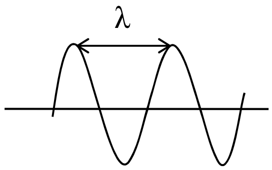
<u>Atomic Structure and Periodicity</u>

Chapter 7

<u>Electromagnetic Radiation</u>
-radiant energy that exhibits wavelike behavior and travels at the speed of light in a vacuum (3×10^8m/s)

<u>Wavelength</u> – (λ, lambda)
-the distance between two consecutive peaks or troughs in a wave.



<u>Frequency</u> – (ν, nu)
-the number of waves, per second that pass a point in space
-since all electromagnetic radiation travels at the speed of light, short wave lengths have high frequency
-for electromagnetic radiation:

$C = \lambda\nu$

λ = wavelength, in meters (1m = 10^9nm)
ν = frequency, in cycles per second (1/s, called hertz)
C = the speed of light, 3×10^8m/s (Hz)

<u>At the End of the 19th Century!</u>
-matter and energy were thought to be distinct

<u>Matter</u>- consists of particles
- particles have mass and a position that can be specified

<u>Energy</u> - in the form of light (electromagnetic radiation) was described as a wave
- it is mass less and delocalized
- its position in space can not be specified
- but, experimental results at the beginning of the 20th century suggest this is wrong!

<u>Max Plank</u>
-heated solids to high temperature until they gave off visible light
-postulated that energy could be gained or lost only in whole number multiples of the quantity hν (h = Plank's constant = 6.626×10^{-34}Js)
-therefore, the change in energy for a system (ΔE):

$\Delta E = nh\nu$ ($\Delta E = h\nu$, on formula sheet)

n = an integer
h = Planks constant
ν = the frequency of the radiation absorbed or emitted

-energy was thought to be continuous, not quantized, but this was contradictory to that idea
-each "particle" of energy, hν, is called a quantum
-it was concluded that the transfer of energy can only occur in whole quanta (like whole particles)

(7.2 p292 – READ IT!)

$\lambda = 4.50\times10^{2}$nm

What is the increment of energy (the quantum) that is emitted at 4.50×10^{2}nm by CuCl?

<u>Albert Einstein</u>:
-he proposed that electromagnetic radiator is quantized
-he said it can be viewed as a stream of "particles" called <u>PHOTONS</u>
-the energy of a photon can be calculated:
$E_{photon} = h\nu$

But $C = \lambda\nu$

So $\nu = \frac{C}{\lambda}$

$\therefore E_{photon} = \frac{hC}{\lambda}$

- in Einstein's theory of relativity:

$E = mc^2$

or $m = \frac{E}{C^2}$

- you can, therefore, calculate the <u>mass</u> associated with a given quantity of energy:
-

$$E_{photon} = \frac{hC}{\lambda}$$

$$M = \frac{E}{C^2} = \frac{\frac{hC}{\lambda}}{C^2} = \frac{hC}{\lambda}$$

- as such, the apparent mass of a photon with wavelength λ is

$$M = \frac{h}{\lambda C}$$

<u>In summary, then</u>

1. Energy is quantized. It only occurs in discrete units called quanta.
2. Electromagnetic radiation shows wave properties and certain characteristics of particulate matter. (This is referred to as the "dual nature of light")

The next question to be asked was:
"Can particles have wave properties?"

<u>Louis de Broglie</u>

-for electromagnetic radiation $M = \frac{h}{\lambda C}$

- for a particle moving at velocity, V, $M = \frac{h}{\lambda V}$

- therefore to calculate the wavelength of a particle moving at a velocity of V:

$$\lambda = \frac{h}{mv}$$

The deBroglie Equation (on formula sheet)

<u>7.3</u> (p294) Compare the wavelength for an electron (mass=9.11×10^{-31}kg) traveling at a speed of 1.0×10^{7}m/s with that for a ball (mass=0.10kg) traveling at 35m/s.

- from 7.3, λ of the ball is incredibly short compared to its environment
- wavelength of the electron is very small but on the same order as the spacing between

- toms in a typical solid
- x-rays directed at crystals produce patterns of constructive and destructive interference
- this can only occur if the electron has a wavelength
- this verified Broglies relationship (at least for an electron)
- it is now believed that all matter obeys deBroglies equation but most particles have such small wavelengths they can not be experimentally verified.

Today believed:

1. Energy is really a form of matter
2. All matter shows both wave and particle properties
    - Large particles (a baseball) exhibit predominantly particle properties
    - Very small particles (a photon) exhibit predominantly wave properties
    - Particles of intermediate mass (electrons) show both wave and particle properties

The Bohr Model (Niels Bohr)

- proposed electrons moved around the nucleus in certain allowed orbits
- he calculated the amount of energy associated with each orbit

$$E = -2.178\times10^{-18}\,J\left(\frac{z^2}{n^2}\right)$$

n= an integer (the larger the number the bigger the orbit radius)
z= nuclear charge
E= the amount of energy for an electron in that orbit

(negative sign means the energy of the electron is less than it would be if it were an infinite distance from the nucleus where there is no interaction and the energy is zero)

On formula sheet: $$E_n = \frac{-2.178\times10^{-18}\,J}{n^2}$$ This is for a H atom where z=1

- this equation can be used to calculate the change in energy of an electron when it changes orbits

Ex. For an electron in an excited atom of H where n=6, returning to ground state where n=1.

for n=6

$$E = -2.178\times10^{-18}\,J\left(\frac{1^2}{6^2}\right) = -6.05\times10^{-20}\,J$$

for n=1

$$E = -2.178\times10^{-18}\,J\left(\frac{1^2}{1^2}\right) = -2.178\times10^{-18}\,J$$

- n=1 has more negative energy that n=6 because the electron is more tightly bound to the nucleus

$$\Delta E = E_f - E_i$$

$$\Delta E = E_1 - E_6 = -2.178\times10^{-18}\,J - \left(-6.05\times10^{-20}\,J\right)$$

$$\Delta E = -2.117\times10^{-18}\,J$$

- here the negative sign for the change means energy is lost (more stable state)

Derived on page 299

$$\Delta E = -2.178\times10^{-18}\,J\left(\frac{1}{n^2_{final}} - \frac{1}{n^2_{initial}}\right)$$

- as the change n=6→n=1 occurs energy is carried away from the atom by the emission of a photon
- the photons wavelength can be calculated

$\Delta E = h\nu$, but $C = \lambda\nu$ or $\nu = \dfrac{C}{\lambda}$ so: $\Delta E = h(\dfrac{C}{\lambda})$

λ= wavelength

C= 3x10[3]

h= 6.626x10[-34]

ν= velocity

Solving for λ: $\lambda = \frac{hc}{\Delta E}$

$$\lambda = \frac{(6.626x10^{-34}\, J \cdot s)(3x10^{8}\, \frac{m}{s})}{2.117x10^{-18}\, J} = 9.383x10^{-8}\, m$$

- the mass of the photon can be calculated

$$\lambda = \frac{h}{mv}$$

or $M = \frac{E}{C^2}$ as an alternate

7.4 Calculate the energy required to excite the hydrogen electron from level n=1 to level n=2. Also calculate the wavelength of light that must be absorbed by a hydrogen atom in the ground state to reach this excited state.

$\Delta E = 1.634x10^{-18}$

$\lambda = 1.217x10^{-7}$

Important Points from the Bohr Model

1) It shows that energy levels are quantized in a hydrogen atom that only circular orbits are allowed
2) As the electron is brought closer to the nucleus it replaces energy

- (Unfortunately when Bohr's model was applied to other atoms, it did not work!)
- It was historically important because it showed quantization of energy in atoms could be explained using simple assumptions

- But electrons do not move around their nucleus in circular orbits.

Bohr Model of the Atom (Niels Bohr)
-Electrons move in circular orbits around the nucleus
-Bohr calculated the amount of energy associated with each orbit in a hydrogen atom
-these values were used to establish the energy emitted as electrons moved from orbit to orbit was "quantized"
(but….)

Heisenberg Uncertainty Principle (Werner Heisenberg)

There is a fundamental limitation to just how precisely you can know both the position and the momentum of a particle at any given time.

-the result is that you cannot know the exact position or pathway of an electron
-the electron does not move around the nucleus in a well defined orbit or path

(**Bohr was wrong!!**)

Erwin Schrodinger

-calculated a "wave function" for the electron
-describes the region in an atom where the electron will probably be found
-also called an "**orbital**"

Modern Day Atomic Theory-

Electrons are in:

1. Principal Energy Levels
   a. Labeled $1 \rightarrow 7$
   b. Represent a distance from the nucleus and an amount of energy
   PEL= 1 –closest to the nucleus, least amount of energy
   PEL=7 --farthest from the nucleus, greatest amount of energy

(PEL= 8,9,10 are possible but at present there are not atoms large enough to need that many PEL's)

(PEL's are made up of…)

Sublevels

-a division of a principle energy level

-name s.p.d.+f

-energy wise, within a given PEL,
s<p<d<f

(sublevels are made up of …)

Orbitals

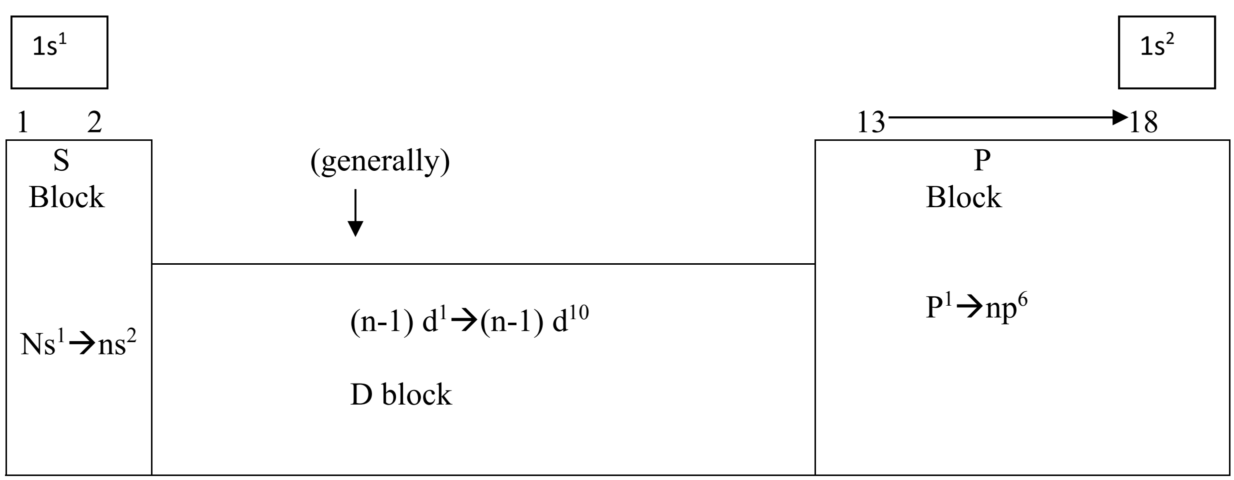
-a region in space that can hold 2 electrons that are spinning in opposite directions
-different sublevels contain different numbers of orbitals.

S=1 (spherical)
P=3 (figure 8-shaped)
D=5 (text p 309)
F=7
(G=9?) speculation

-again this is a mathematical calculation (Schrodinger)

Electron Configurations

- a series of numbers and letters that describe probable locations of electrons in an atom.
- the periodic table is set up by atomic number <u>and electron configuration</u>
- filling order can be determined by positioning on the periodic table.
- where n = the number of outermost PEL+period



F block	$f^1 \rightarrow f^{14}$

4f
5f

-another method of determining filling order is:

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f (5g?)
6s 6p 6d 6f
7s

<u>Exceptions in filling order:</u>

1. (n)s fills before (n-1)d
   Ex. $4s^2$, $3d^1$

2. In the Transition Metals

-filling the d sublevels

Sc $4s^2$, $3d^1$ Fc $4s^2$, $3d^6$
Ti $4s^2$, $3d^2$ Co $4s^2$, $3d^7$
V $4s^2$, $3d^3$ Ni $4s^2$, $3d^8$
*Cr $4s^1$, $3d^5$ Cu $4s^1$, $3d^{10}$ considered the end of transition elements
Mn $4d^2$, $3d^5$ Zn $4s^2$, $3d^{10}$

-atoms are more stable with a <u>½ filled or full sublevel.</u>

<u>In the p, d and f blocks</u>

-because electrons are mutually repulsive
-no orbital gets a 2^{nd} electron until each orbital contains 1 electron
-all unpaired electrons in a sublevel are spinning in the same direction

Hund's Rule
(Frederick Hund 1896-   )German physicist

The most stable arrangement of electrons in sublevels is the one with the greatest number of parallel spins.

Lanthanide and Actinide Series
-follow the elements lanthanum and actinium
-filling of the 4f and 5f sublevels
-elements within each series have similar properties because electrons are being added to the <u>3rd from the outermost</u> sublevel.

(n-2)f

(another way to indicate the location of a single electron is to use…)

Quantum Numbers
-a series of 4 numbers that are used to describe the position of an electron in an atom

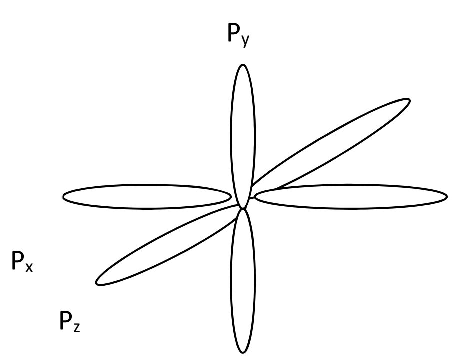
1. Principal quantum number (n)
-this indicates which principal energy level the electron is in
-the possible values are n=1→7

2. Angular Momentum Quantum Number (ℓ)
-this indicates what type (shape) of sublevel the electron is in

s, ℓ=0   d, ℓ=2

p, ℓ=1   f, ℓ=3

3. Magnetic Quantum Number (m_ℓ)
-designates which particular orbital within the sublevel the electron is in
-the values for m_ℓ are + ℓ→- ℓ, integers including o.
Ex.



m_ℓ : P_x= 1

P_y =0

P_z=-1

-for: s m_l =0 p m_l =+1, 0, -1

d m_l = +2, +1, 0, -1, -2 f m_l =3, =2, =1, 0, -1, -2, -3

4. Electron Spin Quantum Number (m_s)

-electron spins on their axes in one of 2 opposite directions.

-the values for m_s are +1/2 and -1/2

Pauli Exclusion Principle (Wolfgang Pauli 1900-1958)

In a given atom, no two electrons can have the same 4 quantum numbers.

-If n, l, & m_l are the same, the electrons must be spinning in opposite directions.

POSIBLE SETS OF QUANTUM NUMBERS

	n	l	M_l	M_s
1s	**1**	**0**	**0**	**+, - ½**
2p	**2**	**1**	**1, 0, -1**	**+, - ½**
3d	**3**	**2**	**+2 --> -2**	**+, - ½**
4f	**4**	**3**	**+3 → -3**	**+, - 1/2**

(The most important electrons are the…)

Valence Electrons

- the electrons in the outermost principal energy level of an atom
- these are the electrons that are usually involved in bonding

*transition elements also use electrons from the "d" sublevel in the second from outermost PEL

Ex. Cu^{+2} $3d^9$ $4s^1$

- for the representative elements (groups 1,2 + 13-18) the <u>ones digit</u> of the <u>group number</u> is the number of valence electrons of the elements in the group.
- The elements in a group have similar properties because they have the same number of valence electrons
- Inner electrons are called “core” electrons.

(When atom’s react, often times electrons and lost by an atom. This requires energy to overcome the attraction of the nucleus for the electron…)

Ionization Energy

-the energy required to remove and electron from a gaseous atom or ion

$X_{(g)}$ + energy -→ $X^{+}_{(g)} + e^{-}$

-the most loosely held electron is removed by the addition of the **1st ionization energy.**

- 2^{nd}, 3^{rd}, 4^{th}, etc, electrons are removed by 2nd, 3^{rd}, 4^{th} etc, ionization energies.

Forces Influencing the Electron in an Atom

- each electron is moving in a field that is the result of two forces
  1. attraction to the nucleus ($\cancel{Z}$ = nuclear charge)
  2. repulsion by the other electrons

Ex $^{4}_{2}He$ 1^{st} ionization energy = 2372kJ/mol
2^{nd} ionization energy = 5248kJ/mol
Why such difference?

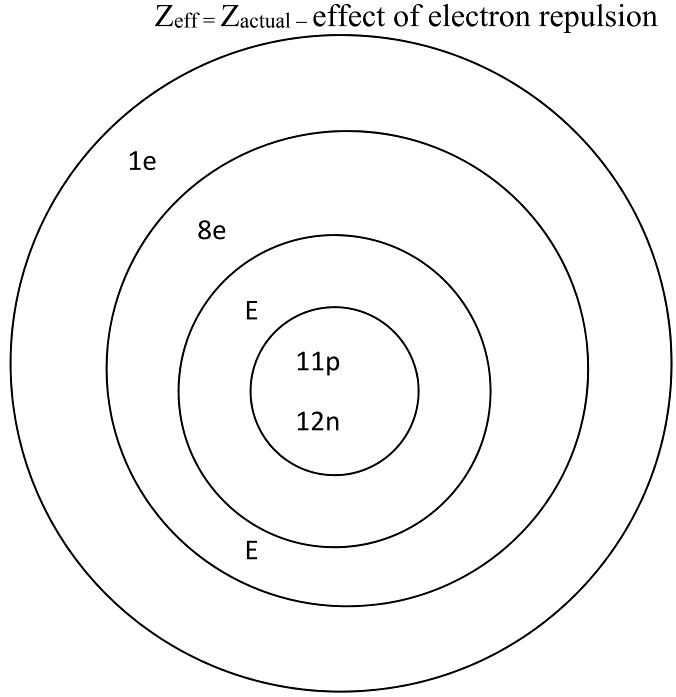
- 1^{st} electron to be removed is attracted to the nucleus but repelled by the 2^{nd} electron.
- 2^{nd} electron experiences nuclear attraction but NO repulsion so it requires more energy to remove it.

Z = nuclear charge = the number of protons @ +1
(This effect of repulsion is called…)

Effective Nuclear Charge (Z_{eff})

- The net result of the nuclear attraction and the electron – electron repulsion.
- Inner electrons repel outer electrons (often called "shielding")
- The greater the number of electrons between a specific electron and the nucleus, the weaker the effective nuclear charge (Z_{eff})

$Z_{eff} = Z_{actual} -$ effect of electron repulsion



- for 1s' e Z_{eff} = 10.3
- for 3s' e Z_{eff} = 1.84

(Greater than 1.0 because sometimes the e has to move closer to the nucleus.)

Ex: For Al:

$Al_{(g)} \rightarrow Al^{+}_{(g)}$ + e-	I_1 = 580 kJ/mol
$Al^{+}_{(g)} \rightarrow Al^{+2}_{(g)}$ + e-	I_2 = 1815kJ/mol
$Al^{+2}_{(g)} \rightarrow Al^{+3}_{(g)}$ + e-	I_3 = 2740kJ/mol
$Al^{+3}_{(g)} \rightarrow Al^{+4}_{(g)}$ + e-	I_4 = 11,600kJ/mol

$Z_{eff} = Z_{actual} - Z_{repulsion}$

- As electrons are moved the amount of repulsion <u>decreases</u>.
- As repulsion decreases, Z_{eff} increases.

Therefore, <u>more</u> energy is required to remove successful electrons.

Why is I_4 so much greater?

- The 4th electron is a <u>core</u> electron, not a valence electron.
- Held more tightly because:

1) There is <u>less</u> repulsion
2) It is in an energy level that is <u>closer</u> to the nucleus

<u>Trends in Ionization Energy</u>

-moving left to right across a peiod, <u>generally</u> 1st ionization energy <u>increases</u>

-adding protons so Z_{eff} <u>increases</u>

Ex

Na	490kj/mol
Mg	735
Al	580*
Si	780
P	1060
S	1005**
Cl	1255
Ar	1525

*Al < Mg

-full s sublevel provides <u>more effective shielding</u>

(lowers Z_{eff})

** S < P

-<u>greater repulsion</u> as 2nd electron is added to an orbital already containing 1 electron (lowers Z_{eff})

-moving <u>down a group</u>, generally 1st ionization energy <u>decreases</u>

-electron being removed is farther from the nucleus

-electrons are shielded by a greater number of core electrons (lowers Z_{eff} !)

7.9 (p325)

Consider:

Ne $1s^2, 2s^2, 2p^6$
Na $1s^2, 2s^2, 2p^6, 3s^1$
Mg $1s^2, 2s^2, 2p^6, 3s^2$

Which atom has:

a) The largest 1^{st} ionization energy?
   Ne: less shielding of outer most electron

b) The smallest 2^{nd} ionization energy?
   Mg: still removing a valence electron rather than a core electron.

Electron Affinity

-the energy released when an electron is added to a gaseous atom

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

Therefore the greater the amount pf electron repulsion:

1. The smaller the ionization energy
2. The smaller the electron affinity

(another periodic property is..)

Atomic Radius

-one half the distance between 2 neighboring atoms in the solid state
-from left to right across a period, generally,
    -radius decreases
    -as protons are added, Z_{eff} increases
-down a group, generally
    -radius increases
    -as n becomes larger, the valence shell is larger

(Mendelyev set up first periodic table as an attempt at organizing information..)

General Information from the Periodic Table

1. The placement of an element on the periodic table allows for the derivation of its electron configuration
    (exceptions: Cr + Cu groups)

2. Placement of an element on the chart allows for a general determination of properties
   Metals→ -lose e-, form positive ions
   -have low ionization energy

Nonmetals → -gain e-, form negative ions
-have high ionization energy and electron affinity

3. Certain groups are important enough to be named:

1 – Alkali metals
2 – Alkaline Earth Metals
17 – Halogens
18 – Inert Gases

3. Representative elements (groups 1,2 +13-18) have similar properties within each group because similar properties within each group because each element in the group has the same number of valence electrons:

Ex) Group I – Alkali Metals

-most chemically active metals
-down the group

1. ionization energy decreases
2. atomic radius increases
3. density increases
4. melting point increases
5. react with nonmetalsto form ionic solids

*6. $2M + 2H_2O \rightarrow 2MOH + H$
**7. hydroxides are strong bases