary, secondary or tertiary.

a. C_2H_5OH

Alcohol: C_2H_5OH **Ethanol**
Primary Alcohol

Product of Fermentation

b. 2-propanol
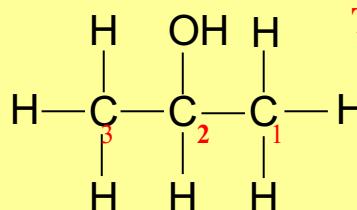
The –OH group is at carbon-2.

Rubbing Alcohol

Secondary Alcohol

$CH_3CH(OH)CH_3$

c. C_6H_5OH

Alcohol with Benzene
Benzenol (or Phenol)
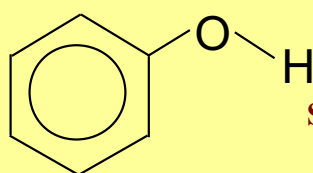
Secondary Alcohol

d. 1,2-ethandiol
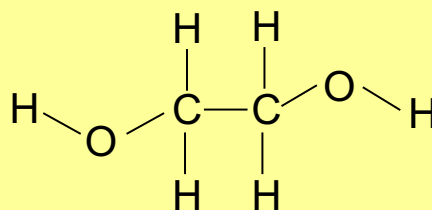
The –OH groups are at both carbons.

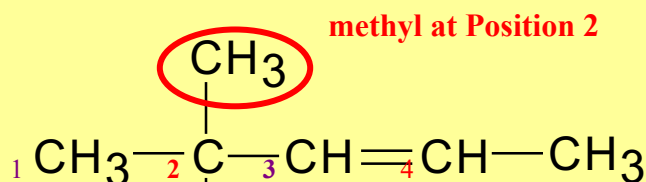**Commonly known as ethylene glycol (Automobile Antifreeze)**

Primary Alcohol $CH_2(OH)CH_2(OH)$

e. $CH_3C(CH_3)OHCHCHCH_3$

First, we draw the structural formula.

methyl at Position 2

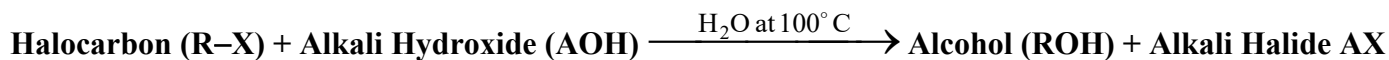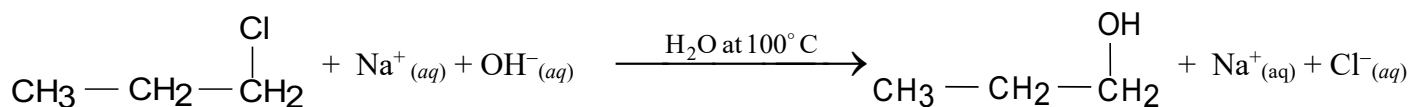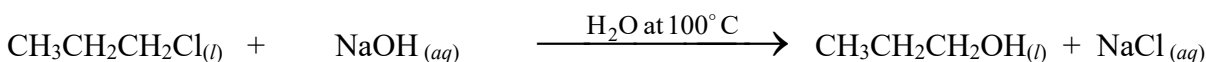**hydroxyl at Position 2**

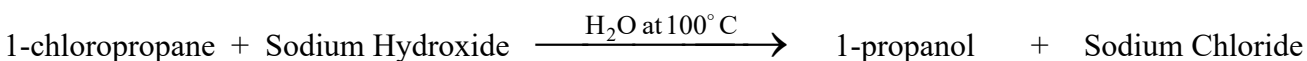**Root Name: 3-penten-2-ol**
Positions of the double bond
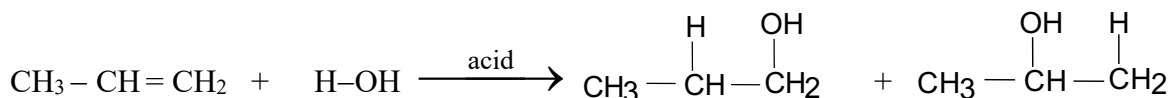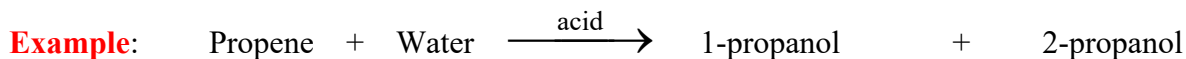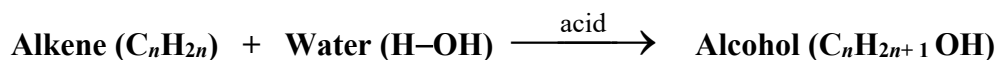
2-methyl-3-penten-2-ol

Tertiary Alcohol

Hydroxyl group takes precedent over alkene double bond when numbering carbon chain

Reactions of Alcohols:

1. **Alcohol Substitution Reaction**: - a reaction where a base (AOH) is reacting with a halocarbon (R–X) to form alcohol (ROH) and an alkali halide (AX) under the aqueous condition of water at high temperature.

Halocarbon (R–X) + Alkali Hydroxide (AOH) $\xrightarrow{\text{H}_2\text{O at } 100°\text{C}}$ **Alcohol (ROH) + Alkali Halide AX**

Example:

1-chloropropane + Sodium Hydroxide $\xrightarrow{\text{H}_2\text{O at } 100°\text{C}}$ 1-propanol + Sodium Chloride

$CH_3CH_2CH_2Cl_{(l)}$ + $NaOH_{(aq)}$ $\xrightarrow{\text{H}_2\text{O at } 100°\text{C}}$ $CH_3CH_2CH_2OH_{(l)}$ + $NaCl_{(aq)}$

$$CH_3 - CH_2 - \overset{\displaystyle Cl}{\underset{|}{C}H_2} + Na^+{}_{(aq)} + OH^-{}_{(aq)} \xrightarrow{\text{H}_2\text{O at } 100°\text{C}} CH_3 - CH_2 - \overset{\displaystyle OH}{\underset{|}{C}H_2} + Na^+{}_{(aq)} + Cl^-{}_{(aq)}$$

2. **Hydration Addition:** - when water (H–OH) is added across a double bond to form an alcohol under acidic condition.

Alkene (C_nH_{2n}) + Water (H–OH) $\xrightarrow{\text{acid}}$ **Alcohol (C_nH_{2n+1} OH)**

Example: Propene + Water $\xrightarrow{\text{acid}}$ 1-propanol + 2-propanol

$C_3H_{6(g)}$ + $HOH_{(l)}$ $\xrightarrow{\text{acid}}$ $CH_3CH_2CH_2OH_{(l)}$ + $CH_3CH(OH)CH_{3(l)}$

$$CH_3 - CH = CH_2 + H\text{–}OH \xrightarrow{\text{acid}} CH_3 - \overset{\displaystyle H}{\underset{|}{C}H} - \overset{\displaystyle OH}{\underset{|}{C}H_2} + CH_3 - \overset{\displaystyle OH}{\underset{|}{C}H} - \overset{\displaystyle H}{\underset{|}{C}H_2}$$

3. **Fermentation**: - the conversion of sugar or starch into ethanol with the aid of an enzyme.

Glucose ($C_6H_{12}O_6$) $\xrightarrow{\text{enzyme (yeast)}}$ **Ethanol (C_2H_5OH) + Carbon Dioxide (CO_2)**

Ethers: - organic compounds containing a hydroxyl functional group, (**R–O–R'**), substituted for a hydrogen atom. (**R and R' – represent the two alkyl groups.**)
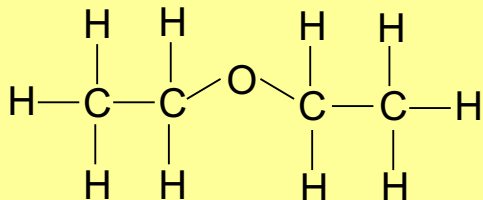- **polar molecules** (due to oxygen's two lone pairs); **very soluble in water** (hydrogen bonding between water and ether)
- naming of ethers starts with the two alkyl groups (in alphabetical order) ending with **ether.**
- hydrocarbons with two similar alkyl groups can use the prefix **di~**.
Note: **If R–O– is a substituent because of higher precedent functional group, it is called *prefix of R–oxy.***

Example 2: Name the following ethers or give the molecular formula or vice-versa. Provide a structural formula for these compounds.
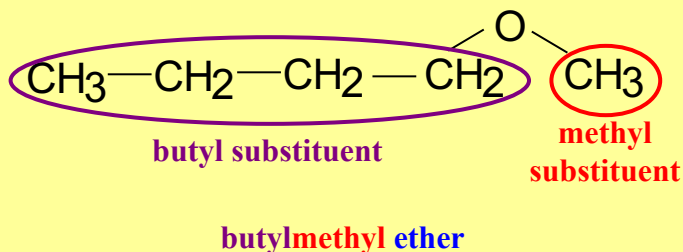
a. diethyl ether
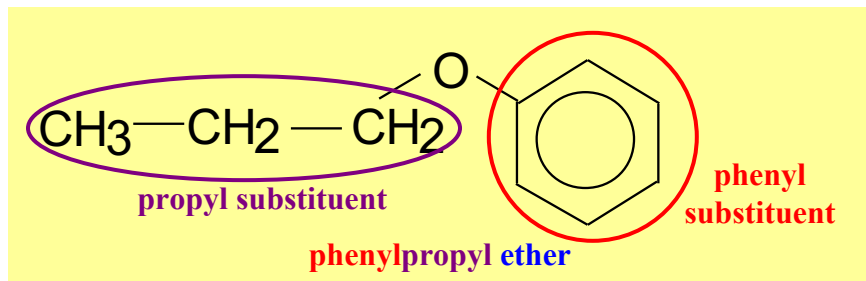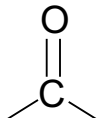
Ether with two ethyl groups: $C_2H_5OC_2H_5$

Used as anaesthetic in the past. We now use methylpropyl ether for anaesthetic).

b. $C_4H_9OCH_3$

CH_3—CH_2—CH_2—CH_2 CH_3

butyl substituent   methyl substituent

butylmethyl ether

c. $C_3H_7OC_6H_5$

CH_3—CH_2—CH_2

propyl substituent   phenyl substituent

phenylpropyl ether

Carbonyl Group: - a   [C=O]   group.

Aldehydes: - compound containing a carbonyl group with at least one hydrogen atom (**R-CHO**) attached to it.

Note that it is CHO *as aldehyde not* C−OH *as alcohol.*
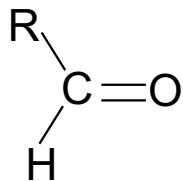
- **polar molecules** (due to oxygen's two lone pairs); **very soluble in water** (hydrogen bonding between water and carbonyl group).
- **Aromatic aldehydes are commonly used as artificial flavours.**
- naming of aldehydes starts with the prefix of the number of carbon in the longest chain including the –C=O group but end with the suffix ~*al* (like in **al** -dehyde).

Note: The aldehyde carbonyl group takes precedent in the root naming over any substituents (hydroxy, oxy, alkyl and halogen substituents).

Example 3: Name the following aldehydes or give the molecular formula or vice-versa. Provide a structural formula for these compounds.
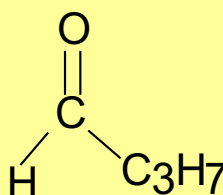
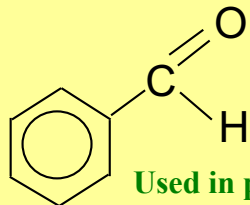a. methanal

Aldehyde: Methanal (1-Carbon)   **HCHO**
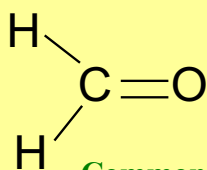
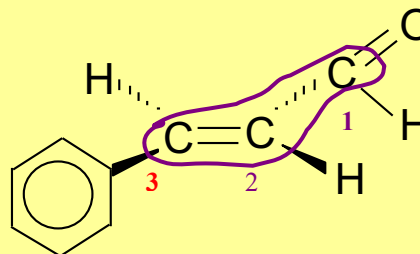Commonly known as formaldehyde. Used as embalming fluid in mortuary.

b. C_3H_7CHO

Aldehyde: 4-Carbons   **Butanal**

c. C_6H_5CHO

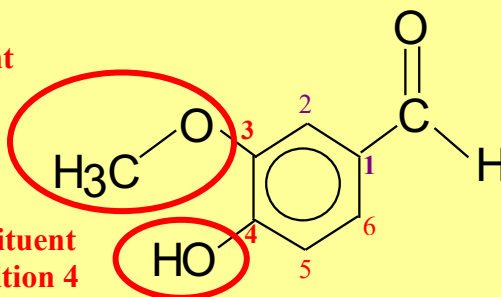Aldehyde: Benzene (C_6H_5-) **Benzenal**

Used in peaches, cherries and almond flavours.

d. *trans*-3-phenyl-2-propenal (cinnamaldehyde)

OHCCHCH(C_6H_5)
**Used as cinnamon flavour.**

e. 4-hydroxy-3-methoxy-benzenal

(CH$_3$–O–) as substituent
*meth*oxy at Position 3

Aldehyde Functional Group takes precedent over ether or alcohol functional groups.

(−OH) as substituent
hydroxy at Position 4

Used in vanilla oil.

Ketones: - compound containing a carbonyl group with no hydrogen atom **(R-C=OR')** attached to it. *Note that it is R–C=OR' as ketone not R–O–R' as ether.*
  - **polar molecules** (due to oxygen's two lone pairs); **very soluble in water** (hydrogen bonding between water and carbonyl group).
  - **Aromatic ketones are commonly used as artificial flavours.**
  - naming of ketones starts with the prefix of the number of carbon in the longest chain including the –C=O group but end with the suffix *~one* (like in ket~**one**). The carbonyl position along the longest carbon chain must be indicated.
  Note: The ketone carbonyl group takes precedent in the root naming over any substituents (hydroxy, oxy, alkyl and halogen substituents).
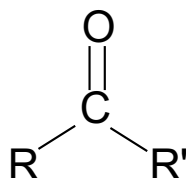
Example 4: Name the following ketones or give the molecular formula or vice-versa. Provide a structural formula for these compounds.
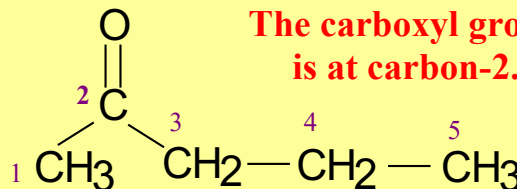
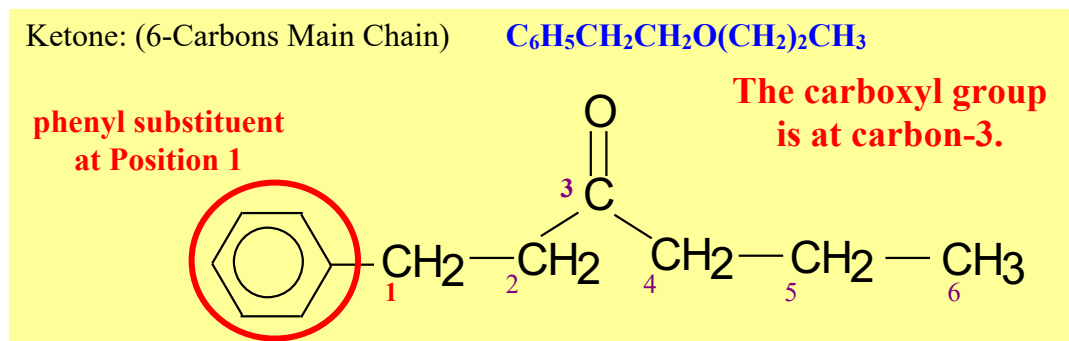a. CH_3COCH_3

Ketone: (3-Carbons)   **Propanone**
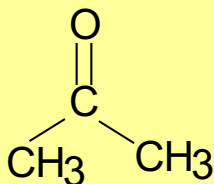
No need to label 2-propanone because the ketone carboxyl group can only exist in this case at carbon 2. Otherwise it would be an aldehyde.

b. 2-pentanone

Ketone: (5-Carbons)   **CH$_3$CO(CH$_2$)$_2$CH$_3$**

The carboxyl group is at carbon-2.

c. 1-phenyl-3-hexanone

Ketone: (6-Carbons Main Chain) $C_6H_5CH_2CH_2O(CH_2)_2CH_3$

phenyl substituent at Position 1

The carboxyl group is at carbon-3.

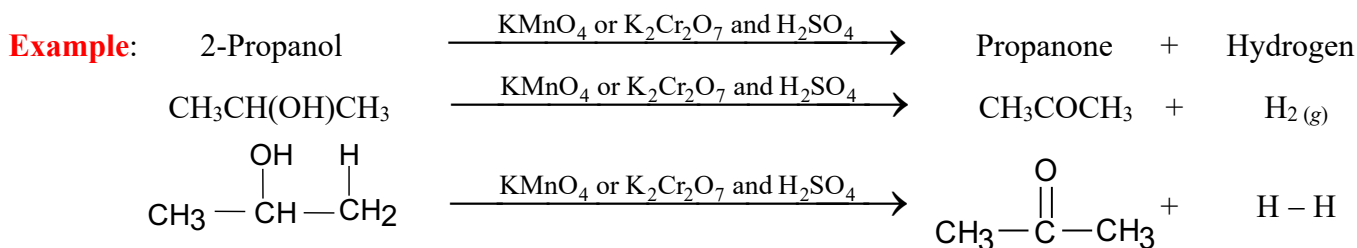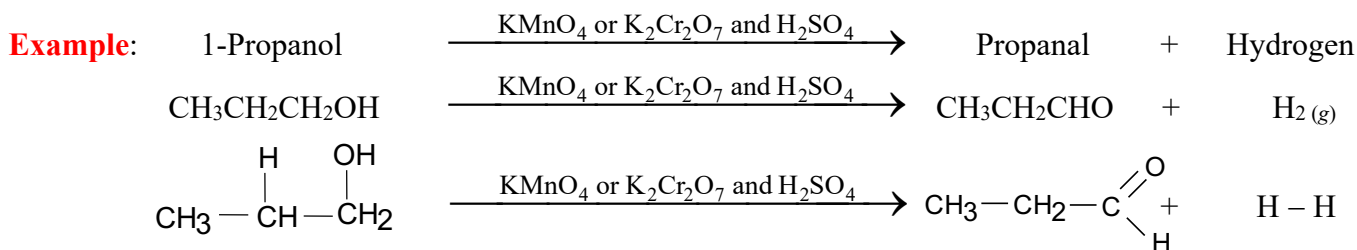**Elimination Reactions**: - reactions that turn saturated hydrocarbons into unsaturated ones using oxidizing agent like $KMnO_4$ or $K_2Cr_2O_7$ in an acidic environment.
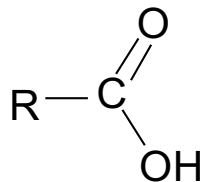
Dehydrations: - elimination reactions where primary alcohols are turned into aldehydes or secondary alcohols are converted to ketones by removing hydrogen.

Primary Alcohol $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ **Aldehyde + Hydrogen**

Secondary Alcohol $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ **Ketone + Hydrogen**

Example: 1-Propanol $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ Propanal + Hydrogen

$CH_3CH_2CH_2OH$ $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ CH_3CH_2CHO + $H_{2 (g)}$

 $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ + $H-H$

Example: 2-Propanol $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ Propanone + Hydrogen

$CH_3CH(OH)CH_3$ $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ CH_3COCH_3 + $H_{2 (g)}$

 $\xrightarrow{KMnO_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ + $H-H$

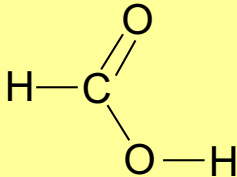**Carboxylic Acids**: - compound containing a carbonyl group **(R-COOH)**.
   - **polar molecules** (due to oxygens' four lone pairs); **very soluble in water** (hydrogen bonding between water and carbonyl group).
   - naming of carboxylic acid starts with the prefix of the number of carbon in the longest chain including the –COOH group but end with the suffix ~*oic acid* (like in carb~**o**~xyl~**ic acid**).
   Note: The carboxylic acid group takes precedent in the root naming over any substituents (hydroxy, oxy, alkyl and halogen substituents).

Example 5: Name the following carboxylic acid or give the molecular formula or vice-versa. Provide a
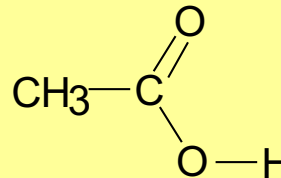structural formula for these compounds.

a. methanoic acid

b. CH_3COOH

Carboxylic Acid: (Methanoic Acid) –1 carbon

HCOOH

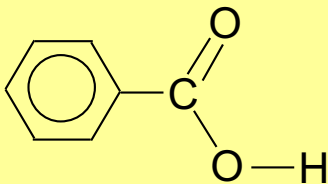Carboxylic Acid: (2 carbons) **Ethanoic Acid**
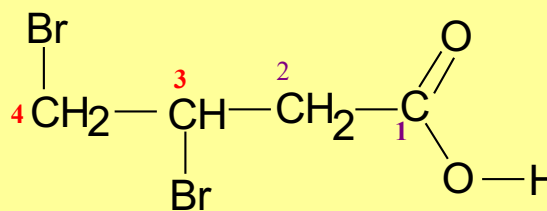
**Commonly
known as Acetic
Acid (Vinegar)**

c. C_6H_5COOH

d. 3,4-dibromo-butanoic acid

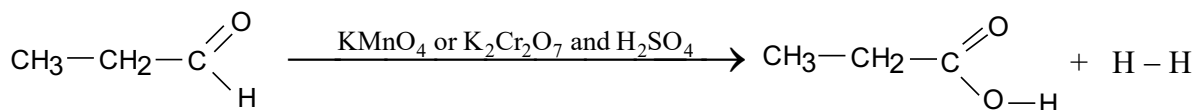Carboxylic Acid with Benzene

Benzenoic Acid

CH₂BrCHBrCH₂COOH

Formation of Carboxylic Acid: - from the elimination reaction of aldehydes.

$$\text{Aldehyde} \xrightarrow{\text{KMnO}_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4} \text{Carboxylic Acid + Hydrogen}$$

Example: Propanal $\xrightarrow{\text{KMnO}_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ Propanoic Acid   + Hydrogen

CH_3CH_2CHO $\xrightarrow{\text{KMnO}_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ CH_3CH_2COOH + $H_{2\,(g)}$

 $\xrightarrow{\text{KMnO}_4 \text{ or } K_2Cr_2O_7 \text{ and } H_2SO_4}$ + H – H

Ester: - compound containing a carbonyl group **(RCOOR')**.
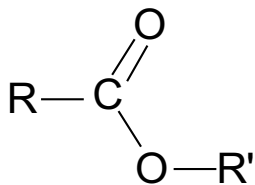
- **polar molecules** (due to oxygens' four lone pairs); **very soluble in water**
(hydrogen bonding between water and carbonyl group).
- commonly use as artifical flavorings.
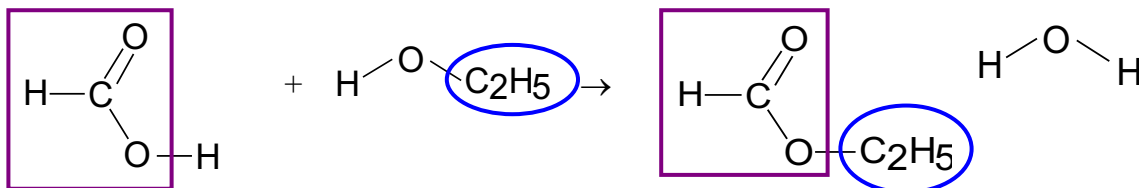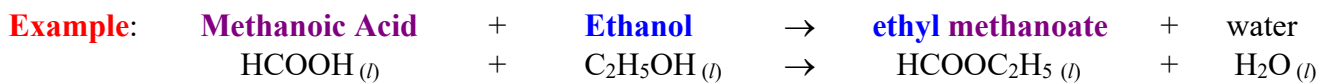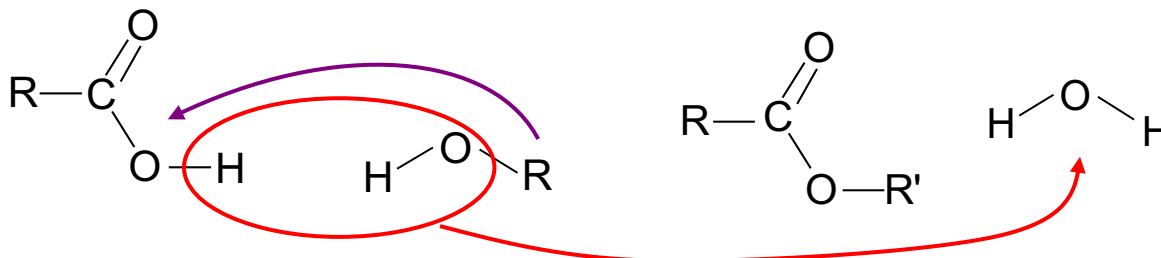- **form when alcohol is reacted with carboxylic acid.**
- naming of ester starts with the **alkyl group −R'**, then the <u>prefix of the number of
carbon in the longest chain</u> including and connected to the RCOO− group and ends
with the suffix *~oate*.
*Note: The ester group takes precedent in the root naming over any substituents
(hydroxy, oxy, alkyl and halogen substituents).*

Esterification (Ester Condensation): - when **alcohol reacts with carboxylic acid to form ester and water** (condensation because water is produced).
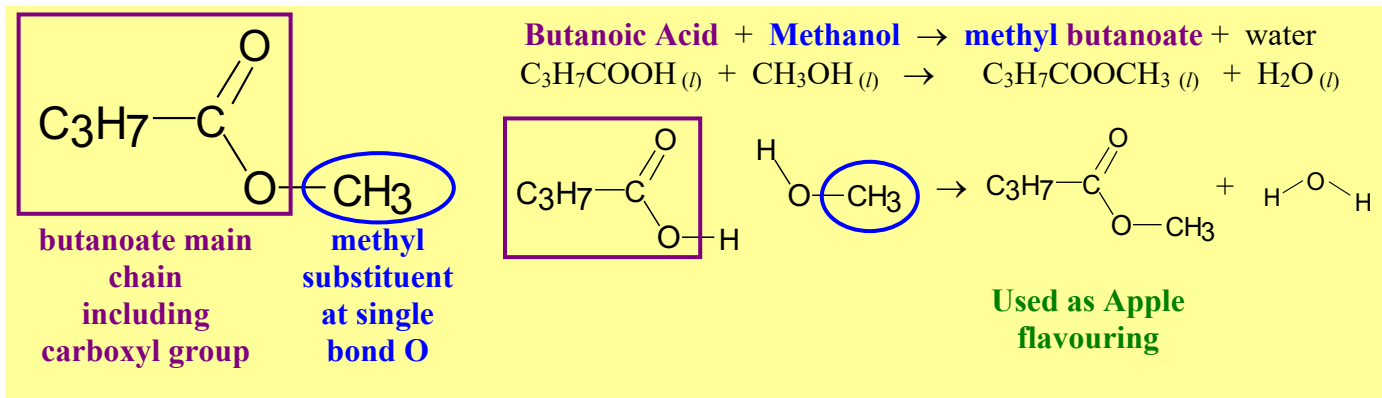- the alcohol chain becomes the alkyl group of the ester (R').
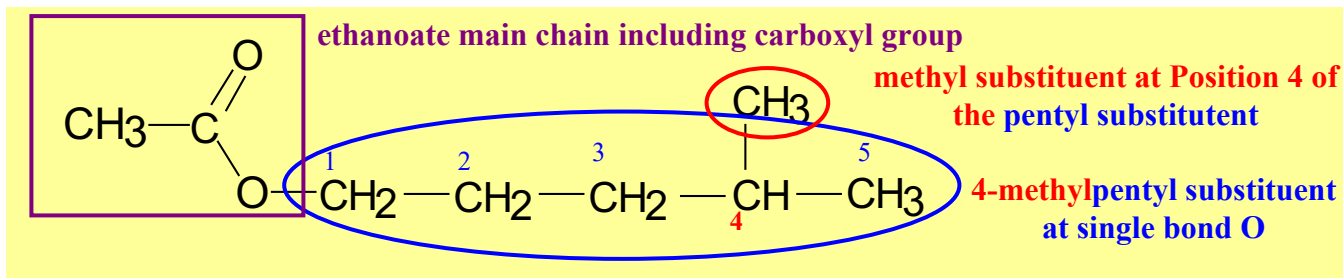- the carboxylic acid chain becomes main carbon chain for the ester functional group.

Carboxylic Acid (RCOOH) + Alcohol (R'OH) → Ester (RCOOR') + H$_2$O

Example: **Methanoic Acid**   +   **Ethanol**   →   **ethyl methanoate**   +   water
                   HCOOH $_{(l)}$ +   C$_2$H$_5$OH $_{(l)}$ →   HCOOC$_2$H$_5$ $_{(l)}$ +   H$_2$O $_{(l)}$
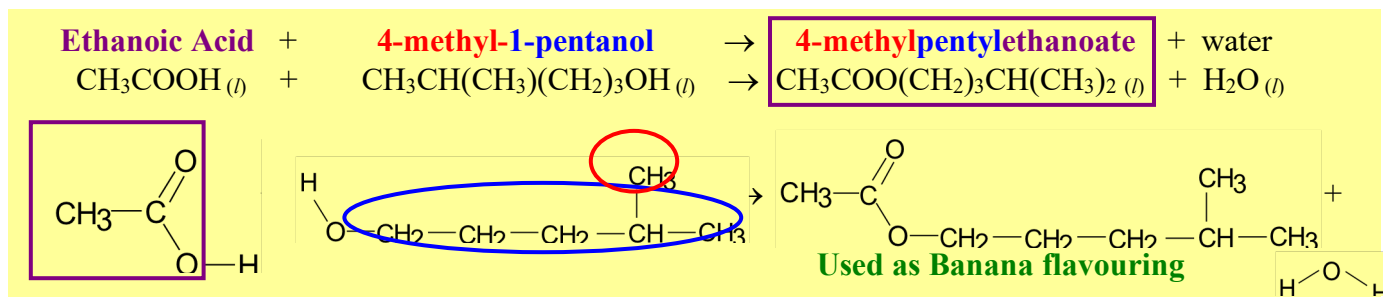

Used as Rum flavouring

Example 6: Name the following esters or give the molecular formula or vice-versa. Provide a structural formula for these compounds. Suggest an esterification reaction to produce each ester below.
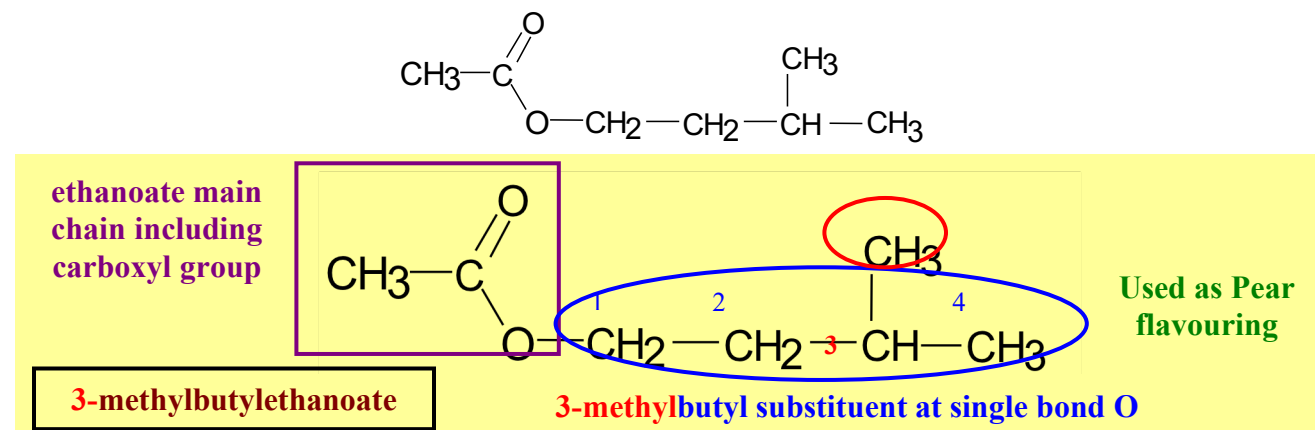
a.   methyl butanoate

Butanoic Acid + Methanol → methyl butanoate + water
C$_3$H$_7$COOH $_{(l)}$ + CH$_3$OH $_{(l)}$ → C$_3$H$_7$COOCH$_3$ $_{(l)}$ + H$_2$O $_{(l)}$

butanoate main chain including carboxyl group   **methyl substituent at single bond O**

Used as Apple flavouring

b.   CH$_3$COO(CH$_2$)$_3$CH(CH$_3$)$_2$

ethanoate main chain including carboxyl group

methyl substituent at Position 4 of the pentyl substitutent

4-methylpentyl substituent at single bond O

Ethanoic Acid +   **4-methyl-1-pentanol**   →   **4-methylpentylethanoate**   +   water

$CH_3COOH_{(l)}$ + $CH_3CH(CH_3)(CH_2)_3OH_{(l)}$ → $CH_3COO(CH_2)_3CH(CH_3)_{2\ (l)}$ + $H_2O_{(l)}$

Used as Banana flavouring

Example 7: Name the following organic compound given the structural formula below.

ethanoate main chain including carboxyl group

3-methylbutylethanoate

3-methylbutyl substituent at single bond O
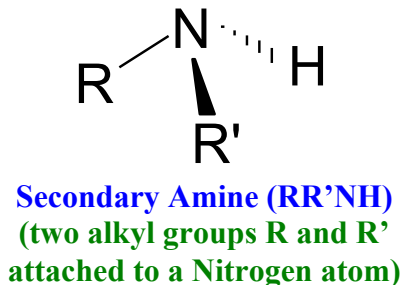
Used as Pear flavouring

Amine: - compound containing a nitrogen atom attaching to one, two or three alkyl groups.
       - **polar molecules** (due to nitrogen's lone pair)
       - have fish-like odour.

Primary Amine (RNH_2)
(one alkyl group R attached to a Nitrogen atom)
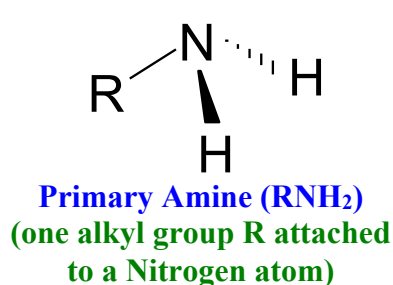
Naming with alkyl group follow by suffix ~*amine*.

Secondary Amine (RR'NH)
(two alkyl groups R and R' attached to a Nitrogen atom)
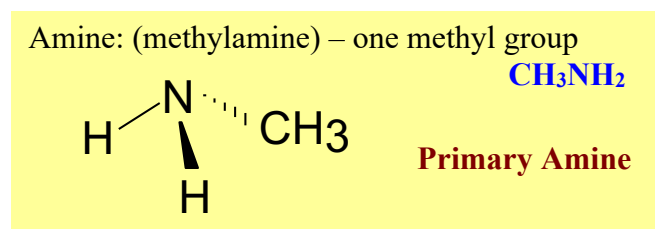
Naming with the longest chain of carbons takes the root name (*alkanamine*) and the other chain becomes a substituent.
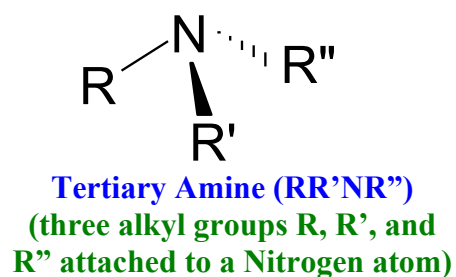
Tertiary Amine (RR'NR")
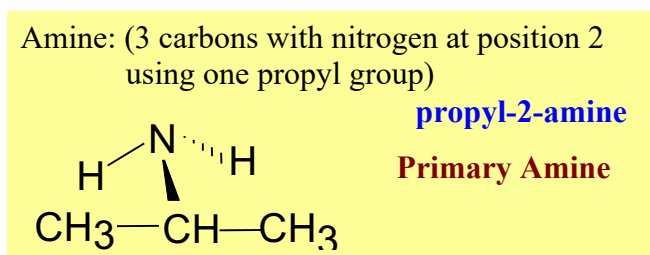**(three alkyl groups R, R', and R" attached to a Nitrogen atom)**

Naming with the longest chain of carbons takes the root name (*alkanamine*) and the other chains become substituents.

Example 8: Name the following amides or give the molecular formula or vice-versa. Provide a structural formula for these compounds. Indicate whether the amine is primary, secondary or tertiary.
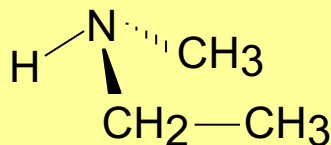
a. methylamine

Amine: (methylamine) – one methyl group

CH_3NH_2

Primary Amine

b. $CH_3CH(NH_2)CH_3$

Amine: (3 carbons with nitrogen at position 2 using one propyl group)

propyl-2-amine

Primary Amine

c. methylethylamine

Amine: (methyl ethyl amine) – one methyl group and one ethyl group

$C_2H_5NH(CH_3)$
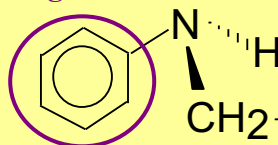
Secondary Amine

d. $C_6H_5NHC_3H_7$

Amine: (a phenyl group and a propyl group)

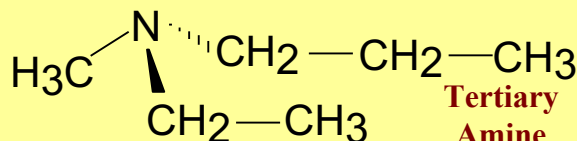**phenyl is the longest chain**   **propylphenylamine**

Secondary Amine

e. methylethylpropylamine

Amine: (methyl ethyl propyl amine) – one methyl group, one ethyl group, and one propyl group
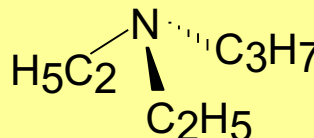
$C_3H_7N(CH_3)(C_2H_5)$

Tertiary Amine

f. $C_3H_7N(C_2H_5)(C_2H_5)$

Amine: (one propyl group, two ethyl groups)

diethylpropylamine

Tertiary Amine

Hydrocarbons from Earth

Fossil Fuel: - hydrocarbon fuels that came from fossils of decayed organisms.

1. **Natural Gas**: - fossil fuel that consists of mainly small alkanes (80% methane, 10% ethane, 4% propane, 2% butane, 4% nitrogen).
   - usually burns efficiently (complete combustion).

   Complete Combustion: - where the products of combustion are carbon dioxide and water vapour only.
   -characterized by a blue flame.

   Example: Propane burns completely. $C_3H_{8\,(g)} + 5\ O_{2\,(g)} \rightarrow 3\ CO_{2\,(g)} + 4\ H_2O_{(g)}$
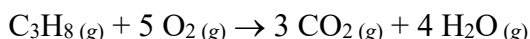
   Incomplete Combustion: - where the main product of combustion is carbon monoxide, along with carbon dioxide and water vapour.
   - happens when carbon particles started to form during combustion and deposited as soot as they cooled, or when there is insufficient oxygen.
   - characterized by a yellow flame.

   Example: Incomplete combustion of Propane. $C_3H_{8\,(g)} + 4\ O_{2\,(g)} \rightarrow 2\ CO_{(g)} + CO_{2\,(g)} + 4\ H_2O_{(g)}$

2. **Petroleum (Crude Oil)**: - fossil fuels that consist mainly of heavier alkanes along with small amounts of aromatic hydrocarbons, and organic compounds that contain sulfur, oxygen and nitrogen.
   - gasoline is composed of 40% of crude oil, whereas natural gas is composed of only 10%.

Fractional Distillation: - a method of heating
crude oil in a tall column to separate its
different components by their different
boiling points.
- lighter alkanes in the natural gas will rise up to
the top of the column because of their low
boiling points.
- the heavier, fuel and lubricating oils will boil
off at the bottom of the column due to their high
boiling points.
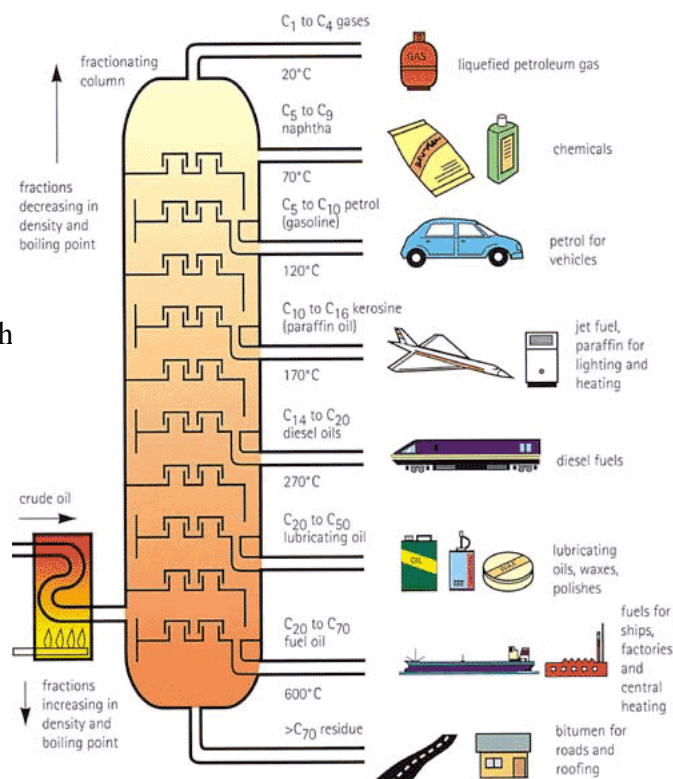
Petroleum Refining: - a process to isolate different types of fuel from crude oil using fractional
distillation or cracking.

Cracking: - a chemical process whereby bigger alkanes are broken up into smaller ones using a catalyst
and heat.
- since gasoline and natural gas only consists of 50% of crude oil, cracking is necessary to
convert heavier fuel to more common fuel used in today's world.

Example: The Cracking of Hexadecane. $C_{16}H_{34} + 2\ H_2 \xrightarrow{\text{catalyst and heat}} C_8H_{18} + C_8H_{18}$
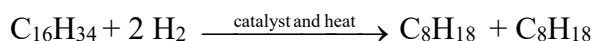
Reforming: - a chemical process where smaller alkanes are combined together and hydrogen is
removed to form heavier alkanes or changed unbranched alkanes into branched alkanes.
- branched alkanes are easier to burn and has a higher octane value in gasoline. (isooctane
or 2,2,4-trimethylpentane has the best octane rating – assigned as 100)

3. **Coal**: - a carbon-based mineral consists of very dense hydrocarbon ring compounds with high molar
masses.
- leaves a lot of soot and burns incompletely.
- usually contains 7% sulfur and when combusted with oxygen gives off SO_2 and SO_3, which is
the main source of air pollution and acid rain.

Assignment
24.4 pg. 1053−1054 #34 to 42

Chapter 25: Synthetic Organic Polymers

25.1: Properties of Polymers

Polymers: - are large organic molecules that are often chainlike.
- include plastics (Polyethylene, Polyvinyl chloride [PVC]), synthetic fibres (polyesters, nylon), and a wide variety of modern day materials (Teflon, synthetic rubber, polypropylene, polyurethane).

25.2: Synthetic Organic Polymers

Monomers: - small units that are the building blocks of the chainlike polymers. (*Mono* means one unit)
- usually contain a set of double bond or active functional groups on either end of the monomer molecule.
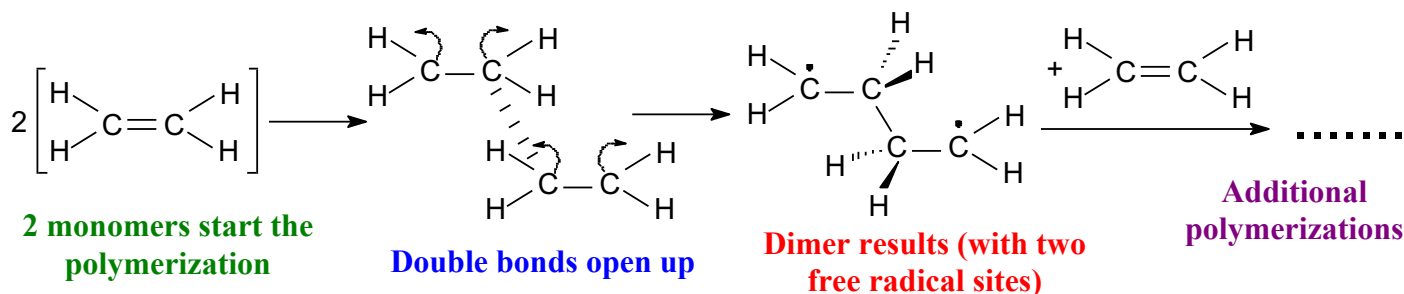
Polymerization: - molecules react with one another much like train carts hooking up to form a long train.

Dimers: - the resulting molecule when two monomer molecules combined (*Di* means two units) which can undergo further polymerization with other monomers.
- dimer is usually a **free radical** (a molecule with unpaired electron(s)), which allows it to "hook" up more monomer for further polymerization.
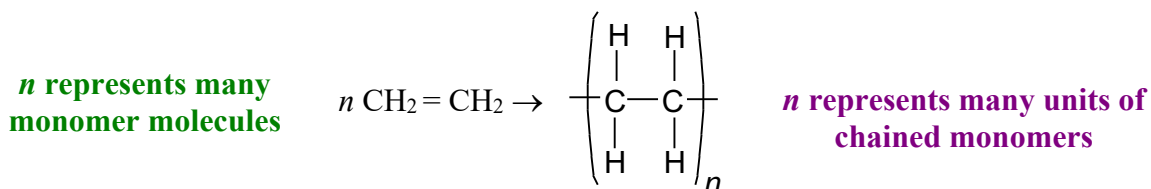
Addition Polymerization: - polymerization process involving the addition of monomers across their double bonds.

Example: The Polymerization of **Ethene** into *Polyethylene*. **(Addition Polymerization)**

2 monomers start the polymerization   **Double bonds open up**   **Dimer results (with two free radical sites)**   **Additional polymerizations**

(Check out animation at https://www.youtube.com/watch?v=4V1GYCqkJg0)

Condensed Notation for Polymerization of Ethene into Polyethylene:

***n* represents many monomer molecules** $n\,CH_2 = CH_2 \rightarrow$ ***n* represents many units of chained monomers**

Homopolymer: **-** a polymer that is made up of only ***one type of monomer***.
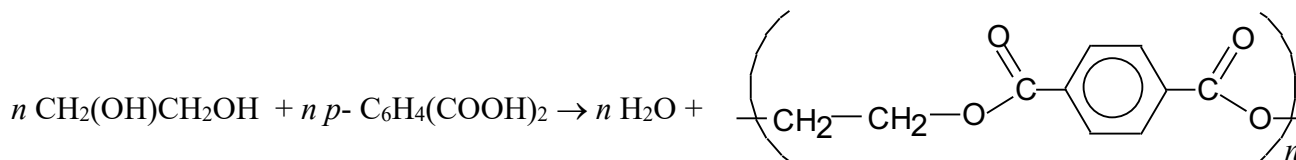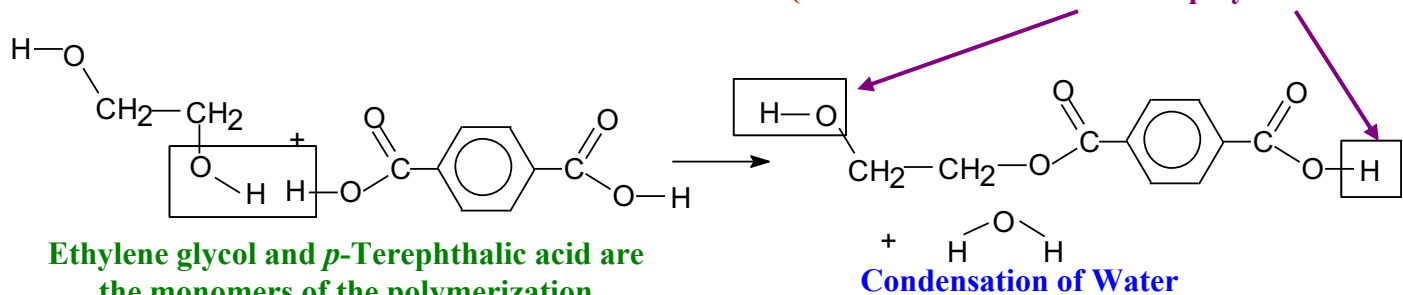- examples: Polyethylene and Polyvinyl chloride

Copolymer: - a polymer that is made up of ***two or more types of monomer***.
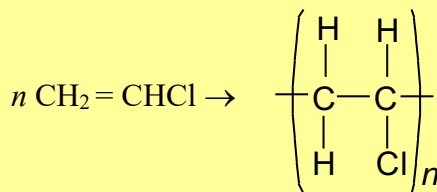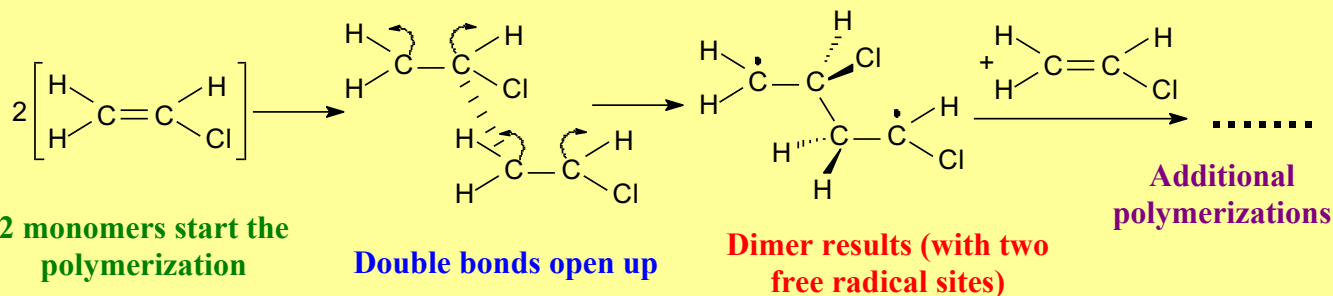
Condensation Polymerization: - polymerization process involving the esterification of monomers across their carboxylic acid functional group with the alcohol function group.

Example: The Polymerization of **Ethylene glycol** and *p*-**Terephthalic acid** into *Polyester*. **(Condensation Polymerization)**

**Dimer results (with two sites for additional polymerizations)**

Ethylene glycol and *p*-Terephthalic acid are the monomers of the polymerization

Condensation of Water

$$n\ CH_2(OH)CH_2OH\ +\ n\ p\text{-}\ C_6H_4(COOH)_2 \rightarrow n\ H_2O\ +$$

Example 1: Describe the polymerization of **Chloroethene (Vinyl Chloride)** into *Polyvinyl chloride (PVC)*.

2 monomers start the polymerization

Double bonds open up

Dimer results (with two free radical sites)

Additional polymerizations

$$n\ CH_2 = CHCl \rightarrow$$

Atactic Polymer: - polymer where the initial monomers are added randomly along the chain, resulting substituents ($-R$) end up in unsystematic positions.
- these polymers do not pack well. As such, they are rubbery and soft, amorphous (change shape easily), has low melting point and dissolve in solvents easily.
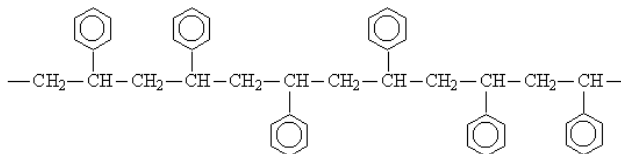
Atactic Polystyrene

Syndiotactic Polymer: - polymer where the initial monomers are added alternately along the chain,
resulting substituents (−R) are on the left and right side of the polymer.
- these polymers has the higher melting point and is somewhat crystalline compared to the atactic polymers. They are also stronger and more rigid. They do not dissolve readily in solvents.
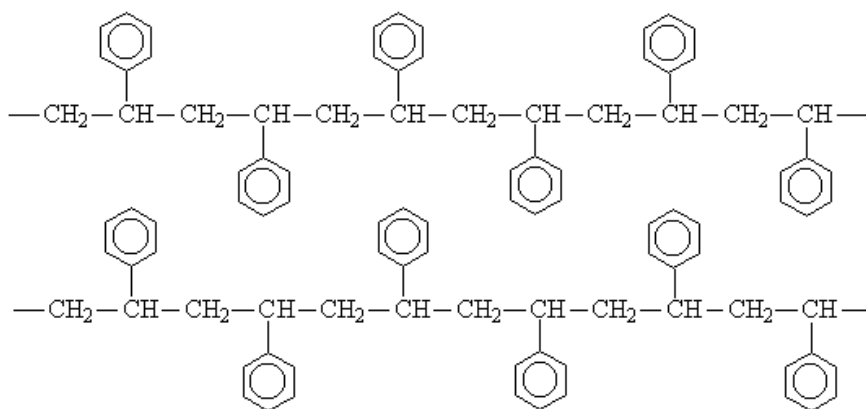
Syndiotactic Polystyrene (two chains shown)

Isotactic Polymer: - polymer where the initial monomers are added systematically along the chain,
resulting substituents (−R) are all on the same side of the polymer.
- these polymers has the highest melting point and are the most crystalline. They are very strong and very rigid. They do not dissolve in solvents.
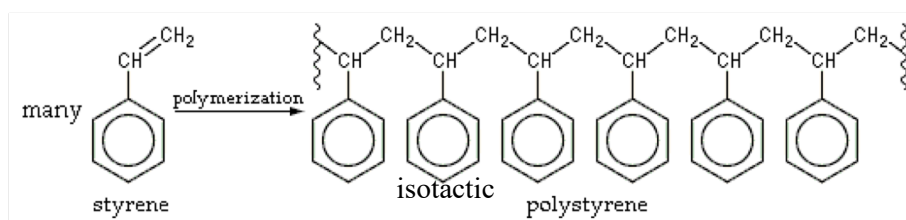
Assignment
25.1 pg. 1081 #3 and 4
25.2 pg. 1081 #7 to 12