

BROOKS/COLE  
CENGAGE Learning

William L. Masterton  
Cecile N. Hurley  
<http://academic.cengage.com/chemistry/masterton>

Chemistry  
Principles and Reactions  
Sixth Edition  
Masterton | Hurley

## Chapter 6

### Electronic Structure and the Periodic Table

Edward J. Neth • University of Connecticut

## Atomic Spectra

- Under certain circumstances, atoms can generate light, which is transmitted through space
  - Fireworks displays
  - Neon lights
  - Sodium vapor streetlights

## Review

- Chapter 2: Structure of the Atom
  - Nucleus: protons and neutrons
  - Surrounding the nucleus: electrons
- Electron Arrangements in Atoms
  - Energy levels
  - Spatial locations
- Considerations
  - Single electron in the hydrogen atom
  - Multiple electrons in other atoms

## Fireworks



## Arranging Electrons in Atoms

- Electron configuration
  - The electron configuration associates the energy level with the number of electrons in each level
- Orbital diagrams
  - Orbital diagrams show the arrangement of electrons within each energy level
- The periodic table
  - Electron configurations can be deduced from the periodic table
  - Properties of atoms can be related to the electron configuration

## The Wave Nature of Light

- Wavelength ( $\lambda$ )
  - Distance between two successive crests or troughs in the light wave
  - Measured in nanometers ( $1 \text{ nm} = 10^{-9} \text{ m}$ )
- Frequency ( $\nu$ )
  - Number of successive crests or troughs (wave cycles) that pass a point in a unit of time
  - If  $10^8$  cycles pass in one second, the frequency is  $10^8/\text{s}$  or  $10^8\text{Hz}$

## Wavelength-Frequency Relationship

- The speed at which a wave moves through space is found by multiplying the wavelength by the frequency:

$$\lambda \nu = c$$

- $c$  is the speed of light in a vacuum,  $2.998 \times 10^8$  m/s
- To use this equation,
  - Frequency must be in  $s^{-1}$
  - Wavelength must be in m

## The Electromagnetic Spectrum

- The human eye can see light covering only a narrow region of the electromagnetic spectrum (400-700 nm)
  - We see the red glow of a barbecue grill, but most of the radiation is emitted above 700 nm as infrared radiation, also known as heat
  - We cannot see the radiation responsible for sunburn (ultraviolet, below 400 nm) or X-rays (even shorter wavelength)

Figure 6.1

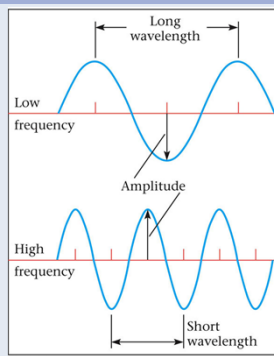
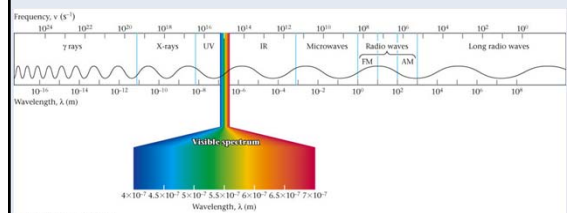


Figure 6.2



## Example 6.1

**Example 6.1** You sit in your back yard on a warm summer evening watching the red sky ( $\lambda = 625$  nm) at sunset and listening to music from your CD player. The laser in the latter has frequency  $3.84 \times 10^{14} s^{-1}$ .

- What is the frequency of the radiation from the red sky?
- What is the wavelength of the laser in nm?

**Strategy** Use the equation:  $\lambda \nu = c$ , taking  $c = 2.998 \times 10^8$  m/s. Note that  $\lambda$  must be expressed in meters.

### SOLUTION

- $\lambda = 625 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} = 6.25 \times 10^{-7} \text{ m}$   
 $\nu = \frac{2.998 \times 10^8 \text{ m/s}}{6.25 \times 10^{-7} \text{ m}} = 4.80 \times 10^{14} s^{-1} = 4.80 \times 10^{14} \text{ Hz}$
- $\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{3.84 \times 10^{14} s^{-1}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 781 \text{ nm}$

## The Particle Nature of Light; Photon Energies

- Before the 20<sup>th</sup> century, light was explained in terms of waves only
- Experiments from 1900-1910 showed that light has properties not explained by waves
  - Max Planck, blackbody radiation
  - Albert Einstein, photoelectric effect
- Today, we consider light to be a stream of particles called photons, whose energy,  $E$ , is given by

$$E = h\nu = \frac{hc}{\lambda}$$

- $h$  is the Planck constant,  $6.626 \times 10^{-34}$  J·s

## Energy and Wavelength

- Note that energy and wavelength are inversely related
  - As the wavelength becomes longer, energy decreases
  - As the wavelength becomes shorter, energy increases
- Low energy
  - Infrared, microwave
- High energy
  - Ultraviolet, X-ray

## Gaseous Elements

- Elements can be put in to the gas phase at high energy
  - Resulting emission of light is **not continuous**
  - Consider sodium
    - Two strong lines in the yellow region: 589.0 and 589.6 nm
    - Light is colored only **yellow**
  - **Line Spectra**

## Example 6.2

**Example 6.2** Graded

Sodium vapor lamps are commonly used to illuminate highways because of their intense yellow-orange emissions at 589 nm.

• (a) Calculate the energy, in joules, of one photon of this light.  
 •• (b) Calculate the energy, in kilojoules, of one mole of such photons.  
 ••• (c) To sense visible light, the optic nerve needs at least  $2.0 \times 10^{-17}$  J of energy to trigger impulses that reach the brain. How many photons of the sodium lamp emissions are needed to "see" the yellow light?

**Strategy** Use the equation  $E = hc/\lambda$ . In part (b), remember to use Avogadro's number.

**SOLUTION**

(a)  $E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{5.89 \times 10^{-7} \text{ m}} = 3.37 \times 10^{-19} \text{ J}$

This may seem like a tiny amount of energy, but bear in mind that it comes from a single photon.

(b)  $E = \frac{3.37 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} = 203 \text{ kJ}$

This is roughly comparable to the energy effects in chemical reactions about 240 kJ of heat is evolved when a mole of  $\text{H}_2$  burns, for instance.

(c) From (a) you obtain the conversion factor:

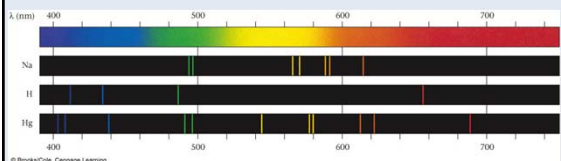
$$\frac{3.37 \times 10^{-19} \text{ J}}{1 \text{ photon}}$$

Using that, we have

$$2.0 \times 10^{-17} \text{ J} \times \frac{1 \text{ photon}}{3.37 \times 10^{-19} \text{ J}} = 59 \text{ photons}$$

Not too many photons are needed to sense the light.

## Figure 6.3



## Atomic Spectra

- Sir Isaac Newton
  - 17<sup>th</sup> Century
  - Showed that white light from the sun can be separated into color components by a prism
  - The resulting spectrum is **continuous** (unbroken) from 400 to 700 nm

## Line Spectra

- The fact that photons making up atomic spectra have only certain discrete wavelengths implies that they can have only discrete energies because
 
$$E = h\nu = \frac{hc}{\lambda}$$
- Photons are produced when an electron moves from one energy level to another within the atom
- Electronic energies are **quantized**: they are limited to specific values

## Atomic Spectrum of Hydrogen

- Hydrogen has a single electron and therefore a simple atomic spectrum
  - Multi-electron atoms have complex spectra
- When hydrogen is energized at high voltage, atoms emit radiation
  - Wavelengths can be grouped into series
  - First series was discovered by Johann Balmer (the Balmer Series)

## Mathematics of the Bohr Model

- The energy of the hydrogen electron is given by

$$E_n = \frac{-R_H}{n^2}$$

- $E_n$  is the energy of the electron
- $R_H$  is the Rydberg constant,  $2.180 \times 10^{-18}$  J
- $n$  is an integer called the principal quantum number

Table 6.1

**Table 6.1** Wavelengths (nm) of Lines in the Atomic Spectrum of Hydrogen

Ultraviolet (Lyman Series)	Visible (Balmer Series)	Infrared (Paschen Series)
121.53	656.28	1875.09
102.54	486.13	1281.80
97.23	434.05	1093.80
94.95	410.18	1004.93
93.75	397.01	
93.05		

© Brooks/Cole, Cengage Learning

## Notes on the Bohr Model

- Zero energy is the point at which the proton and electron are infinitely separated; energy must be absorbed to reach this state, so all states below it have negative energy.
- The ground state is the lowest energy state for the hydrogen atom, where  $n = 1$ . Any  $n$  value above 1 corresponds to an excited state.
- When an electron emits energy as a photon of light, it falls from a higher  $n$  to a lower  $n$ .

## The Hydrogen Atom

- Niels Bohr (1885-1962)
  - Theoretical explanation of the hydrogen spectrum
  - 1922 Nobel Prize in physics
- The Bohr Model
  - Hydrogen consists of a central proton about which moves the electron
  - Electrostatic attraction of proton for electron likened to centrifugal force of circular motion of the electron
  - Electrons occupy fixed orbits around the nucleus

## Energy Release

- The difference in energy between two states in the hydrogen atom is the energy of the photon released in the transition between those states

$$\Delta E = h\nu = E_{hi} - E_{lo}$$

- Combining Bohr's equation for two states produces the Rydberg equation for the hydrogen atom

$$\nu = \frac{R_H}{h} \left[ \frac{1}{n_{lo}^2} - \frac{1}{n_{hi}^2} \right]$$

- $h$  is the Planck constant,  $6.626 \times 10^{-34}$  J·s

### Example 6.3

**Example 6.3** Calculate the wavelength in nanometers of the line in the Balmer series that results from the transition  $n = 4$  to  $n = 2$ .

**Strategy** Use Equation 6.4 to find the frequency;  $n_{\text{lo}} = 2$ ,  $n_{\text{hi}} = 4$ . Then use the equation  $\lambda = c/\nu$  to find the wavelength.

**SOLUTION**

$$\nu = \frac{2.180 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} \left[ \frac{1}{4} - \frac{1}{16} \right] = 6.169 \times 10^{14} / \text{s}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{6.169 \times 10^{14} / \text{s}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = \mathbf{486.0 \text{ nm}}$$

**Reality Check** Compare this value with that listed in Table 6.1 for the second line in the Balmer series.

### The Quantum Mechanical Model

- Bohr's theory explains the hydrogen atom very well
- When applied to atoms with two or more electrons, the theory gives only qualitative agreement with experimental data

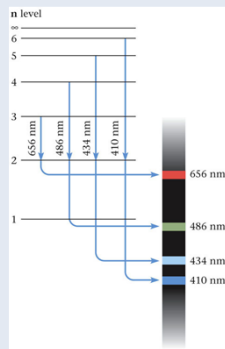
### The Hydrogen Series

- The lines in the hydrogen spectrum are grouped by the value of  $n_{\text{lo}}$ :
  - Balmer series has  $n_{\text{lo}} = 2$
  - Lyman series has  $n_{\text{lo}} = 1$
  - Paschen series has  $n_{\text{lo}} = 3$

### Matter Waves

- deBroglie, 1892-1987
  - If light, which is ordinarily considered a wave, can have the properties of a particle, then electrons, which are ordinarily considered particles, can have the properties of a wave
  - The result was a new branch of physics called **wave mechanics**, which evolved into **quantum mechanics**

### The Balmer Series



### Fundamental Principles of Quantum Mechanics

- The kinetic energy of an electron is inversely related to the volume of the region in space to which it is confined
  - The kinetic energy increase from the shrinking volume of an electron moving toward the nucleus balances the electrostatic attraction to prevent the electron from falling into the nucleus
- It is impossible to specify the exact position of an electron at a given instant
  - We can only specify the probability of finding an electron in a particular region of space

## Schrodinger

- Erwin Schrodinger (1887-1961)
  - 1926
  - Wrote a differential equation to express the wave properties of an atom
    - $\Psi$  is called the wave function
    - It is possible to find the amplitude of the electron wave at various points in space
    - $\Psi^2$  is proportional to the probability of finding an electron at a particular point in space

## Quantum Numbers

- The Schrodinger equation can be solved exactly only for the hydrogen atom
- Approximations allow for solutions of the equation relevant to atoms with two or more electrons
- The solutions result in orbitals, which have an energy, a shape and an orientation in space
- The solutions result in three **quantum numbers**:
  - $n$
  - $\ell$
  - $m_\ell$

## Electron Cloud Diagrams

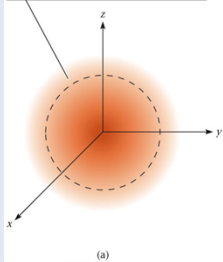
- Electron cloud diagrams are maps of electron density
  - The depth of color is proportional to  $\Psi^2$ , the probability of finding an electron
- Orbitals
  - The orbital represents the region in space where there is a 90% or higher probability of finding an electron
- Pictorial view follows

## First Quantum Number, $n$

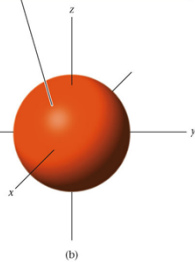
- The principal energy level is specified by the first quantum number,  $n$
- $n = 1, 2, 3, 4, \dots$ 
  - $n = 1$  is the first principal level
  - $n = 2$  is the second principal level, and so on ...

Figure 6.4

In this rendering the depth of color is proportional to the probability of finding the electron at a given point. The dotted line encloses the volume within which there is a 90% probability of finding the electron.



In this rendering the orbital encloses the volume within which there is a 90% probability of finding the electron; the electron density within the orbital is not shown.



## The Second Quantum Number, $\ell$

- Each principal energy level (specified by  $n$ ) has one or more sublevels
  - The sublevel is specified by the quantum number  $\ell$
  - $\ell$  is derived from  $n$ :
    - $\ell = 0, 1, 2 \dots (n-1)$
    - In the  $n$ th principal level, there are  $n$  sublevels
  - Instead of using numbers, the sublevels are given letter designations
    - For  $\ell = 0, 1, 2, 3$  we use s, p, d, f

## Combining n and $\ell$

- n and  $\ell$  are combined to indicate the principal and subsidiary levels
  - 1s means  $n = 1$  and  $\ell = 0$
  - 2s means  $n = 2$  and  $\ell = 0$
  - 2p means  $n = 2$  and  $\ell = 1$

**Table 6.2** Sublevel Designations for the First Four Principal Levels

n	1	2	3	4
$\ell$	0	0 1	0 1 2	0 1 2 3
Sublevel	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f

© Brooks/Cole, Cengage Learning

## Sublevels s through f

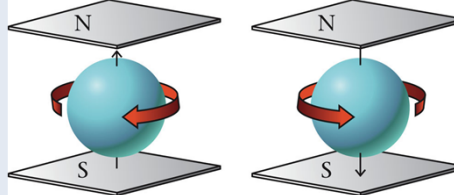
- For an s sublevel,  $\ell = 0$ , so  $m_\ell = 0$
- For a p sublevel,  $\ell = 1$  so  $m_\ell = -1, 0, \text{ or } 1$
- For a d sublevel,  $\ell = 2$  so  $m_\ell = -2, -1, 0, 1, \text{ or } 2$
- For an f sublevel,  $\ell = 3$  so  $m_\ell = -3, -2, -1, 0, 1, \text{ or } 2$

## Relative Energy

- For atoms with more than one electron, the energy is dependent on both n and  $\ell$ 
  - $ns < np < nd < nf$
- Recall that as n increases, energy increases
  - 2s is higher energy than 1s
- Combining both
  - 2p is higher energy than 2s

## The Fourth Quantum Number, $m_s$

- The last quantum number is associated with the electron spin
  - Two spins are possible, clockwise and counterclockwise
  - There are two values of  $m_s$ ,  $+\frac{1}{2}$  and  $-\frac{1}{2}$



## The Third Quantum Number, $m_\ell$

- Each sublevel contains one or more orbitals, which differ from one another in the value of the third quantum number,  $m_\ell$
- Just as  $\ell$  depends on n,  $m_\ell$  depends on  $\ell$ 
  - $m_\ell = \ell \dots +1, 0, -1, \dots -\ell$
  - There are  $2\ell + 1$  orbitals per sublevel

## The Pauli Exclusion Principle

- No two electrons in the same atom may have the same set of four quantum numbers
  - Two electrons may occupy an orbital; these will differ in spin
  - The spins of two electrons in an orbital will be opposite to each other

Table 6.3

n	$\ell$	$m_\ell$	$m_s$
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (2p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of $m_\ell$
3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (3p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of $m_\ell$
	2 (3d)	-2, -1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of $m_\ell$
4	0 (4s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (4p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of $m_\ell$
	2 (4d)	-2, -1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of $m_\ell$
	3 (4f)	-3, -2, -1, 0, +1, +2, +3	$\pm\frac{1}{2}$ for each value of $m_\ell$

© Brooks/Cole, Cengage Learning

### Atomic Orbital Shapes and Sizes

- Recall that an orbital is a physical representation of the region in space where there is a 90% probability of finding an electron
- We will consider the shapes of two types of orbitals in this chapter
  - s orbitals are spherical, differing only in size (they become larger as n increases)
  - p orbitals consist of two lobes along an axis
    - There are three axes – x, y and z
    - There are three p orbitals –  $p_x$ ,  $p_y$ , and  $p_z$

### Example 6.4

**Example 6.4** Consider the following sets of quantum numbers (n,  $\ell$ ,  $m_\ell$ ,  $m_s$ ). Which ones could not occur? For the valid sets, identify the orbital involved.

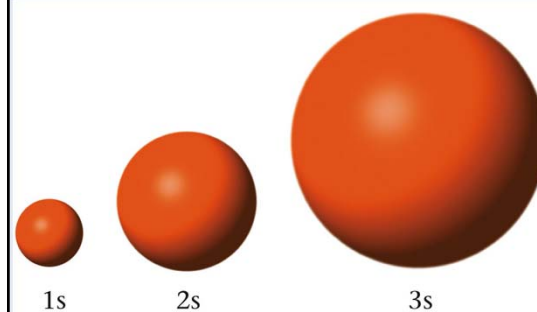
- (a) 3, 1, 0,  $+\frac{1}{2}$     (b) 1, 1, 0,  $-\frac{1}{2}$     (c) 2, 0, 0,  $+\frac{1}{2}$   
 (d) 4, 3, 2,  $+\frac{1}{2}$     (e) 2, 1, 0, 0

**Strategy** Use the selection rules for the four quantum numbers to find the sets that could not occur. For the valid sets, identify the principal level and sublevel.

**SOLUTION**

- (a) valid; 3p    (b) not valid;  $\ell$  cannot equal n    (c) valid; 2s  
 (d) valid; 4f    (e) not valid;  $m_s$  cannot be zero

### Shape of s-orbital



© Brooks/Cole, Cengage Learning

### Example 6.5

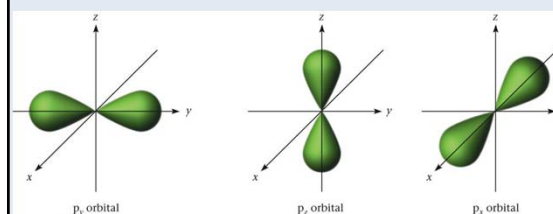
- Example 6.5**  
 (a) What is the capacity for electrons of an s sublevel? A p sublevel? A d sublevel? An f sublevel?  
 (b) What is the total capacity for electrons of the fourth principal level?

**Strategy** Since two electrons fill an orbital, multiply the number of orbitals in the sublevel by 2 to find its capacity. To find the total capacity of the principal level, add those of the individual sublevels.

**SOLUTION**

- (a) s sublevel: 1 orbital  $\times$   $2e^-$ /orbital =  $2e^-$   
 p sublevel: 3 orbitals  $\times$   $2e^-$ /orbital =  $6e^-$   
 d sublevel: 5 orbitals  $\times$   $2e^-$ /orbital =  $10e^-$   
 f sublevel: 7 orbitals  $\times$   $2e^-$ /orbital =  $14e^-$   
 (b)  $2e^-(4s) + 6e^-(4p) + 10e^-(4d) + 14e^-(4f) = 32e^-$

### Shapes of p-orbitals



© Brooks/Cole, Cengage Learning

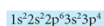


## Shapes and Sizes

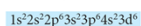
**Example 6.6** Find the electron configurations of the sulfur and iron atoms.

**Strategy** Determine the number of electrons in the atom from its atomic number. Using the energy diagram in Figure 6.8, fill the appropriate sublevels.

**SOLUTION** The sulfur atom has atomic number 16, so there are  $16e^-$ . Two electrons go into the 1s sublevel, two into the 2s sublevel, and six into the 2p sublevel. Two more go into the 3s sublevel, and the remaining four go into the 3p sublevel. The electron configuration of the S atom is



The iron atom has 26 electrons. Proceeding as above, the electron configuration must be

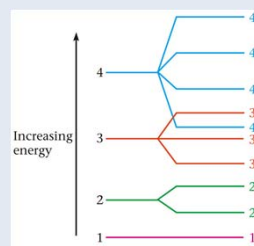


The 4s sublevel fills before the 3d sublevel.

**Reality Check** You can use the periodic table to check your answer. See Figure 6.9 and the accompanying discussion.

## Predicting Electron Configurations

- Predictions apply to gaseous atoms in the ground state
- Energy of sublevel determines order of assignment



## Shapes and Sizes (cont'd)

**Example 6.7** For the iodine atom, write

- (a) the electron configuration. (b) the abbreviated electron configuration.

**Strategy** To obtain the electron configuration, use Figure 6.9. Go across each period in succession, noting the sublevels occupied, until you get to iodine. To find the abbreviated configuration, start with the preceding noble gas, krypton.

**SOLUTION**

(a) Period 1: the 1s sublevel fills ( $1s^2$ )

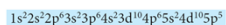
Period 2: the 2s and 2p sublevels fill ( $2s^2 2p^6$ )

Period 3: the 3s and 3p sublevels fill ( $3s^2 3p^6$ )

Period 4: the 4s, 3d, and 4p sublevels fill ( $4s^2 3d^{10} 4p^6$ )

Period 5: the 5s and 4d sublevels fill; five electrons enter the 5p ( $5s^2 4d^{10} 5p^5$ )

Putting it all together, the electron configuration of iodine must be



(b) [Kr] accounts for the first 36  $e^-$ : [Kr]  $5s^2 4d^{10} 5p^5$

## Electron Configuration from Sublevel Energies

- Once the order of filling of sublevels is known, the electron configuration is readily obtained
  - Experimental evidence provides the relative energies of sublevels
  - Sublevels are ordinarily filled before proceeding to the next energy sublevel
- Examples
  - H,  $1s^2$       He,  $1s^2$
  - Li,  $1s^2 2s^1$       Be,  $1s^2 2s^2$
  - B,  $1s^2 2s^2 2p^1$       C,  $1s^2 2s^2 2p^2$

## Electron Configuration in Atoms

- By applying the rules from which quantum numbers derive, it is possible to assign quantum numbers to each electron in an atom
  - Electron configuration:  $1s^2 2s^2 2p^5$
  - Coefficient is n
  - Letter is  $m_l$
  - Superscript is the number of electrons

## The Transition Metals

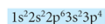
- Consider Ar:  $1s^2 2s^2 2p^6 3s^2 3p^6$ 
  - The next electron enters the 4s
    - K:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
    - Ca:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
  - With the transition metals, the 3d fills after the 4s
    - Sc:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
  - Following the transition metals, the 4p fills
    - Ga:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

## Example 6.6

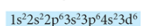
**Example 6.6** Find the electron configurations of the sulfur and iron atoms.

**Strategy** Determine the number of electrons in the atom from its atomic number. Using the energy diagram in Figure 6.8, fill the appropriate sublevels.

**SOLUTION** The sulfur atom has atomic number 16, so there are  $16e^-$ . Two electrons go into the 1s sublevel, two into the 2s sublevel, and six into the 2p sublevel. Two more go into the 3s sublevel, and the remaining four go into the 3p sublevel. The electron configuration of the S atom is



The iron atom has 26 electrons. Proceeding as above, the electron configuration must be



The 4s sublevel fills before the 3d sublevel.

**Reality Check** You can use the periodic table to check your answer. See Figure 6.9 and the accompanying discussion.

## Table 6.4

**Table 6.4** Abbreviated Electron Configurations of Group 1 and 2 Elements

Group 1		Group 2	
${}^3\text{Li}$	[He] $2s^1$	${}^4\text{Be}$	[He] $2s^2$
${}^{11}\text{Na}$	[Ne] $3s^1$	${}^{12}\text{Mg}$	[Ne] $3s^2$
${}^{19}\text{K}$	[Ar] $4s^1$	${}^{20}\text{Ca}$	[Ar] $4s^2$
${}^{37}\text{Rb}$	[Kr] $5s^1$	${}^{38}\text{Sr}$	[Kr] $5s^2$
${}^{55}\text{Cs}$	[Xe] $6s^1$	${}^{56}\text{Ba}$	[Xe] $6s^2$

© Brooks/Cole, Cengage Learning

## Abbreviated Electron Configurations

- To save writing, abbreviated electron configurations are written
  - Start with the preceding noble gas
  - Complete the configuration with the rest of the electrons in the element
    - S is [Ne] $3s^2 3p^4$
    - Ni is [Ar] $4s^2 3d^8$

## Notes on The Periodic Table

- Elements in Group 1 and 2 fill an **s sublevel**
- Elements in Groups 13-18 fill a **p sublevel**
- Elements of the transition metals fill a **d sublevel**
- The two sets of 14 elements each at the bottom of the periodic table fill f sublevels with a principal quantum number **two less than the period number**
  - First row: lanthanides
  - Second row: actinides

## Filling of Sublevels and the Periodic Table

- By using the periodic table, it is possible to quickly write an electron configuration for any element
  - Consider the Group 1 elements
    - All have the outer configuration  $s^1$
  - Consider the Group 2 elements
    - All have the outer configuration  $s^2$
- Atoms of elements in a group have the same distribution of electrons in the outermost principal energy level

## Example 6.7

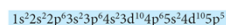
**Example 6.7** For the iodine atom, write

- (a) the electron configuration. (b) the abbreviated electron configuration.

**Strategy** To obtain the electron configuration, use Figure 6.9. Go across each period in succession, noting the sublevels occupied, until you get to iodine. To find the abbreviated configuration, start with the preceding noble gas, krypton.

**SOLUTION**

- (a) Period 1: the 1s sublevel fills ( $1s^2$ )  
 Period 2: the 2s and 2p sublevels fill ( $2s^2 2p^6$ )  
 Period 3: the 3s and 3p sublevels fill ( $3s^2 3p^6$ )  
 Period 4: the 4s, 3d, and 4p sublevels fill ( $4s^2 3d^{10} 4p^6$ )  
 Period 5: the 5s and 4d sublevels fill; five electrons enter the 5p ( $5s^2 4d^{10} 5p^5$ )  
 Putting it all together, the electron configuration of iodine must be



- (b) [Kr] accounts for the first  $36e^-$ : [Kr]  $5s^2 4d^{10} 5p^5$

## Exceptions

- Some elements have electron configurations that differ from those expected from the application of the rules we have seen
  - Cr is actually  $[\text{Ar}]4s^13d^5$
  - Cu is actually  $[\text{Ar}]4s^13d^{10}$
- These differences arise because
  - The energy levels of the orbitals are close to each other
  - There is a gain in stability by producing a half-filled or a filled shell where possible

## Notes

- In all filled orbitals, the two electrons have opposed spins
- Within a given sublevel there are as many half-filled orbitals as possible
  - This is a direct consequence of Hund's Rule
- Hund's rule is based on experiment
  - Substances with **unpaired** electrons are **paramagnetic**
  - Substances with **all paired** electrons are **diamagnetic**

## Orbital Diagrams of Atoms

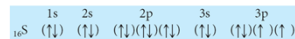
- One step beyond the assignment of electrons to orbitals is the depiction of electrons in orbitals
  - Parentheses indicate orbitals ( )
  - Arrows, up and down, indicate electrons ( $\uparrow\downarrow$ )
    - Recall the  $m_s$  quantum number
    - One electron in an atom has  $m_s = \frac{1}{2}$  and the other has  $m_s = -\frac{1}{2}$
  - Hund's Rule
    - Maximize unpaired spins where possible

## Example 6.8

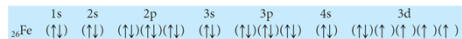
**Example 6.8** Construct orbital diagrams for atoms of sulfur and iron.

**Strategy** Start with the electron configuration, obtained as in Section 6.5. Then write the orbital diagram, recalling the number of orbitals per sublevel, putting two electrons of opposed spin in each orbital within a completed sublevel, and applying Hund's rule where sublevels are partially filled.

**SOLUTION** Recall from Example 6.6 that the electron configuration of sulfur is  $1s^22s^22p^63s^23p^4$ . Its orbital diagram is



The atomic number of iron is 26; its electron configuration is  $1s^22s^22p^63s^23p^64s^23d^6$ . All the orbitals are filled except those in the 3d sublevel, which is populated according to Hund's rule to give four unpaired electrons.



**Reality Check** To construct an orbital diagram, start with the electron configuration and apply Hund's rule.

Figure 6.10

Atom	Orbital diagram						Electron configuration
B	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow$ )	( )	( )	( )	$1s^22s^22p^1$
C	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow$ )	( $\uparrow$ )	( )	( )	$1s^22s^22p^2$
N	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow$ )	( $\uparrow$ )	( $\uparrow$ )	( )	$1s^22s^22p^3$
O	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow$ )	( $\uparrow$ )	( )	$1s^22s^22p^4$
F	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow$ )	( )	$1s^22s^22p^5$
Ne	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	( $\uparrow\downarrow$ )	$1s^22s^22p^6$
	1s	2s	2p				

## Electron Arrangements in Monatomic Ions

- In forming an ion, electrons are **removed from (cation)** or **added to (anion)** sublevels in the highest principal energy level

## Main Group Ions and Noble Gas Structures

- Cations of Group 1 form +1 ions
- Cations of Group 2 form +2 ions
- Nitrogen forms a -3 ion
- Elements in the oxygen family form -2 ions
- Halogens form -1 ions

## Example 6.9

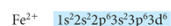
**Example 6.9** Give the electron configuration of

- (a)  $\text{Fe}^{2+}$     (b)  $\text{Br}^-$

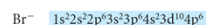
**Strategy** First obtain the electron configuration of the corresponding atom, as in Section 6.5. Then add or remove electrons from sublevels of highest  $n$ .

**SOLUTION**

- (a) As pointed out in Example 6.6, the electron configuration of iron is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ . Two electrons are removed from the 4s sublevel to form  $\text{Fe}^{2+}$ :



- (b) The electron configuration of Br ( $Z = 35$ ) is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ . An electron is added to the 4p sublevel to form  $\text{Br}^-$



This is the electron configuration of the noble gas krypton,  $Z = 36$ .

Figure 6.11 – Noble Gas Configurations

					$\text{H}^+$	$\text{He}$
$\text{Li}^+$	$\text{Be}^{2+}$		$\text{N}^{3-}$	$\text{O}^{2-}$	$\text{F}^-$	$\text{Ne}$
$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{Al}^{3+}$		$\text{S}^{2-}$	$\text{Cl}^-$	$\text{Ar}$
$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Sc}^{3+}$		$\text{Se}^{2-}$	$\text{Br}^-$	$\text{Kr}$
$\text{Rb}^+$	$\text{Sr}^{2+}$	$\text{Y}^{3+}$		$\text{Te}^{2-}$	$\text{I}^-$	$\text{Xe}$
$\text{Cs}^+$	$\text{Ba}^{2+}$	$\text{La}^{3+}$				

## Periodic Trends

- The chemical and physical properties of elements are a periodic function of atomic number
  - Recall that the number of electrons is equal to the atomic number of an element
- Properties to be considered
  - Atomic radius (and ionic radius)
  - Ionization energy
  - Electronegativity

## Transition Metal Cations

- Transition metal cations do not form ions with noble-gas configurations
  - Cations do form, with charges ranging from +1 to higher numbers
  - The outer s electrons are lost before the d electrons; this is the first-in, first-out rule
- Consider Mn
  - Mn is  $[\text{Ar}]4s^2 3d^5$
  - $\text{Mn}^{2+}$  is  $[\text{Ar}]3d^5$

## Atomic Radius

- The “size” of an atom is a difficult to define term
- The radius of an atom can be defined and measured, assuming the atom is a sphere
- The trend for the radius of the atom is
  - A decrease in radius across a period
  - An increase in radius down a group

Figure 6.12

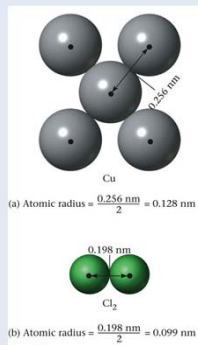
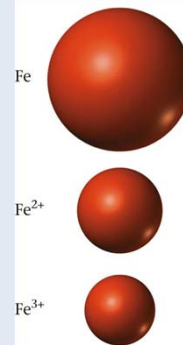


Figure 6.14



### Trends in Atomic Radius

- The increase in radius down a group can be explained by the screening of the electron from the positive charge on the nucleus in the outer shell by the inner electrons; **the effective nuclear charge decreases**
- The decrease in radius across a period can be explained by the fact that electrons are being added to the same principal energy level and do not screen as well; **the effective nuclear charge increases**

### Example 6.10

**Example 6.10** Using only the periodic table, arrange each of the following sets of atoms and ions in order of increasing size.

- (a) Mg, Al, Ca    (b) S, Cl, S<sup>2-</sup>    (c) Fe, Fe<sup>2+</sup>, Fe<sup>3+</sup>

**Strategy** Recall that radius decreases across a period and increases moving down a group. An atom is larger than the corresponding cation but smaller than the corresponding anion.

**SOLUTION**

- (a) Compare the other atoms with Mg. Al, to the right, is smaller than Mg. Ca, below Mg, is larger. The predicted order is **Al < Mg < Ca**.
- (b) Compare with the S atom. Cl, to the right, is smaller. The S<sup>2-</sup> anion is larger than the S atom. The predicted order is **Cl < S < S<sup>2-</sup>**.
- (c) Compare with the Fe<sup>2+</sup> ion. The Fe atom, with no charge, is larger. The Fe<sup>3+</sup> ion, with a +3 charge, is smaller. The predicted order is **Fe<sup>3+</sup> < Fe<sup>2+</sup> < Fe** (Figure 6.14).

### Ionic Radius

- Cations are smaller than the atoms from which they form**
  - Fewer electrons mean increased effective nuclear charge on those that remain
- Anions are larger than the atoms from which they form**
  - More electrons mean that there is more electron-electron repulsion so the size of the ion increases relative to that of the atom

### Ionization Energy

- The ionization energy is a measure of difficulty in removing an electron from a gaseous atom
- $M(g) \rightarrow M^+(g) + e^-$ 
  - ionization energy increases across a period from left to right
  - ionization energy decreases down a family from top to bottom

Figure 6.15

					17	18	
					H 1312	He 2372	
Li 520	Be 900	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 738	Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	As 944	Se 941	Br 1140	Kr 1351
Rb 403	Sr 550	In 558	Sn 709	Sb 832	Te 869	I 1009	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 716	Bi 703	Po 812	At 812	Rn 1037

## Electronegativity

- Electronegativity is the ability of an atom to attract electrons
  - Linus Pauling
    - Fluorine is the most electronegative element
    - Cs is the least electronegative element
  - As electronegativity increases, the formation of an anion becomes more likely
- Trends
  - Electronegativity increases across a period
  - Electronegativity decreases down a family

## Example 6.11

**Example 6.11** Consider the three elements C, N, and Si. Using only the periodic table, predict which of the three elements has

- the largest atomic radius; the smallest atomic radius.
- the largest ionization energy; the smallest ionization energy.

**Strategy** Because these three elements form a block,



in the periodic table, it is convenient to compare both nitrogen and silicon with carbon. Recall the trends for atomic radius and ionization energy.

**SOLUTION**

- C is larger than N but smaller than Si. Silicon must be the largest atom and nitrogen the smallest.

Table 6.5

**Table 6.5** Electronegativity Values

H							—*
2.2							
Li	Be	B	C	N	O	F	—*
1.0	1.6	2.0	2.5	3.0	3.5	4.0	
Na	Mg	Al	Si	P	S	Cl	—*
0.9	1.3	1.6	1.9	2.2	2.6	3.2	
K	Ca	Sc	Ge	As	Se	Br	Kr
0.8	1.0	1.4	2.0	2.2	2.5	3.0	3.3
Rb	Sr	Y	Sn	Sb	Te	I	Xe
0.8	0.9	1.2	1.9	2.0	2.1	2.7	3.0
Cs	Ba						
0.8	0.9						

\*The noble gases He, Ne, and Ar are not listed because they form no stable compounds.

## Example 6.11

- C has a smaller ionization energy than N but a larger ionization energy than Si. Hence, Si has the smallest ionization energy and N the largest.

**Reality Check** Check these answers against Figure 6.13 and 6.15.

## Key Concepts

- Relate wavelength, frequency and energy
- Use the Bohr model to identify lines in the hydrogen spectrum
- Identify the quantum numbers of electrons in atoms
- Derive the electron capacity of energy levels
- Write electron configurations, full and abbreviated, for atoms and ions
- Draw orbital diagrams for atoms and ions
- Identify periodic trends in radii, ionization energy and electronegativity