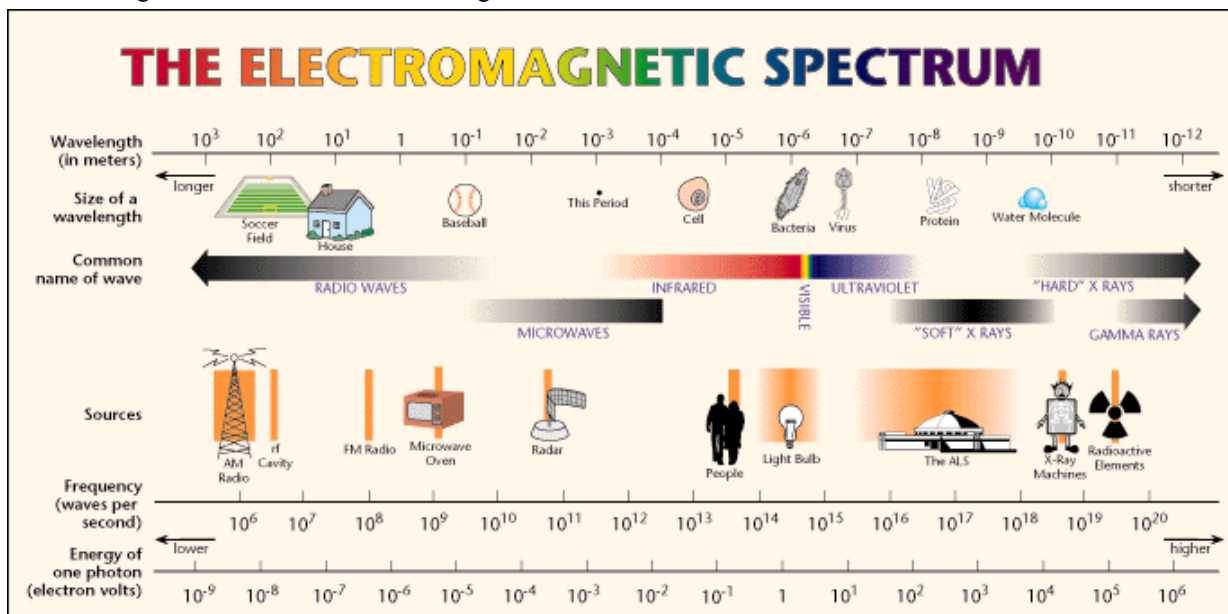**Name** _____   **AP CHEM**   __/__/__

Chapter 7 Outline – Atomic Structure and Periodicity

Electromagnetic Radiation
- One way energy travels through space is by electromagnetic radiation.
- The electromagnetic spectrum represents the total range of electromagnetic radiation ranging from the longest radio waves to the shortest gamma waves.
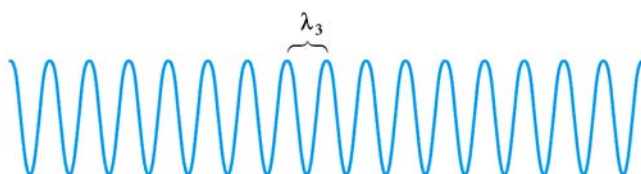

- Waves have three primary characteristics: wavelength, (λ – Greek Lamda), frequency (ν – Greek Nu),and speed of light (c).
- Wavelength, (λ), is the distance between consecutive peaks or troughs in a wave.
- Frequency, (ν), is the number of waves that pass a specific point in space per second.
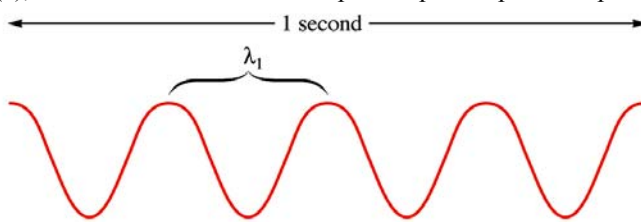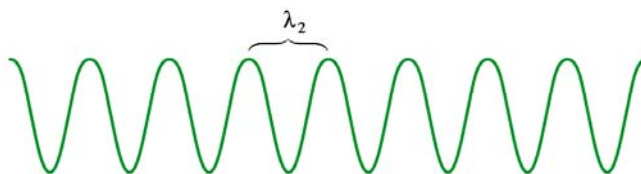
- $\lambda \nu = c$, λ = wavelength in meters, ν = frequency in cycles per second, c = speed of light (2.9979×10^8 m/s)
- Calculating Radiation: Example: The red colors in fireworks are due to the emission of light with wavelengths around 650 nm when strontium salts are heated. Calculate the frequency of red light with the wavelength of 6.50×10^2 nm.

  $\lambda \nu = c$

  6.50×10^2 nm $\div 10^9 = 6.50 \times 10^{-7}$

  $(6.50 \times 10^{-7}$ m$) \nu = 2.9979 \times 10^8$ m/s

  $\nu = 4.61 \times 10^{14}$ s^{-1} $= 4.61 \times 10^{14}$ Hz
- You try: WMZQ operates at frequency of 98.7 MHz (megahertz). Calculate the wavelength distance between waves.

- Try another: What is the frequency in hertz of blue light having a wavelength of 425 nm?


The Nature of Matter
- At the end of the 19th Century, the idea prevailed that matter and energy were distinct. Matter consisted of particles and energy consisted of waves. Particles had mass and their location could be identified. Waves were massless and delocalized.
- At the beginning of the 20th century, however, certain experimental results suggested that this picture was incorrect.
- Max Planck (1858 – 1947). While studying the radiation profiles emitted by solid bodies heated to incandescence, Plank found that the results could not be explained in terms of the physics of his day. Planck could account for his observations only by postulating that energy can be gained or lost only in whole number, multiples of the quantity $h\nu$, where h is a constant called Planck's constant, determined to have the value 6.626×10^{-34} J·s.
- $\Delta E = nh\nu$; ΔE = the change in energy; n is an integer (1,2,3..); h is Planck's constant , and ν is the frequency of the electromagnetic radiation absorbed or emitted.
- Planck discovered that energy is quantized and can occur in discrete units of size $h\nu$. Each of these small "packets" of energy is called a quantum.
- Einstein suggested that electromagnetic radiation can be viewed as a stream of particles called photons. The energy of photons is given by the expression: $E_{photon} = h\nu = \dfrac{hc}{\lambda}$ where h is Planck's constant, ν is the frequency and λ is the wavelength.
- In a related development, Einstein derived the theory of relativity. $E = mc^2$. E= energy, m= mass, c = the speed of light; the main significance of this theory is that energy has mass.
- In 1922 Arthur Compton (1892 – 1962) performed experiments involving collisions of X-rays and electrons that showed that photons do exhibit the expected mass.
- Two important conclusions can be made from the work of Planck & Einstein:
  - Energy is quantized. It can occur in discrete units called quanta.
  - Electromagnetic radiation, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well. This phenomenon is sometimes referred to as the dual nature of light.
- Diffraction results when light is scattered from a regular array of points or lines.
- When an x-ray is directed onto a crystal. The scattered radiation produces a diffraction pattern of bright spots and dark areas on a photographic plate.
- Energy is a form of matter and all matter shows the same type of properties. All matter exhibits both particulate and wave properties. Large matter exhibit predominately particulate properties. The associated wavelength is so small that it is not observed. Very small "bits of matter", such as photons, while showing some particulate properties exhibit predominately wave properties. Pieces of matter with intermediate mass, such as electrons, show clearly both the particulate and wave properties of matter.

The Atomic Spectrum of Hydrogen

- A continuous spectrum results when white light is passed through a prism. A continuous spectrum contains all wavelengths of visible light.
- A line spectrum is a spectrum showing only certain discrete wavelengths.

(a)

(b)
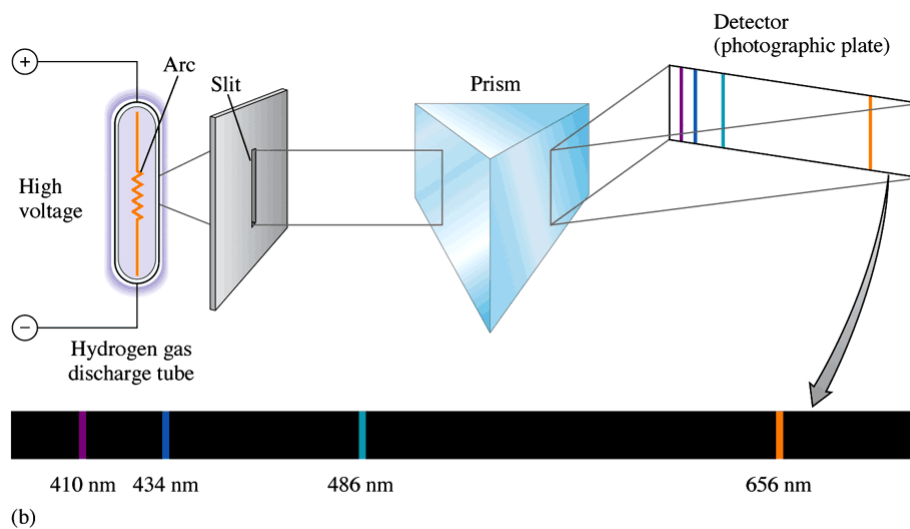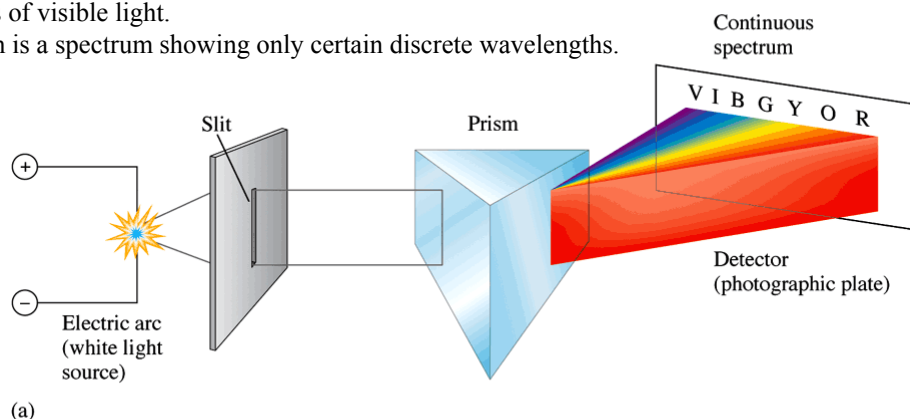
The Bohr Model

- In 1913, Danish physicist Niels Bohr (1885 – 1962) developed a quantum model for the hydrogen atom.
- Bohr proposed that the electron in a hydrogen atom moves around the nucleus only in certain allowed circular orbits.
- Bohr reasoned that the tendency of the revolving electron to fly off the atom must be just balanced by its attraction for the positively charged nucleus.
- Bohr found that his model would fit the experimental results if he assumed that the angular momentum of the electron could only occur in specific increments.
- Bohr's model gave hydrogen atom energy levels consistent with the hydrogen emission spectrum.
- The most important equation to come from Bohr's model is the expression for the energy levels available to the electron in the hydrogen atom: $E = -2.178 \times 10^{-18} J (Z^2/n^2)$, n = an integer (the larger the value of n, the larger the orbit radius; Z is the nuclear charge.
- This equation is used to calculate the change in energy of an electron when the electron changes orbit.
- For example: Calculate the change in energy corresponding to a change from level n= 6 to n=1.

   For $n = 6$
   $E = -2.178 \times 10^{-18} J (Z^2/n^2)$
   $E = -2.178 \times 10^{-18} J (1^2/6^2)$
   $E = -6.050 \times 10^{-20} J$

For n = 1
$E = -2.178 \times 10^{-18} \text{ J } (Z^2/n^2)$
$E = -2.178 \times 10^{-18} \text{ J } (1^2/1^2)$
$E = -2.178 \times 10^{-18} \text{ J}$

$\Delta E = E_{final} - E_{initial}$
$\Delta E = (-2.178 \times 10^{-18} \text{ J}) - (-6.050 \times 10^{-20} \text{ J})$
$\boldsymbol{\Delta E = -2.117 \times 10^{-18} \text{ J}}$
The negative sign indicates that the electron has lost energy and is now in a more stable state. The energy is carried away from the atom by the production (emission) of a photon.

- You try: Calculate the energy required to excite the hydrogen electron from level n=1 to level n=2.

- Two important points about the Bohr Model:
  - The model correctly fits the quantized energy levels of the hydrogen atom and postulates only certain allowed circular orbits for the electron.
  - As the electron becomes more tightly bound, its energy becomes more negative relative to the zero-energy reference state (corresponding to the electron being at infinite distance from the nucleus). As the electron is brought closer to the nucleus, energy is released from the system.
- At first Bohr's model appeared to be very promising. The energy levels calculated by Bohr closely agreed with the values obtained from hydrogen emission spectrum. However, when Bohr's model was applied to atoms other than hydrogen, it did not work at all.
- It was concluded that Bohr's model is fundamentally incorrect.
- It is important to realize, however, that the current theory of atomic structure is in no way derived from the Bohr model. Electrons do not move around the nucleus in circular orbits.

The Quantum Mechanical Model of the Atom
- By the mid-1920's it had become apparent that the Bohr model could not be made to work.
- Heisenberg, de Broglie and Schrödinger were at the forefront of developing an alternative model.
- The approach they developed became known as the wave mechanics or, more commonly, quantum mechanics.
- To Schrödinger and de Broglie, the electron bound to the nucleus seemed similar to a standing wave, and they began research on a wave mechanical description of the atom.
- Heisenberg's mathematical analysis led him to a surprising conclusion: There is a fundamental limitation to just how precisely we can know both the position and momentum of a particle at a given time. This is known as the Heisenberg uncertainty principle. The more accurately you know a particle's position, the less accurately you can know its momentum and vice versa.

- It is therefore not appropriate to assume that the electron is moving around the nucleus in a well defined orbit as in the Bohr model.
- Although the wave function itself has no easily visualized meaning, the square of the function indicates the probability of finding an electron near a particular point in space.
- The square of the wave function is most conveniently represented as a probability distribution, in which the intensity of color is used to indicate the probability value near a given point in space. The probability distribution for hydrogen is shown to the upper right.
- The diagram is also known as an electron density map; electron density and electron probability mean the same thing.
- The size of an orbital cannot be defined precisely, since the probability never becomes zero. The definition most often used by chemists to describe the size of the hydrogen 1s orbital is the radius of the sphere that encloses 90% of the total electron probability. That is, 90% of the time the electron is inside this sphere.
- An orbital is difficult to define at the introductory level. Technically it is a wave function. However, it is most helpful to picture an orbital as a three dimensional electron density map. That is, an electron in a particular atomic orbital is assumed to exhibit the electron probability indicated by the orbital map.

(a)

(b)

y-axis: Probability (R^2)

x-axis: Distance from nucleus (r)
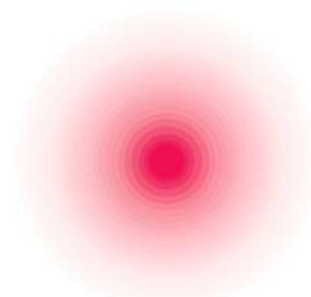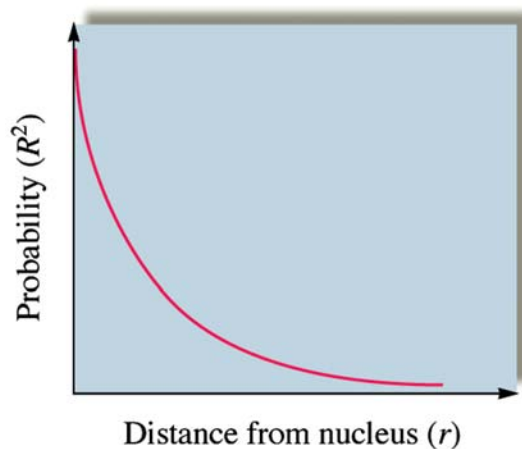
Quantum Numbers
- Quantum numbers are used to describe the various properties of atomic orbitals.
- **The principle quantum number (n)** has integral values: 1,2,3…. The principle quantum number is related to the size and energy of the orbital. As n increases, the orbital becomes larger and the electron spends more time farther from the nucleus.
- **The angular momentum quantum number (ℓ)** has integral values from 0 to n-1 for each value of n. This quantum number is related to the shape of the atomic orbitals. It is sometimes referred to as subshell.
- **The magnetic quantum number (m_ℓ)** has integral values between ℓ and -ℓ including zero. The value of m_ℓ is related to the orientation of the orbital in space relative to the other orbitals in the atom.
- Example: Write a set up quantum numbers to represent the electrons of sodium, cobalt and boron.
  - **Na: 3, 0, 0**
  - **Co: 4, 2, 1**
  - **B: 2, 1, -1**
- **You Try:** Write a set up quantum numbers to represent the electrons of zirconium, barium and iodine.

Angular Momentum Quantum Number	
Value of ℓ	Letter used
0	s
1	p
2	d
3	f
4	g

Orbital Shapes and Energies

- S orbitals have a characteristic spherical shape. When an atom contains more that one s orbital, the orbitals are separated by a node or nodal surface.
- Nodes are areas of an atom with zero electron probability.
- P orbitals have two lobes separated by a node at the nucleus. P orbitals are labeled P_x, P_y and P_z for the axis it lies on.

- D orbitals first occur in the third energy level (n=3). The five d orbitals have the shapes shown below.

- F orbitals first appear in the fourth energy level. Their shapes are complex. These orbitals are not used in bonding. Their shape is included here for completeness.

- 6 -

- The energy of a particular orbital is determined by its n value. Thus, all orbitals with the same value of n have the same energy. Orbitals with the same amount of energy are called degenerate orbitals.

Electron Spin and the Pauli Principle
- The concept of electron spin was developed by Samuel Goudsmit and George Uhlenbeck while they were graduate students at the University of Leyden in the Netherlands.
- They found a fourth quantum number was needed to account for the details of the emission spectra of atoms. The spectral data indicated that the electron has a magnetic moment with two possible orientations when the atom is placed in an external magnetic field.
- The new quantum number adopted to describe this phenomenon, called the **electron spin quantum number (m_s)** can have only one of two values, $+\frac{1}{2}$ and $-\frac{1}{2}$.
- The main significance of electron spin is connected with the postulate of Austrian physicist Wolfgang Pauli: **In a given atom no two electrons can have the same set of four quantum numbers**. This is called the **Pauli Exclusion Principle**. Since electrons in the same orbital have the same n, ℓ, m_ℓ values, this postulate states that they must have different values of m_s. Since only two values of m_s are allowed, **an orbital can hold only two electrons and they must have opposite spins**.

The History of the Periodic Table
- The greatest triumph of the quantum mechanical model is its ability to account for the arrangement of the elements in the periodic table.
- The periodic table was originally developed to represent patterns observed in the chemical properties of the elements.
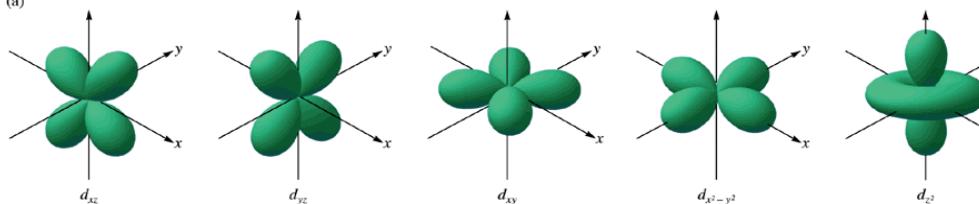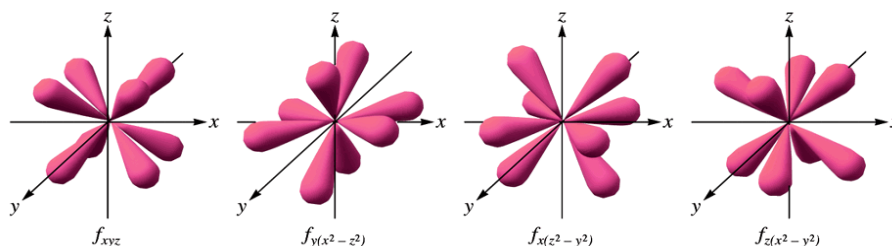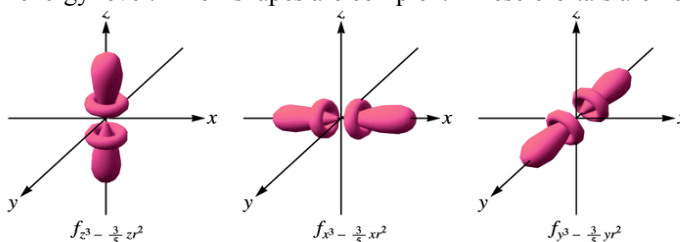- The first to recognize patterns was Johann Dobereiner (1780-1849) who found several groups of three elements that have similar properties. Ca, Sr & Ba (atomic weights: 40, 88, 137) = $(40 + 137) \div 2 = 88$; Li, Na & K (atomic weights: 7, 23, 39) = $(7 + 39) \div 2 = 23$; Cl, Br & I (35, 80, 127) = $(35 + 127) \div 2 = 81$
- John Newlands suggested that the elements should be arranged in octaves, based on the idea that certain properties seemed to repeat for every eight element in a way similar to the musical scale which repeats for every eight tone.
- The present form of the periodic table was conceived independently by two chemists: German, Julius Lothar Meyer (1830-1895) and Russian, Dmitri Ivanovich Mendeleev. Mendeleev is usually give most of the credit because he was able to make predictions about still yet to be discovered elements. Mendeleev also corrected atomic masses of some elements.
- The current arrangement of elements is different from Mendeleev's table in that elements are now organized by increasing atomic number.

The Aufbau Principle and the Periodic Table
- Electron configurations are used to indicate the arrangement of electrons around the nucleus of an atom in its ground state.
- You must know how to write electron configurations by an elements location on the periodic table.
- Example: Write the electron configuration for chlorine. $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^5$
- You try. Write the electron configuration for aluminum and iron.

- **The Aufbau Principle**: as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to these hydrogen-like orbitals.
- **Hund's Rule:** (named for F.H. Hund) states that the lowest energy configuration for an atom is having the maximum number of unpaired electrons allowed by the Pauli principle in a particular set of degenerative orbitals.
- By convention, the unpaired electrons are represented as having parallel spins (with spin up).
- Example: Note the orbital diagram for Oxygen: O: $1s^2 2s^2 2p^4$

- You try: Write the orbital diagram for carbon.

- To use the short cut version of electron configuration, go back to the last noble gas that was passed, put its symbol in brackets and begin with the outer s orbital.
- For example write the electron configuration abbreviated version for Cobalt:
    Co: $[Ar] 4s^2 3d^7$
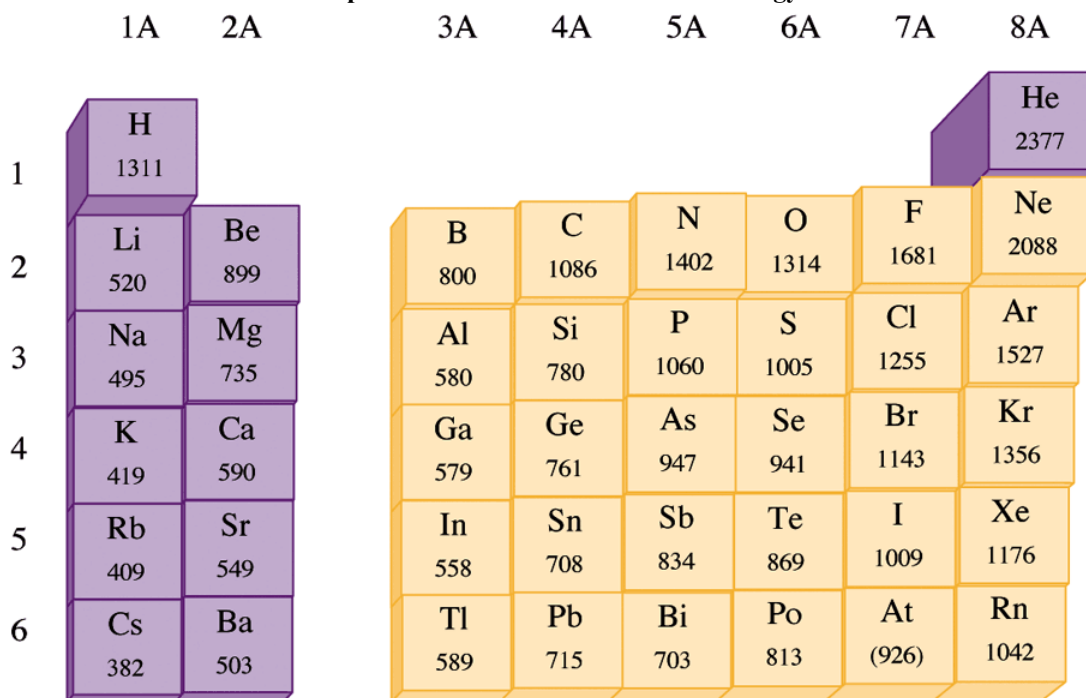- You try: Write the abbreviated electron configuration for iodine.

- Abbreviated electron configurations show the valence electrons. **Valence electrons are the electrons in the outer energy level of an atom**. These electrons are found in s and p orbitals. Valence electrons are important because they are involved in bonding.
- **Inner electrons** are known as **core electrons**.
- The elements in the same vertical column of the periodic table have the same valence electron configuration.
- Some transition metals show **exception** in their electron configurations. **Chromium's electron configuration is: $[Ar]4s^1 3d^5$ instead of $[Ar]4s^2 3d^4$ and Copper's electron configuration is: $[Ar]4s^1 3d^{10}$ instead of $[Ar]4s^2 3d^9$. In these elements, an electron is moved from the s to the d subshell so the orbitals are half-filled.**
- After lanthanum, which has the electron configuration: $[Xe]6s^2 5d^1$, a group of 14 elements called the lanthanide series, or lanthanides, occurs. This series of elements corresponds to filling of the seven 4f orbitals.
- After actinium, which has the electron configuration: $[Rn]7s^2 6d^1$, a group of 14 elements called the actinide series, or actinides, occurs. This series of elements corresponds to filling of the seven 4f orbitals.

Periodic Trends in Atomic Properties
- **Ionization Energy is the energy required to remove an electron from a gaseous atom or ion:**
    o $X(g) \rightarrow X^+(g) + e^-$
- Consider the energy required to remove several electrons in succession from aluminum in the gaseous state:
    o $Al(g) \rightarrow Al^+(g) + e^-$ $I_1 = 580$ kJ/mol
    o $Al^+(g) \rightarrow Al^{2+}(g) + e^-$ $I_2 = 1815$ kJ/mol
    o $Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$ $I_3 = 2740$ kJ/mol
    o $Al^{3+}(g) \rightarrow Al^{4+}(g) + e^-$ $I_4 = 11,600$ kJ/mol
- In a stepwise ionization process, it is always the highest-energy electron (the one bound least tightly) that is removed first. The first ionization energy, I_1, is the energy required to remove the highest-energy electron of an atom.
- Note that as more electrons are removed, the successive ionization energies increase. This is because as the atoms lose an electron they become positively charged. This increase in positive charge binds the remaining electrons more firmly.
- **The big increase in aluminum's ionization energy between I_3 and I_4 is because in the fourth step a core electron is being removed. Core electrons are bound more tightly than valence electrons.**

- **Left to right across a period, first ionization energy increases. Increasing the number of protons and electrons in the same principle energy level increases the attraction between the protons and the electrons, making it more difficult to remove an electron.**
- **First ionization energy decreases in going down a group. This is due to the fact that the electrons being removed are further from the nucleus.**
- The diagram below shows the trends in ionization energies (kJ/mol) for the representative elements. **Note the discontinuities in ionization energy in going across a period. In period two, discontinuities exist between beryllium and boron and nitrogen and oxygen. The decrease in ionization energy going from Be to B is due to the fact that the s subshell electrons shield the nucleus from the p subshell electron in boron making its first ionization energy lower. The reason for the decrease in ionization energy when going from nitrogen to oxygen is due to the fact that oxygen has one doubly filled orbital. The extra electron repulsions make its first ionization energy lower.**

	1A	2A		3A	4A	5A	6A	7A	8A
1	H 1311								He 2377
2	Li 520	Be 899		B 800	C 1086	N 1402	O 1314	F 1681	Ne 2088
3	Na 495	Mg 735		Al 580	Si 780	P 1060	S 1005	Cl 1255	Ar 1527
4	K 419	Ca 590		Ga 579	Ge 761	As 947	Se 941	Br 1143	Kr 1356
5	Rb 409	Sr 549		In 558	Sn 708	Sb 834	Te 869	I 1009	Xe 1176
6	Cs 382	Ba 503		Tl 589	Pb 715	Bi 703	Po 813	At (926)	Rn 1042

- **Electron Affinity is the energy change associated with the addition of an electron to a gaseous atom.**
  - $X(g) + e^- \rightarrow X^-(g)$
- The figure below shows the electron affinity values for the atoms among the first 20 elements that form stable, isolated negative ions.
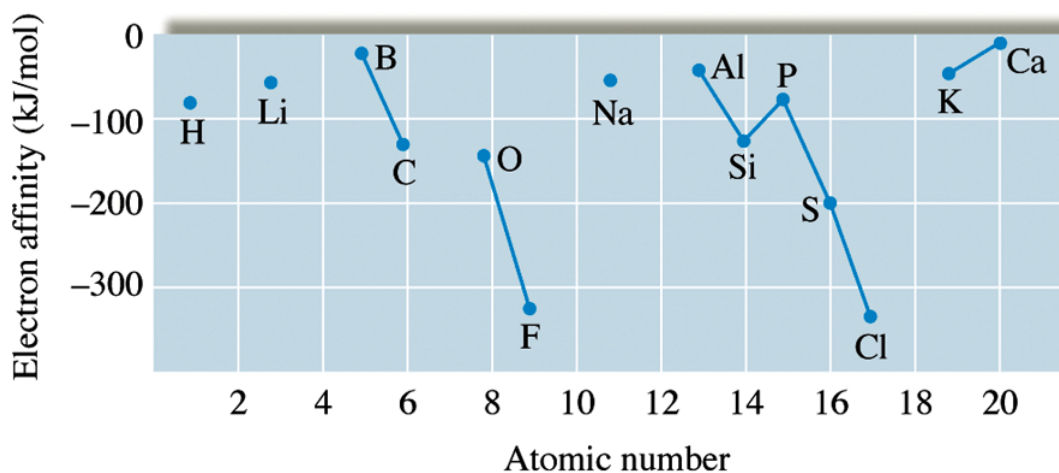
- **When the addition of an electron makes the atom more stable, energy is given off.** This is true for most of the elements. **When the addition of an electron makes the atom less stable, energy must be put in. That's because the added electron must be placed in a higher energy level, making the element less stable. This is the case for elements with full subshells, like the alkaline earth metals and the noble gases.**
- **When moving left to right across a period, the energy given off when an electron is added increases. Electron affinities do not change much down a group.**
- **The most reactive metals have the smallest ionization energy (Fr). The most reactive non-metals have the largest ionization energy and are the most exothermic when they gain electrons (F).**
- Just as the size of an orbital cannot be specified exactly, neither can the size of an atom. **Atomic radius is defined as half the distance between like atoms located next to one another.**
- **Atomic radius decreases left to right across a period**. This is because as you go across a period, more protons and more electrons are added, increasing the attraction between them and bringing them closer together.
- **Atomic radius increases down a group because more energy levels are being added.**