

# Chapter 7- Atomic Structure & Periodicity

## Study Guide

Zumdahl finds the material in this chapter to be among the most interesting and useful in all of chemistry. The coverage of the electromagnetic spectrum leads into the electronic structure of atoms. From this information, we can rationalize, and predict, such properties of atoms as size, ionization energy, and the way in which they will form bonds (a discussion which continues in chapters 8 and 9).

### 7.1 Electromagnetic Radiation

Electromagnetic Radiation is the **only** source of information from celestial objects other than the Moon, Mars and Venus. We can't directly touch the stars, but we can receive their radiation and learn from this.

Define:

**Electromagnetic Radiation-**

**Wavelength-**

**Frequency-**

The relationship between frequency and wavelength is  $\nu = c/\lambda$

Wavelength ( $\lambda$ ) (lambda) is in meters.

Frequency ( $\nu$ ) (nu) is in  $\text{sec}^{-1}$  or Hz.

Speed of light ( $c$ ) is equal to  $2.9979 \times 10^8 \text{ m/s}$  or  $3.00 \times 10^8 \text{ m/s}$  (3 sig figs)

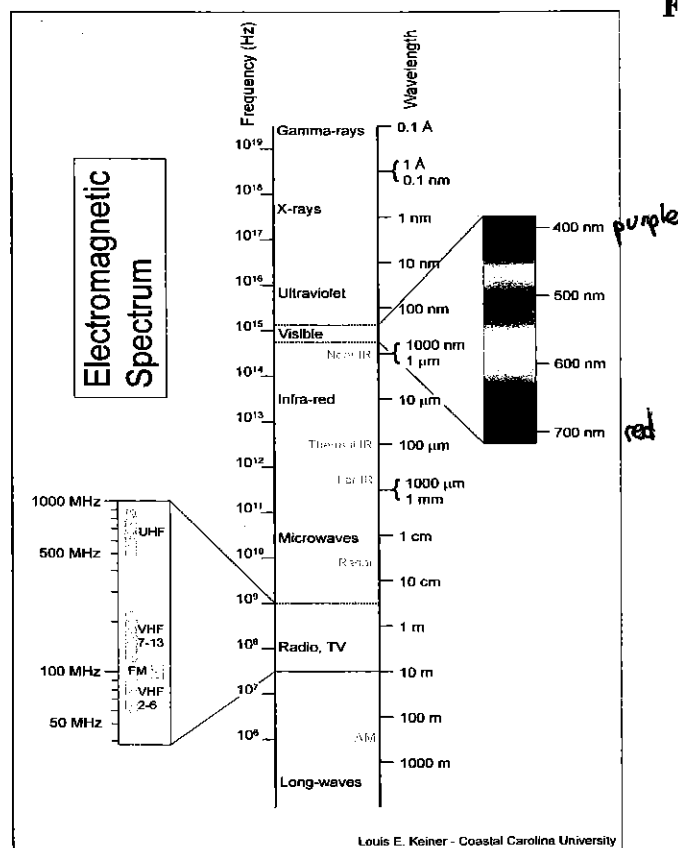


Figure 7.1 The Electromagnetic Spectrum

#### Example 7.1 A True False on the Electromagnetic Spectrum

Answer the following with "true" or "false"

1. Blue Light has a shorter wavelength than red light.
2. X-rays have lower frequencies than radio waves.
3. Microwaves have higher frequencies than gamma rays.
4. Visible radiation composes the major portion of the electromagnetic spectrum.

### Example 7.1 B Wavelength-Frequency Conversion

Photosynthesis (use of sun's light in plants to convert  $\text{CO}_2$  and  $\text{H}_2\text{O}$  into glucose and oxygen) uses light with a frequency of  $4.54 \times 10^{14}$  Hz. What wavelength does this correspond to?

**Solution:** Since  $v = c/\lambda$ , so  $\lambda = c/v$

$$\lambda = 3.00 \times 10^8 \text{ m/s} / 4.54 \times 10^{14} \text{ s}^{-1} = 6.61 \times 10^{-7} \text{ m.}$$

Since  $1 \text{ m} = 1 \times 10^9 \text{ nm}$ ,  $6.61 \times 10^{-7} \text{ m} = 661 \text{ nm}$

### Problems:

1. The visible region of the spectrum goes from 400 nm to 700 nm. What is the frequency range of the visible spectrum?  $1 \text{ m} = 1 \times 10^9 \text{ nm}$
2. Calculate:
  - a. The frequency of blue light of wavelength  $4.5 \times 10^2 \text{ nm}$ .
  - b. The wavelength of green light of frequency  $5.7 \times 10^{14} \text{ Hz}$ .

## 7.2 The Nature of Matter

There are two critically important equations introduced at the beginning of this section of your textbook. The first one is:

$$\Delta E = h\nu$$

Where  $\Delta E$  is the change in energy for a system (in Joules **PER PHOTON**),  
 $h$  is Planck's constant ( $6.626 \times 10^{-34} \text{ Js}$  or  $6.626 \times 10^{-34} \text{ kg m}^2/\text{s}$ ) and  
 $\nu$  is the frequency of the wave (in Hz or  $\text{s}^{-1}$ )

Only certain specific amounts of energy can be gained or lost in a substance. These **quanta** have magnitudes that depend on the substance. Given the observed frequency change, the change in energy can be calculated for the absorption or emission of "**photons**" (the term used if the quanta of energy are viewed as **particles**).

From Section 7.1, you know that  $\nu$  and  $\lambda$  are related by  $\nu = c/\lambda$ . Therefore,

$$\Delta E = h\nu = hc/\lambda$$

This is the 2<sup>nd</sup> equation you should know. These two equations are among the most important in all of chemistry, as you shall see in succeeding chapters.

### Example 7.2 A Interconverting Between Energy, Frequency and Wavelength

Sodium atoms have a characteristic yellow color when excited in a flame. The color comes from the emission of light of 589.0 nm.

- What is the frequency of this radiation?
- What is the energy of this radiation per photon? Per mole of photons?

#### Solution:

a.  $v = c/\lambda = 3.00 \times 10^8 \text{ m/s} / 5.890 \times 10^{-7} \text{ m} = 5.090 \times 10^{14} \text{ s}^{-1}$

b.  $\Delta E = hv = 6.626 \times 10^{-34} \text{ Js} \times 5.090 \times 10^{14} \text{ s}^{-1} = 3.373 \times 10^{-19} \text{ J}$

This value is *per photon*. There are  $6.02 \times 10^{23}$  photons/mole photons (Avogadro's number). To convert  $\Delta E$  per mole, multiply the  $\Delta E$  by Avogadro's number and convert J to kJ.

$$[(3.373 \times 10^{-19} \text{ J})(6.02 \times 10^{23} \text{ photons/mole})] / 1000 \text{ J/kJ} = 203.1 \text{ kJ/mole}$$

### De Broglie's Equation

Let's review your textbook's derivation of the de Broglie's equation. The goal is to relate wavelength ( $\lambda$ ) to mass ( $m$ ) of a particle.

$$E = mc^2 \text{ and } E = hc/\lambda$$

$$mc^2 = hc/\lambda$$

This gives us  $m = h/\lambda c$ , or for a particle which is not moving at the speed of light ( $c$ ), but rather at some velocity ( $v$ ), **de Broglie's equation** is:

$$m = h/\lambda v \text{ or } \lambda = h/mv$$

### Example 7.2 B de Broglie's Equation

What is the wavelength of an electron (mass =  $9.11 \times 10^{-31} \text{ kg}$ ) traveling at  $5.31 \times 10^6 \text{ m/s}$ ?

#### Solution:

Before we "plug and chug," recall that  $1 \text{ J} = 1 \text{ kgm}^2/\text{s}^2$

$$\lambda = h/mv = (6.626 \times 10^{-34} \text{ kgm}^2/\text{s}) / [(9.11 \times 10^{-31} \text{ kg})(5.31 \times 10^6 \text{ m/s})] = 1.37 \times 10^{-10} \text{ m} = 0.137 \text{ nm}$$

#### Problems:

- A photon of yellow light has a wavelength of 585 nm. Calculate the:
  - Frequency.
  - Energy difference in joules per photon (particle).
  - Energy difference in kilojoules per mole of photons.

2. Red light with a wavelength of 6708 Å (Angstroms) is emitted when lithium is heated in a flame.
  - a. What is the frequency of this radiation? ( $1 \times 10^{10} \text{ Å} = 1 \text{ m}$ )
  
  - b. What is the energy of this radiation per photon? Per mole of photons?
  
3. The first ionization energy of potassium is 419 kJ/mole. Do x-rays with a wavelength of 80.0 nm have sufficient energy to ionize potassium?
  
  
  
  
  
  
  
  
  
  
4. Compare the velocity of an electron (mass =  $9.11 \times 10^{-31} \text{ kg}$ ) and a neutron (mass =  $1.67 \times 10^{-27} \text{ kg}$ ), both with de Broglie wavelengths of 0.100 nm ( $1 \text{ J} = 1 \text{ kgm}^2/\text{s}^2$ )
  
  
  
  
  
  
  
  
  
  
5. Calculate:
  - a. The de Broglie wavelength of a golf ball with a mass of .220 kg traveling at 44.6 m/s.
  
  
  
  
  
  
  
  
  
  
  - b. The wavelength of a thoroughbred racehorse, which weighs 600 pounds with a speed of 40 miles/hour.

### 7.3 The Atomic Spectrum of Hydrogen

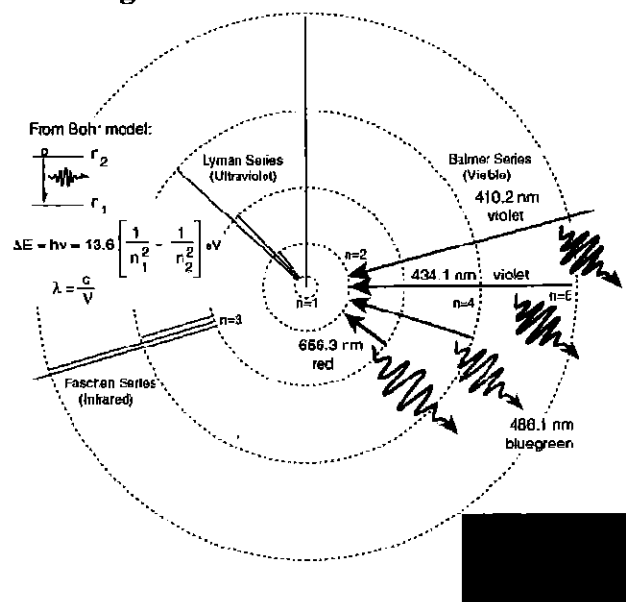
The key idea presented in this section is the difference between a continuous spectrum and a discrete or line spectrum.

- A **continuous spectrum** contains all the wavelengths over which the spectrum is continuous.
- A **line spectrum** contains certain specific wavelengths, which are characteristic of the substance emitting those wavelengths.

It is concluded in your textbook that the fact hydrogen has a line spectrum shows that only certain energy transfers are allowed in hydrogen. **There are specific energy levels, which the hydrogen electron can shift.** These energy levels are said to be **quantized**.

## 7.4 The Bohr Model

At the beginning of this section, your book discusses Neils Bohr's reasoning for relating the **energy levels** to the observed **wavelengths** emitted by the hydrogen atom. Although Bohr's ultimate conclusions have since been enhanced, his work represented a great leap forward in 1913. **Figure 7.2 The Bohr Model**



Here are the major aspects of the Bohr Model of Atomic Structure (Based upon the hydrogen atom):

- The electron is held in a region of empty space within the atom by the electrostatic force of attraction between it and the positively charged nucleus (Coulomb's Law is obeyed).
- The path of the electron is circular. The electron experiences a centripetal force equal to the electrostatic force (Newton's Laws hold).
- The electron possesses angular momentum ( $mvr$ ) which is quantized in units of  $(h)/(2\pi)$ . This is a key assumption without justification (except that it works).
- Only certain orbits are possible, as a result of the above assumption. The radius of the orbits can assume only certain values that Bohr could calculate.
 
$$R = (5.29 \times 10^{-11})N^2 \text{ meters}$$
- Each allowable orbit represents a specific energy state for the electron, which Bohr could calculate.
 
$$E_N = (-2.178 \times 10^{-18} \text{ J/particle})/N^2 \text{ or } E_N = (-1312 \text{ kJ/mole})/N^2$$

**E = energy**  
**N = an integer related to orbital position. The farther out from the nucleus, the higher the value of N. If an electron is given enough energy, it goes away from the nucleus. We say it is ionized, and n = infinity.**
- Each successive orbit represents a state of higher energy than the one beneath it. The smallest orbit in the hydrogen atom represents the lowest possible energy state for the atom ( $N = 1$ ). This is called the ground state. The highest energy state is  $n = \text{infinity}$ , where an electron is ionized.
- By absorbing a "quantum" of energy the electron can "jump" from the ground state to an orbit of higher energy. The atom is said to be in the excited state.
 
$$\Delta E = E_{hi} - E_{low}$$
- When the electron "jumps" back to an orbit of lower energy, a "quantum" of energy is emitted as light. The wavelength of the light can be calculated.
- Each line in the hydrogen spectrum corresponds to a particular "jump" the electron makes between one orbit and another.

**Example 7.4A Energy Levels in the Bohr Atom**

Calculate the energy corresponding to the  $N = 3$  electronic state in the Bohr hydrogen atom.

**Solution:** In the hydrogen atom, where  $N = 3$ .  $E_N = (-2.178 \times 10^{-18} \text{ J/particle})/N^2 =$

$$E_3 = (-2.178 \times 10^{-18} \text{ J/particle})/3^2 = -2.42 \times 10^{-19} \text{ J}$$

**Example 7.4B Changes in Energy in the Bohr Atom**

Calculate the energy change corresponding to the excitation of an electron from the  $N = 1$  to  $N = 3$  electronic state in the hydrogen atom.

**Solution:** In this problem, we need the change in energy.

$$\Delta E = E_{\text{hi}} - E_{\text{low}} = E_3 - E_1$$

There are two possible approaches to the calculation. The first is to calculate each energy separately and take the difference. The second is to subtract the equations, and then factor can calculate the change using one equation.

**Approach 1:**  $\Delta E = -2.178 \times 10^{-18} \text{ J} [1/3^2] - (-2.178 \times 10^{-18} \text{ J} [1/1^2])$

**Approach 2:**  $\Delta E = -2.178 \times 10^{-18} \text{ J} [1/3^2 - 1/1^2] = -2.178 \times 10^{-18} \text{ J} [-8/9]$

Both approaches will equal  $\Delta E = + 1.936 \times 10^{-18} \text{ J}$

The “+” sign is very important! It means energy was **absorbed** to excite the electron. In other words, the system has **gained energy**.

**Example 7.4C Wavelength from Energy in Bohr Atom**

What wavelength of electromagnetic radiation is associated with the energy change in promoting an electron from the  $N = 1$  to  $N = 3$  level in the hydrogen atom? (Use the value of  $\Delta E$  from the previous example.)

**Solution:**  $\Delta E = hc/\lambda$  so  $\lambda = hc/\Delta E$

$$\lambda = (6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})/1.936 \times 10^{-18} \text{ J} = 1.026 \times 10^{-7} \text{ m} = \mathbf{102.6 \text{ nm}}$$

This energy corresponds to radiation in the ultraviolet region of the spectrum.

(Note: Even if  $\Delta E = \text{“-“}$  (as it will when energy is released), you must assign a “+” sign to  $\lambda$  because you can't have a negative wavelength!)

**Problems:**

- Calculate the wavelength of light emitted in the spectral transition of  $N = 4$  to  $N = 2$  in the hydrogen atom.

7. Make a plot of energy vs  $N$  for the Bohr hydrogen atom for  $N = 1$  to  $N = 50$ .
- What is the energy of the Bohr hydrogen atom when  $N = \text{infinity}$ ?
  - What is the ionization energy for the Bohr hydrogen atom (i.e. the energy required to move an electron from  $N = 1$  to  $N = \text{infinity}$ )?
8. How much energy is required to ionize a mole of hydrogen atoms?
9. Calculate the wavelength of light that must be absorbed by a hydrogen atom in its ground state to reach the excited  $\Delta E = +2.914 \times 10^{-18} \text{ J}$ .
10. What region of the spectrum would you look in to find the radiation associated with the:
- Spectral transition of  $N = 4$  to  $N = 1$  of the Bohr hydrogen atom?
  - Spectral transition of  $N = 3$  to  $N = 2$  of the Bohr hydrogen atom?

## 7.5 The Quantum Mechanical Model of the Atom

The key assumption of the quantum mechanical model regarding electron motion around the hydrogen atom. This assumption is that **the electron is assumed to behave as a standing wave**. Only certain orbits are shaped such that the “wave” (electron) can fit. The **wave function** of an electron represents the allowed coordinates where the electron *may* reside in the atom. Each wave function is called an **orbital**. Your textbook points out that Schrodinger was not certain that treating the electron as a wave would make any sense- the key would be if the model would fit experimental atomic data.

The **Heisenberg uncertainty principle** in your book says that “there is a limit to just how precisely we can know both the position and the momentum of a particle at a given time.” It turns out that when the radiation used to locate a particle hits that particle, it changes momentum. Therefore, the position and momentum cannot both be measured exactly.

## 7.6 Quantum Numbers

### 7.7 Orbital Shapes and Energies (described on separate worksheet)

### 7.8 Electron Spin and the Pauli Principle

#### Definition of a Quantum Number

#### Definition of an Atomic Orbital

1. Principal Quantum Number,  $n$ , gives the primary **energy level**.  $n = 1, 2, 3, 4, 5, 6$
2. Subsidiary Quantum Number aka Angular Momentum Quantum Number,  $\ell$ , gives the **sublevel** (s, p, d, f stuff). ( $\ell = 0, 1, 2, 3, \dots, n-1$ ). The letter comes from history. They describe the spectral line relating to transitions involving these levels; e.g. “s” denotes a “sharp” line.

If  $\ell = 0$ , it refers to a s-sublevel

If  $\ell = 1$ , it refers to a p-sublevel

If  $\ell = 2$ , it refers to a d-sublevel

If  $\ell = 3$ , it refers to a f-sublevel

These are always linked to “ $n$ .” The smallest possible  $\ell$  is always 0, and the largest is always  $n-1$ . Therefore, if you want all possible values for  $\ell$  in the energy level 1 ( $n = 1$ ), then you are allowed to go from 0 to ( $n-1$ ). In this case, you go from 0 to ( $1-1$ ), which is also 0. Thus, there is only one possible sublevel in  $n=1$  and that is  $\ell=0$ .

There are all the sublevels you have to know for all the elements that occur naturally plus all those that have been created so far. Memorize these letter designations because you will need to be able to interchange the two designations quickly.

For multi-electron atoms, energy is dependent on  $\ell$  as on  $n$ . Within a given principal level (same value of  $n$ ) sublevels increase in energy in the order:

3. Magnetic Quantum Number,  $m_\ell$ , gives the orientation of the sub shell  $m_\ell: \ell, \dots, 0, \dots, -\ell$ . This gives each orbital in a sublevel a unique name). So like, there is only one orbital in an s-sublevel ( $\ell = 0$ ) so  $m_\ell$  can only have one value, 0. In a p-sublevel, ( $\ell = 1$ ) so  $m_\ell$  can have possible values, and each orbital can be uniquely named by  $m_\ell = -1, 0, +1$  and so on.



4. Magnetic Spin Quantum Number,  $m_s$ . This differentiates the two electrons that can exist in an orbital.  $m_s$  is not related to  $n$ ,  $l$ , or  $m_l$ . It has only 2 possible values:  $+1/2$  or  $-1/2$ . In combination with the other quantum numbers, it uniquely identifies an electron.

Quantum numbers give unique names to each electron. The orbital-energy level description (you know, the spdf stuff), is a way of looking at all the electrons as belonging to groups. Be comfortable with the fact that the two ideas overlap.

| Quantum Numbers |     |       |              | Orbitals & Shells |                  |
|-----------------|-----|-------|--------------|-------------------|------------------|
| $n$             | $l$ | $m_l$ | $m_s$        | Sublevel          | Specific Orbital |
| 1               | 0   | 0     | $+1/2, -1/2$ | 1s                | s                |
| 2               | 0   | 0     | $+1/2, -1/2$ | 2s                | s                |
| 3               | 0   | 0     | $+1/2, -1/2$ | 3s                | s                |
| 3               | 1   | -1    | $+1/2, -1/2$ | 3p                | p                |
| 3               | 1   | 0     | $+1/2, -1/2$ | 3p                | p                |
| 3               | 1   | +1    | $+1/2, -1/2$ | 3p                | p                |

Etc,

Capacities of Electronic Levels and Sublevels in Atoms

**\*\* A sublevel of quantum number  $l$  has a capacity of  $2(2l+1)$ .** For example, a 3d sublevel ( $l=2$ ) has a capacity of  $2((2 \times 2) + 1) = 10e^-$

**\*\* A principal level of quantum number  $n$  has a capacity of  $2n^2$ .** For example, the total capacity of the fourth principal energy level is  $2(4)^2 = 32e^-$ .

THIS IS JUST BOOKEEPING

It is a way of giving each electron in an atom a unique tag.

GET A GRIP ON THIS!!!

**Example 7.8A Practice with Quantum Numbers**

Which of the following sets of quantum numbers are not allowed? For each incorrect set, state why it is incorrect.

- $n = 3, l = 3, m_l = 0, m_s = -1/2$
- $n = 4, l = 3, m_l = 2, m_s = -1/2$
- $n = 4, l = 1, m_l = 1, m_s = +1/2$
- $n = 2, l = 1, m_l = -1, m_s = -1$
- $n = 5, l = -4, m_l = 2, m_s = +1/2$
- $n = 3, l = 1, m_l = 2, m_s = -1/2$
- $n = 3, l = 2, m_l = -1, m_s = 1$

**Example 7.8 B Electrons in Orbital**

If each orbital can hold a maximum of two electrons (of opposite spin), how many electrons can each of the following hold?

- 2s
- 5p
- 4f
- 3d
- 4d

**Problems:**

- Write a complete set of quantum numbers for each of the 5 electrons of a Boron atom.

12. What are the possible values for  $m_l$  for:

- a.  $l = 2$       b.  $l = 4$       c.  $n = 4$  (all sublevels)

13. What type of electron orbital (s, p, d or f) is designated:

a.  $n = 2, l = 1, m_l = 1$ ?

b.  $n = 4, l = 3, m_l = 0$ ?

c.  $n = 1, l = 0, m_l = 0$ ?

14. Arrange the following sets of quantum numbers in order of increasing energy. If they have the same energy, place them together.

a. 4, 2, -1, +1/2

b. 1, 0, 0, -1/2

c. 3, 1, 1, -1/2

d. 2, 0, 0, +1/2

e. 2, 1, 0, +1/2

f. 3, 1, 1, +1/2

## 7.9 Polyelectronic Atoms

1. What are the three energy contributions that must be considered when describing the helium atom?
2. What does your book mean by the **electron correlation problem**? How do we deal with the problem?
3. What does it take more energy to remove an electron from  $Al^+$  than from  $Al$ ?
4. Why do electrons "prefer" to fill s, p, d and then f within a particular quantum level?
5. What is the **penetration effect** and why is it important?
6. Why does the **3d** orbital have a higher energy than **3p**, even though it has maximum probability closer to the nucleus than the 3p?

## 7.10 The History of the Periodic Table

1. What was the original basis of the construction of the periodic table?
2. What are triads?
3. List the properties that Mendeleev used to predict ekasilicon's position in the periodic table.
4. Several atoms of element 116 have been observed. Based on Table 7.4 in your book, what properties would you predict this element would have?
5. What is the important difference between Mendeleev's table and the modern one?

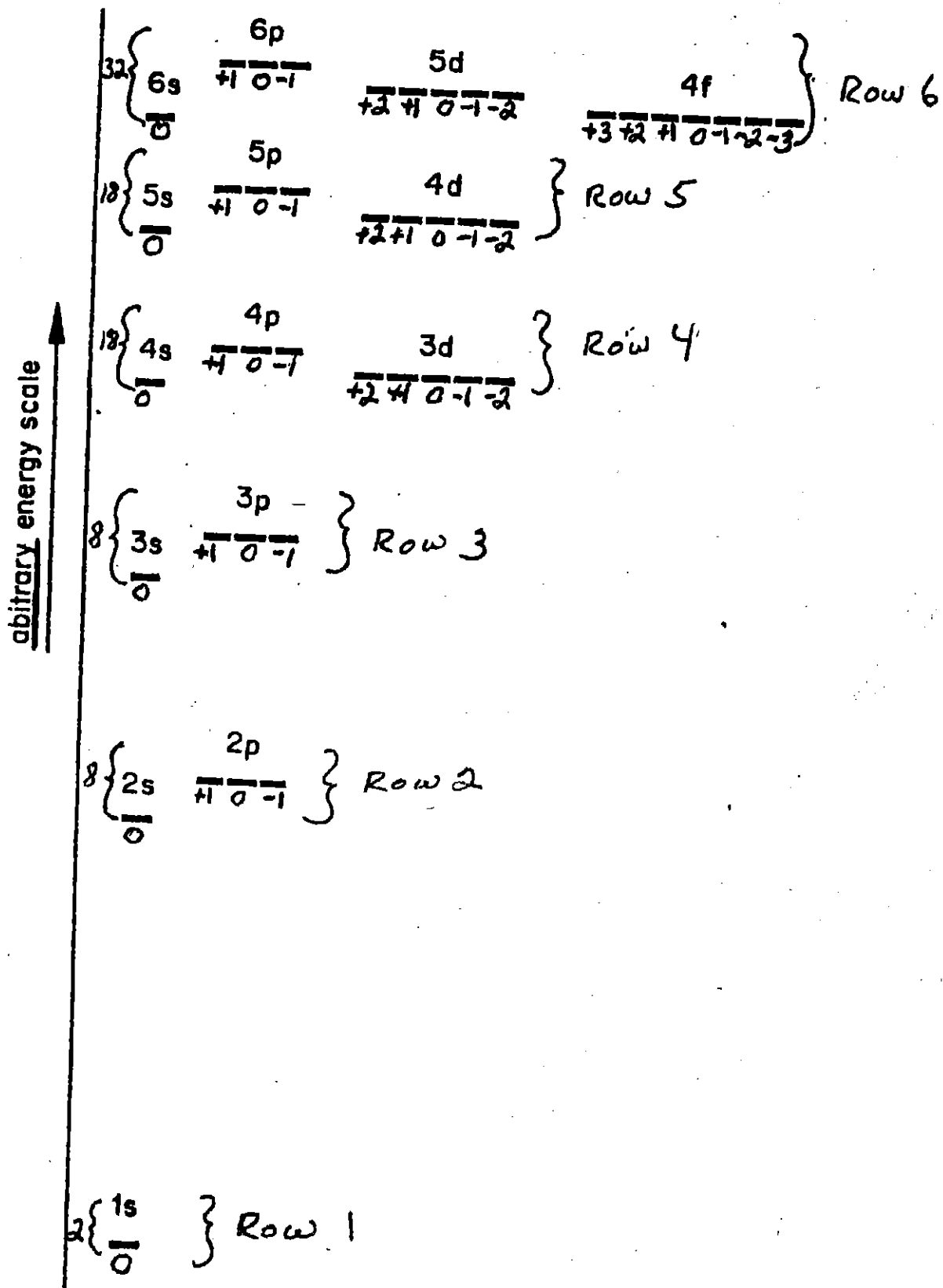
## 7.11 The Aufbau Principle and the Periodic Table

Read the statement of the Aufbau Principle in your book. Your book presents **orbital diagrams** for the 1<sup>st</sup> 10 elements. When constructing orbital diagrams and electron configurations, please keep the following in mind:

Notes: Using the "Order of filling Sublevels" Chart (on next page)

1. The Row number found in the periodic table for the sublevels which are filling are found to the right of the sublevel groupings.
2. The total number of electrons accommodated in each row of the periodic table is given to the left of the sublevel groupings.
3. The principle Quantum number,  $n$ , is the number designation of the sublevel. Example: "4f" implies that  $n = 4$  for this particular "f" sublevel.
4. The magnetic quantum number,  $m_l$  (which identifies a particular orbital within a sublevel) is given below each orbital within the sublevel.
5. The electron is shown as an arrow with opposite vertical orientations (different spins). Up arrow =  $m_s = +1/2$ ; Down arrow =  $m_s = -1/2$
6. Electron populate orbitals singly at first ( $m_s = +1/2$ ), until the sublevel is half-filled and the pairing of electrons with the orbitals occurs (Hund's Rule holds).
7. No two electrons within an atom can have the same set of quantum numbers (Pauli's exclusion principle must hold).

# ORDER OF ELECTRON FILLING



Order of filling sublevels.

There are three exceptions to Aufbau:

1. Cr, Mo, W, according to aufbau, would have  $d^4s^2$  but it's more stable to have 5 half-filled orbitals so it changes to  $d^5s^1$ .
2. Cu, Ag, Au, according to aufbau, it would have  $d^9s^2$  but again, the s electron jumps to the d-orbital to gain stability and thus these guys have an outer electron configuration of  $d^{10}s^1$ .
3. When you begin and end the inner transition metals, starting at the 6<sup>th</sup> period element 56, Barium, now has an electronic configuration of  $[\text{Xe}]6s^25d^1$ . Now the inner-transition metals have to fit in and the electrons for them to go into f-orbitals. That lone d electron is unstable when filling up the f-sublevel and jumps into an f-orbital until the sublevel is full. So Cerium has an electronic configuration  $[\text{Xe}]6s^25d^04f^2$ . When you get to the end, filling up the f-sublevel, the electron pops back into the d-sublevel. So, Letetium has an electronic configuration  $[\text{Xe}]6s^25d^14f^{14}$ .

|                 |                 |                 |                 |                 |                                    |                 |                 |                 |                 |                                     |                  |                 |                 |                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|-----------------|------------------------------------|-----------------|-----------------|-----------------|-----------------|-------------------------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1s <sup>1</sup> |                 |                 |                 |                 |                                    |                 |                 |                 |                 |                                     |                  | 1s <sup>2</sup> |                 |                 |                 |                 |                 |
| 2s <sup>1</sup> | 2s <sup>2</sup> |                 |                 |                 |                                    |                 |                 |                 |                 |                                     |                  | 2p <sup>1</sup> | 2p <sup>2</sup> | 2p <sup>3</sup> | 2p <sup>4</sup> | 2p <sup>5</sup> | 2p <sup>6</sup> |
| 3s <sup>1</sup> | 3s <sup>2</sup> |                 |                 |                 |                                    |                 |                 |                 |                 |                                     |                  | 3p <sup>1</sup> | 3p <sup>2</sup> | 3p <sup>3</sup> | 3p <sup>4</sup> | 3p <sup>5</sup> | 3p <sup>6</sup> |
| 4s <sup>1</sup> | 4s <sup>2</sup> | 3d <sup>1</sup> | 3d <sup>2</sup> | 3d <sup>3</sup> | 4s <sup>1</sup><br>3d <sup>5</sup> | 3d <sup>5</sup> | 3d <sup>6</sup> | 3d <sup>7</sup> | 3d <sup>8</sup> | 4s <sup>1</sup><br>3d <sup>10</sup> | 3d <sup>10</sup> | 4p <sup>1</sup> | 4p <sup>2</sup> | 4p <sup>3</sup> | 4p <sup>4</sup> | 4p <sup>5</sup> | 4p <sup>6</sup> |
| 5s <sup>1</sup> | 5s <sup>2</sup> | 4d <sup>1</sup> | 4d <sup>2</sup> | 4d <sup>3</sup> | 5s <sup>1</sup><br>4d <sup>5</sup> | 4d <sup>5</sup> | 4d <sup>6</sup> | 4d <sup>7</sup> | 4d <sup>8</sup> | 5s <sup>1</sup><br>4d <sup>10</sup> | 4d <sup>10</sup> | 5p <sup>1</sup> | 5p <sup>2</sup> | 5p <sup>3</sup> | 5p <sup>4</sup> | 5p <sup>5</sup> | 5p <sup>6</sup> |
| 6s <sup>1</sup> | 6s <sup>2</sup> | 5d <sup>1</sup> | 5d <sup>2</sup> | 5d <sup>3</sup> | 6s <sup>1</sup><br>5d <sup>5</sup> | 5d <sup>5</sup> | 5d <sup>6</sup> | 5d <sup>7</sup> | 5d <sup>8</sup> | 6s <sup>1</sup><br>5d <sup>10</sup> | 5d <sup>10</sup> | 6p <sup>1</sup> | 6p <sup>2</sup> | 6p <sup>3</sup> | 6p <sup>4</sup> | 6p <sup>5</sup> | 6p <sup>6</sup> |
| 7s <sup>1</sup> | 7s <sup>2</sup> | 6d <sup>1</sup> | 6d <sup>2</sup> | 6d <sup>3</sup> | 7s <sup>1</sup><br>6d <sup>5</sup> | 6d <sup>5</sup> |                 | 6d <sup>7</sup> |                 |                                     |                  |                 |                 |                 |                 |                 |                 |

|                                    |                                    |                                    |                                    |                                    |                                    |                                    |                                    |                                     |                                     |                                     |                                     |                                     |                                     |
|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| 5d <sup>0</sup><br>4f <sup>2</sup> | 5d <sup>0</sup><br>4f <sup>3</sup> | 5d <sup>0</sup><br>4f <sup>4</sup> | 5d <sup>0</sup><br>4f <sup>5</sup> | 5d <sup>0</sup><br>4f <sup>6</sup> | 5d <sup>0</sup><br>4f <sup>7</sup> | 5d <sup>0</sup><br>4f <sup>8</sup> | 5d <sup>0</sup><br>4f <sup>9</sup> | 5d <sup>0</sup><br>4f <sup>10</sup> | 5d <sup>0</sup><br>4f <sup>11</sup> | 5d <sup>0</sup><br>4f <sup>12</sup> | 5d <sup>0</sup><br>4f <sup>13</sup> | 5d <sup>0</sup><br>4f <sup>14</sup> | 5d <sup>1</sup><br>4f <sup>14</sup> |
| 6d <sup>0</sup><br>5f <sup>2</sup> | 6d <sup>0</sup><br>5f <sup>3</sup> | 6d <sup>0</sup><br>5f <sup>4</sup> | 6d <sup>0</sup><br>5f <sup>5</sup> | 6d <sup>0</sup><br>5f <sup>6</sup> | 6d <sup>0</sup><br>5f <sup>7</sup> | 6d <sup>0</sup><br>5f <sup>8</sup> | 6d <sup>0</sup><br>5f <sup>9</sup> | 6d <sup>0</sup><br>5f <sup>10</sup> | 6d <sup>0</sup><br>5f <sup>11</sup> | 6d <sup>0</sup><br>5f <sup>12</sup> | 6d <sup>0</sup><br>5f <sup>13</sup> | 6d <sup>0</sup><br>5f <sup>14</sup> | 6d <sup>1</sup><br>5f <sup>14</sup> |

**Example 7.11 A Electron Configuration**

Write electron configurations for each of the following neutral atoms.

- a. boron                      b. sulfur                      c. vanadium                      d. iodine

**Solution**

- a. B (5 electrons):  $1s^2 2s^2 2p^1$   
b. S (16 electrons):  $1s^2 2s^2 2p^6 3s^2 3p^6$   
c. V (23 electrons):  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$   
d. I (53 electrons):  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$

**Example 7.11 B Shorthand Configurations**

Write the shorthand configuration for the atoms in example 7.11 A, and state how many valence electrons the element has.

**Solution:**

- a. B:  $[\text{He}]2s^2 2p^1$  (3 valence)  
b. S:  $[\text{Ne}]3s^2 3p^4$  (6 valence)  
c. V:  $[\text{Ar}]4s^2 3d^3$  (transition metal, 2 valence)  
d. I:  $[\text{Kr}]5s^2 4d^{10} 5p^5$  (7 valence electrons...n=4 level is complete)

**Problems**

15. Write the electron configurations (ground state) for:

- a. Cl                      b. Cr                      c. Se                      d. Si

16. Write the abbreviated electron configuration for:

- a. Br                      b. Ti                      c. Cd                      d. F

17. Give the symbol of the element of lowest atomic numbers whose ground state has:

- a. A completed d sublevel
- b. Three 4d electrons
- c. Five 3p electrons
- d. One s electron

**Example 7.11 C *Orbital Diagrams***

Draw orbital diagrams for the following:

- a. sodium
- b. phosphorus
- c. chlorine

**Problems**

18. Give the orbital diagram of:

- a. C
- b. Fe
- c. P
- d. Ar

19. Give the number of unpaired electrons in an atom of:

- a. O
- b. Sr
- c. V

20. Write the electron configuration for:

- a. a calcium ion,  $\text{Ca}^{+2}$
- b. a selenium ion,  $\text{Se}^{-2}$
- c. a zirconium ion,  $\text{Zr}^{+2}$
- d. a cobalt (II) ion:  $\text{Co}^{+2}$
- e. a cobalt (III) ion:  $\text{Co}^{+3}$

## 7.12 Periodic Trends and Atomic Properties

**Ionization Energy** increases as successive electrons are removed from an atom because:

1. The value for  $Z_{\text{eff}}$  increases because there are fewer electron-electron repulsions and a higher positive to negative charge ratio than before.
2. Upon going from f to d to p to s electrons, there is a higher penetration effect. For example, the removal of a 3p will require more than the removal of a 3d from the same atom.
3. When you remove all of the electrons from an energy level, you begin removing **core** electrons, which are more tightly bound to the nucleus than valence electrons.

Note that:

1. First ionization energy increases as we go across a period.
2. First ionization energy decreases as we go down a group.
3. There are anomalies that exist, such as the decrease from P to S. (Can you explain why?)

**Electron affinity** is the **change in energy** associated with the addition of an electron to a gaseous atom. In keeping with thermodynamic convention, if the addition is exothermic, the energy change will be negative. Although electron affinity *generally* increases from left to right across a period, there are several exceptions. For example, the electron affinity of phosphorus is lower than sulfur. That is because P is  $3p^3$  (half filled) while S is  $3p^4$ . If you put an extra electron on phosphorus, it must share an orbital, thus forcing electron-electron repulsion. These repulsions already exist in the 3p orbitals of sulfur. The trend in electron affinity is less predictable.

The **atomic radius** of an atom **decreases** from left to right across a period. This is because  $Z_{\text{eff}}$  increases. Atomic radius increases going down a group. This is because of increased orbital size. (See Fig 7.35 in book). You must consider **ionic radius** in terms of the following questions: What will adding an electron do to electron-electron repulsions? What will subtracting an electron do to the effective nuclear charge?



**Example 7.12 A Ionization Energy**

Examine Table 7.5 in book. Justify the large increases in ionization energy at  $I_5$  and  $I_7$  for sulfur.

**Solution**

$I_5$  represents removal of the last 3p electron. The remaining electrons are 3s and core electrons. The 3s electron has a much greater penetration effect than the 3p. Therefore,  $I_5$  is much larger than  $I_4$ .

$I_7$  represents ionization of a core (2p) electron. This electron is much closer to the nucleus, thus requiring more energy to ionize it.

**Example 7.12 B Trends in Atomic Radius**

Order the atoms or ions in the following groups from largest to smallest radius.

- Cs, Si, F, Ca, Ga
- $\text{Ca}^{+2}$ ,  $\Gamma$ , I, Li

**Solution**

- F (smallest), Si, Ga, Ca, Cs (largest)  
Cs is in period 6, group 1  
F is in period 2, group 7
- I is large. Adding an electron forces extreme electron-electron repulsion making it larger. Calcium is large, but taking its 4s electron away markedly increases the  $z_{\text{eff}}$ .  
 $\text{Ca}^{+2}$ , Li, I,  $\Gamma$

**Problems**

21. Order the following groups from smallest to largest radius:

- Ar,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{S}^{-2}$
  - C, Al, F, Si
  - Na, Mg, Ar, P
  - $\Gamma$ ,  $\text{Ba}^{+2}$ ,  $\text{Cs}^+$ , Xe
22. Which of the following will have the most exothermic electron affinity? The least?
- Ge, Si, C
  - Cl,  $\text{Cl}^-$ ,  $\text{Cl}^+$

### 7.13 The Properties of a Group: The Alkali Metals

The goal of your book in this section is to show you how understanding electron configurations and the structure of the periodic table can allow you to predict the properties of this group. This section begins with a review of the information contained in the periodic table.

1. Elements in a group exhibit similar properties.
2. It is primarily the number of valence electrons that determine an atom's chemistry.
3. Electron configurations can be gleaned from the periodic table.
4. Learn the names of the different groups (halogens, active metals, lanthanides, etc). See Figure 7.36 in your book.
5. Metals tend to lose electrons (have low ionization energies). Nonmetals tend to gain electrons. Metalloids (semimetals) have properties of both.

#### *Properties as We Go Down the Alkali Metals*

- A. The first ionization energy decreases.
- B. The atomic radius increases.
- C. The density increases.
- D. The reactivity increases (they lose electrons readily).
- E. The melting and boiling points decrease.

#### **Example 7.13 The Alkali Metals**

Explain the trends that alkali metals follow in properties "A" through "D" above based on your knowledge of electron configurations and atomic structure.

#### **Solution**

- A. First ionization energy: As we go down the group, the valence electron falls in a higher energy level. The nuclear attraction is less, making it easier to ionize the electron.
- B. Atomic radius: Again, the valence electron occupies a higher energy level, thereby being farther from the nucleus.
- C. Density: Atomic Mass increases faster than atomic size.
- D. Reactivity: The electrons are easier to ionize; therefore, reactions which require less energy are possible.