**TOPIC** 

6

# **ELECTRONIC STRUCTURE OF ATOMS**

The content in this topic is the basis for mastering Learning Objectives 1.5, 1.6, 1.7, 1.8, 1.12, 1.13, and 1.15 as found in the Curriculum Framework.

When you finish reviewing this topic, be sure you are able to:

- Calculate wave properties including frequency, wavelength, and energy of a photon
- Write ground state electron configurations of atoms using the periodic table as a guide
- Explain the photoelectric effect and photoelectron spectroscopy (PES)
- Describe electron structure using photoelectron spectroscopy, ionization energy data, and Coulomb's law
- Analyze data that relate ionization energies to electron configurations
- · Explain electron configurations using Coulomb's law
- Identify and distinguish between paramagnetic and diamagnetic electron configurations

# Section 6.1 The Wave Nature of Light

**Electromagnetic radiation** (also called radiant energy or light) is a form of energy having both wave and particle characteristics. It propagates through a vacuum at the speed of light,  $3.00 \times 10^8$  m/s.

Wavelength,  $\lambda$ , is the distance between two adjacent peaks of the wave.

**Frequency**,  $\nu$ , is the number of wavelengths (or cycles) that pass a given point in a second.

The **electromagnetic spectrum** includes all the wavelengths of radiant energy from short gamma rays to long radio waves (see Figure 6.1).

The **visible spectrum** is that part of the electromagnetic spectrum that we can see, generally with wavelengths ranging between about 400 and 700 nm.

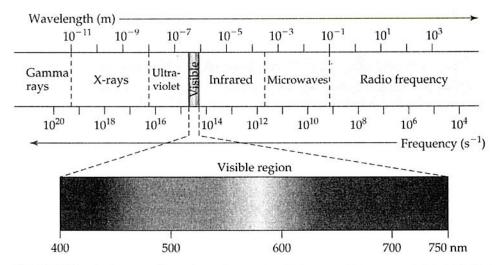


Figure 6.1 The electromagnetic spectrum. As wavelength decreases, frequency and energy increase.

# **Quantized Energy and Photons**

A **quantum** (also called a **photon**) is a specific particle of light energy that can be emitted or absorbed as electromagnetic radiation. The energy of a photon is described by the equation,  $E = h\nu$ . All energy is quantized. That is, matter is allowed to emit or absorb energy only in discrete amounts, whole number multiples of  $h\nu$ .

The **speed of light**, c, in a vacuum is  $3.00 \times 10^8$  m/s.

Table 6.1 shows how the wavelength, frequency, and energy of a single photon of light are related mathematically.

**Table 6.1** Mathematical relationships regarding electromagnetic radiation.

$\nu = c/\lambda$	$E = h\nu$	$E = hc/\lambda$
$\lambda$ = wavelength in nm $\nu$ = frequency in 1/s or hertz; 1 Hz = 1 s <sup>-1</sup>	E = energy of a single photon in joules	
$c = \text{speed of light} = 3.00 \times 10^8 \text{m/s} = 3.00 \times 10^{17} \text{nm/s};$ $1 \text{nm} = 10^{-9} \text{m}$	$h = \text{Planck's constant} = 6.63 \times 10^{-34} \text{J-s}$	

#### Example:

What is the frequency, the energy of a single photon, and the energy of a mole of photons of light having a wavelength of 555 nm?

#### Solution:

First, calculate the frequency from the wavelength using  $\nu = c/\lambda$ . Then, use your answer to calculate the energy of a single photon using  $E = h\nu$ . Finally, multiply the resulting energy by Avogadro's number of photons per mole to obtain the energy of a mole of photons.

Section 6.2

$$\nu = c/\lambda = (3.00 \times 10^{17} \, nm/s)/(555 \, nm) = 5.41 \times 10^{14} \, 1/s$$
  
 $E = h\nu = (6.63 \times 10^{-34} \, Js)(5.41 \times 10^{14} \, 1/s) = 3.58 \times 10^{-19} \, J$   
 $x \, J/mol = (3.58 \times 10^{-19} \, J/photon)(6.02 \times 10^{23} \, photons/mol) = 216,000 \, J/mol = 216 \, kJ/mol$ 



**Common misconception:** When calculating frequency from wavelength, be sure the units for the speed of light match the units for wavelength. For instance, when wavelength is expressed in nanometers, it is convenient to use the value of  $3.00 \times 10^{17}$  nm/s for the speed of light.

## Your Turn 6.1

Explain why the units for frequency are reciprocal seconds, 1/s. Write your answer in the space provided.

The **photoelectric effect** is the emission of electrons from a metal surface that is induced by light energy. Figure 6.2 illustrates the photoelectric effect.

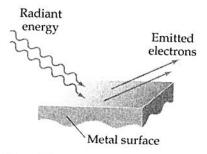


Figure 6.2 The photoelectric effect: Light energy striking a metal causes the surface to emit electrons.

Each type of metal requires a different minimum energy of light to cause the surface to emit electrons because each metal has a unique energy binding its electrons to the surface.

## Line Spectra and the Bohr Model

Section 6.3

An **atomic emission spectrum** (or line spectrum) is a pattern of discrete lines of different wavelengths when the light energy emitted from energized atoms is passed through a prism or diffraction grating. Each element produces a characteristic and identifiable pattern. Figure 6.3 shows the atomic emission spectrum of hydrogen.

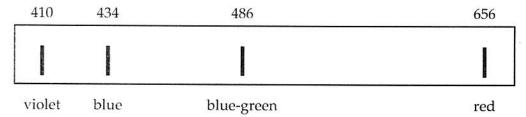
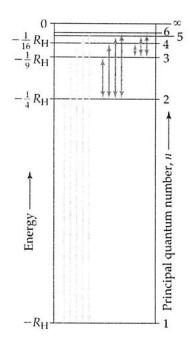


Figure 6.3 The atomic emission spectrum of hydrogen showing the colors and wavelengths of the visible lines.

The Bohr model of the atom (developed by Danish physicist Niels Bohr) explains the origin of the lines of the atomic emission spectrum of hydrogen. Adopting the idea that energies are quantized, Bohr proposed that electrons move in circular, fixed energy orbits around the nucleus. He postulated that each circular orbit corresponds to an "allowed" stable energy state. The ground state is the lowest energy state. Excited states are states of higher energy than the ground state. Energy, in the form of a photon, is emitted or absorbed by an electron only when it changes from one allowed energy state to another. The lines of the atomic emission spectrum of hydrogen result when an electron falls from a higher allowed state to a lower allowed state. The increment between each allowed state is proportional to Planck's constant, the speed of light, and the Rydberg constant,  $R_{\rm H}$  (see Figure 6.4).



**Figure 6.4** Energy levels in the hydrogen atom from the Bohr model. The four transitions with n = 2 as the lower state represent the four lines in the atomic emission spectrum of hydrogen.

The energy transition from allowed states n=3 to n=2 in Figure 6.4 gives rise to the 656 nm line in the atomic emission spectrum of hydrogen. The three transitions immediately to the right of the n=3 to n=2 transition correspond to the other three lines seen in the hydrogen spectrum.

## Your Turn 6.2

The energy transitions shown in Figure 6.4 correspond to which colors and wavelengths of the visible lines of the hydrogen spectrum? Which line corresponds to the largest energy change? Explain. Write your answer in the space provided.

# Section 6.4 The Wave Behavior of Matter

Like light, electrons have characteristics of both waves and particles. Because a wave extends in space, its location is not precisely defined.

The **uncertainty principle**, applied to electrons in an atom, states that it is inherently impossible to simultaneously determine the exact position and momentum of an electron. The best that can be done is to calculate a probability of finding an electron in a certain region of space.

# Section 6.5 Quantum Mechanics and Atomic Orbitals

The **quantum mechanical model** of the atom is a mathematical model that incorporates both wave and particle characteristics of electrons in atoms. It explains the atomic emission spectrum of hydrogen and proposes that electrons in atoms are arranged with certain energies.

The **shell model** is a simple model of the atom that interprets various electronic energies within an atom. Experimental evidence shows that electrons within atoms have different energies and that the electrons are arranged in shells or energy levels at varying distances from the nucleus. Table 6.2 summarizes the shell model of the atom with electrons arranged within energy levels, sublevels, and orbitals.

**Table 6.2.** The shell model of the atom.

Principal Energy Level, <i>n</i>	Sublevel Designation	Number of Orbitals	Number of Electrons
1	1s	1	2
2	2 <i>s</i>	1	2
	2 <i>p</i>	3	6
3	3 <i>s</i>	1	2
	3 <i>p</i>	3	6
	3 <i>d</i>	5	10
4	4s	1	2
	4 <i>p</i>	3	6
	4 <i>d</i>	5	10
	4 <i>f</i>	7	14
5	5 <i>s</i>	1	2
	5 <i>p</i>	3	6
	5 <i>d</i>	5	10
	5 <i>f</i>	7	14
	5 <i>g</i>	9	18

A **principal energy level** is designated 1, 2, 3, 4, 5, and so on. Principal energy level 1 contains electrons that are located closest to the nucleus.

**Energy sublevels** exist within principal energy levels. Sublevels are designated s, p, d, f, g, and so on. Energy level 1 has only an s sublevel. Energy level 2 has two sublevels, s and p. Energy level 3 contains s, p, and d sublevels. Energy level 4 has sublevels s, p, d, and f; and so on.

An **orbital** is a region of space where an electron of a given energy is likely to be found. Each sublevel contains one or more orbitals. Each orbital can contain a maximum of two electrons.

Your Turn 6.3

How many electrons can occupy the following energy levels and sublevels? n = 4, 3d, 5s, and 5f? Write your answers in the space provided.

# Section 6.6 Representations of Orbitals

An **orbital** (or the square of a wave function) is a calculated probability of finding an electron of a given energy in a region of space. Figure 6.5 shows the electron probability distributions of various orbitals.

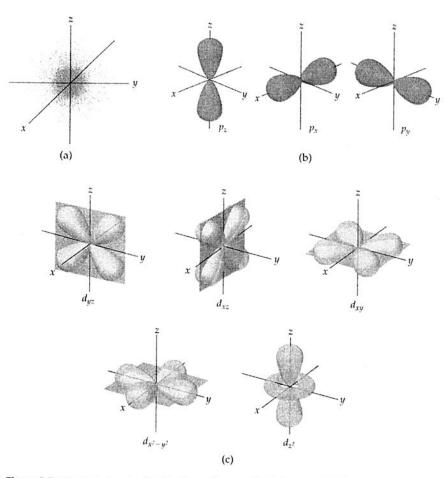


Figure 6.5 Electron-density distributions of an s orbital, three p orbitals, and five d orbitals.

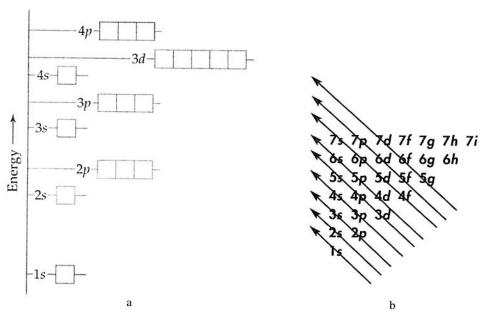


**Common misconception:** An orbital is not the same as an orbit. An orbital is not a defined path of an electron. Rather it is a three-dimensional probability density distribution where an electron is likely to be found in the space surrounding the nucleus of an atom.

# **Many-Electron Atoms**

Section 6.7

In many-electron atoms (atoms other than hydrogen), electron-electron repulsions cause different sublevels to have different energies. Figure 6.6a shows the relative energy levels in many-electron atoms. Figure 6.6b is a convenient device for determining the relative energies, from lowest to highest of each sublevel of a many-electron atom.



**Figure 6.6** (a) Orbital energy levels in many-electron atoms. (b) A device to determine the relative energies of sublevels. The lower energy sublevels start at the bottom of the chart and increase in energy in the direction of the arrows, tail to head.

List the first sixteen energy sublevels shown in Figure 6.6 in order of increasing energy. Write your answer in the space provided.

Your Turn 6.4

# Section 6.8 Electron Configurations

An **electron configuration** is a distribution of electrons among various orbitals of an atom. Table 6.3 shows the electron configurations of some lighter elements.

 Table 6.3
 Electron configurations of several lighter elements.

Element	Total Electrons	Orbital Diagram	Electron Configuration
		1s 2s 2p 3s	
Li	3	11 1	$1s^22s^1$
Be	4	11 11	$1s^22s^2$
В	5	11 11 1	$1s^22s^22p^1$
С	6	11 11 1 1	$1s^22s^22p^2$
N	7	11 11 1 1	$1s^22s^22p^3$
Ne	10	11 11 11 11 1	$1s^22s^22p^6$
Na	11	11 11 11 11 1	$1s^22s^22p^63s^1$

**Paramagnetic** is a term referring to an atom having one or more unpaired electrons. Table 6.3 shows that lithium, boron, carbon, nitrogen, and sodium are all paramagnetic.

Diamagnetic means that all electrons in an atom are paired.

## Your Turn 6.5

Which of the elements listed in Table 6.3 are diamagnetic? Explain. Write your answer in the space provided.

Figure 6.6a or 6.6b can be used to write the ground state electron configurations of most atoms.

Rules for writing ground state electron configurations for atoms using Figure 6.6a or 6.6b are the following:

- Fill the lowest energy level first. Electrons in the same orbital must have opposite spins (different spin quantum numbers). The total number of electrons to be used is the atomic number of the element.
- 2. Place no more than two electrons per orbital to satisfy the Pauli exclusion principle.
- 3. Do not pair electrons in degenerate (same energy) orbitals until each orbital has one electron of the same spin. (This is called Hund's rule.)
- 4. Write the electron configuration by using sublevel designations and superscripts to designate the number of electrons in each sublevel.

#### **Example:**

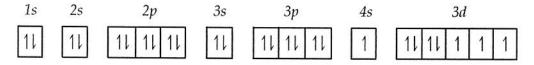
Write the electron configuration for iron.

#### Solution:

The atomic number of iron is 26. Fill twenty-six electrons in the orbital diagram like this:

Write the corresponding ground state electron configuration like this:  $1s^22s^22p^63s^23p^64s^23d^6$ 

An excited state configuration has higher energy than the ground state configuration. Excited state configurations have one or more electrons occupying higher-energy levels than would be predicted from Figure 6.4 or 6.5. For example, one of many possible excited state configurations for iron arises when an electron moves from a 4s sublevel to a 3d sublevel. The excited state orbital diagram looks like this:



 $1s^22s^22p^63s^23p^64s^13d^7$  is an excited state electron configuration.

# Section 6.9 Electron Configurations and the Periodic Table

The periodic table is organized so that elements with similar electron configurations are arranged in columns as shown in Figure 6.7. Electron configurations of most elements can be determined by their location on the periodic table using Figure 6.7.

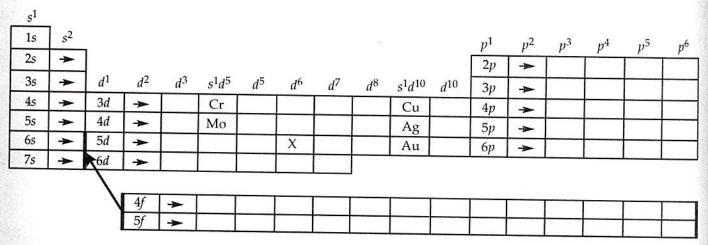


Figure 6.7 Elements on the periodic table are largely arranged according to electron configurations.

### Example:

Write the electron configuration of the element marked by the "X."

#### Solution:

Element "X" is located in the row labeled 5d and the column labeled  $d^6$ , so there are six electrons in the 5d sublevel, the highest occupied sublevel. The electron configuration for element X ends in  $5d^6$ . Write the complete electron configuration by starting at the top left and working left to right and top to bottom until the element X is reached:

$$1s^22s^22p^63s^23p^64\,s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^6$$

A condensed electron configuration for an element shows only electrons occupying the outermost sublevels (the electrons in the same row as the element) and is preceded by the symbol for the noble gas in the row above the element.

#### Example:

Write the condensed electron configuration for element X.

#### Solution:

Element X has these sublevels occupied in its row:  $6s^24f^{14}5d^6$  and the noble gas in the row above is xenon, Xe. The condensed configuration is (Xe)  $6s^24f^{14}5d^6$ .

Your Turn 6.6

In a condensed electron configuration, what does the symbol (Xe) represent? Write your answer in the space provided.

**Common misconception:** Although not tested on the AP exam, the Group 6 atoms, Cr and Mo, are unusual because their ground state outermost electrons are arranged  $s^1d^5$  rather than  $s^2d^4$ . All Group 11 atoms, Cu, Ag, and Au, similarly exhibit  $s^1d^{10}$  ground state configurations rather than  $s^2d^9$ . These configurations arise because the s and d orbitals are very close in energy, and precisely half-filled degenerate d orbitals (as in chromium) and completely full d orbitals (as in copper) experience less electron–electron repulsion than do other partially filled configurations.



The positive nucleus of an atom attracts its negative electrons and this attraction is the basis for the shell model. The energies of atomic orbitals determine the stabilities of atoms and how atoms react.

**Coulomb's law** is a way to estimate the relative forces of attraction between two charged particles such as a nucleus and an electron. Coulomb's law states that the **force of attraction** between two charged particles is related to the **magnitude of their charges** and the **distance** between them:

$$F = kQ_1Q_2/d^2$$

where

F is the force of attraction  $Q_1$  and  $Q_2$  are the charges of the particles d is the distance between the particles k is a constant

It is not appropriate to use Coulomb's law to calculate interactions of electrons because Coulomb's law is a classical model and electrons are governed by quantum mechanics. However, we can use the equation to guide our thinking about the relative magnitudes of forces between charged particles.

The greater the charges of the particles, the greater the force of attraction between them. Also the closer the particles are to each other, the greater the attraction.

A similar equation describes the energy between the particles:

$$E = kQ_1Q_2/d$$

Ionization energy of an electron in an atom is the energy required to remove the electron from the atom. Coulomb's law indicates that the farther an electron is from the nucleus, the lower the energy required to remove that electron. Electrons close to the nucleus are held with a greater force than those that are more distant from the nucleus. Also, higher positive nuclear charges draw electrons closer to the nucleus and hold them with greater force.

### Photoelectron Spectroscopy (PES)

**Photoelectron spectroscopy** is an experimental method used to measure the energies of electrons in atoms. These energies, called binding energies or ionization energies, give direct experimental evidence of the shell model of the atom.

**lonization energy** is the energy required to remove an electron from the ground state of a gaseous atom.

Photoelectron spectroscopy works like the photoelectric effect except that the sample is in the gas phase. When a high-energy photon of a known energy bombards a gaseous atom in a vacuum, the photon ejects an electron from the atom. The spectrometer measures the kinetic energy of the ejected electron. The ionization energy (also called the binding energy) of the electron is calculated using the following equation:

Ionization energy = energy of the photon minus the kinetic energy of the electron.

A typical photoelectron spectrometer uses high-energy photons of about  $12,000 \, kJ/mol$ . Any ionization energy less than the bombarding photons can be measured by the spectrometer.

A **photoelectron spectrum** of an atom is a graph showing energy on the x-axis and relative number of electrons on the y-axis. The photoelectron spectra of the elements having atomic numbers 1 through 5 are shown in Figure 6.8.

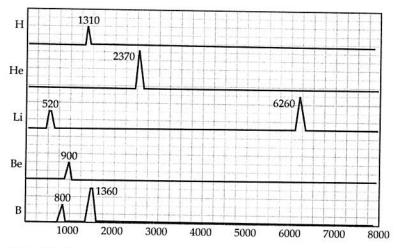


Figure 6.8 Photoelectron spectra of elements 1-5. The numbers are in kJ/mol.

Each signal or peak in a photoelectron spectrum represents the energy of one or more electrons in a given energy sublevel. For example, helium has only one peak in its photoelectron spectrum, indicating that its electrons are contained in only one energy sublevel.

The intensity of each signal at a given energy is interpreted as the number of electrons in that energy level. The signal in the helium photoelectron spectrum is twice the size as the peak in the hydrogen spectrum. This means that there are twice as many electrons in the helium sublevel as there are in the corresponding hydrogen sublevel.

Photoelectron spectroscopy (PES) provides direct evidence for the shell model of the atom and is a useful means to rationalize and explain periodic properties and trends.

Electron configurations of atoms with multiple electrons can be inferred from photoelectron spectra. Table 6.4 uses data from the photoelectron spectra in Figure 6.8 to infer the electron configurations of hydrogen, helium, lithium, beryllium, and boron.

**Table 6.4** Electron configurations from photoelectron ionization energies of lighter elements.

Atom	Electron Configuration	Ionization Energy, kJ/mol			
Н	$1s^1$	1310			
Не	$1s^2$	2370			
Li	$1s^2$	6260			
	$2s^1$	520			
Be	$1s^2$	*			
	$2s^2$	900			
В	$1s^2$	*			
	$2s^2$	1,360			
	2p1	800			

<sup>\*</sup>Because of the relatively high nuclear charges of beryllium and boron, the ionization energies of their 1s electrons are higher than the 12,000 kJ/mol photons typically used by photoelectron spectrometers to eject electrons. Thus, photoelectron spectroscopy does not show corresponding signals for these electrons. This is true for the inner electrons of most heavy atoms.

### Your Turn 6.7

- Explain what the peaks signify in the photoelectron spectra shown in Figure 6.8.
- b. For each signal in the photoelectron spectra shown in Figure 6.8, assign an orbital designation from the electron configuration of each atom.
- c. Use Coulomb's law to explain why the signal in the helium spectrum is at higher energy than the signal in the hydrogen spectrum.

Write your answers in the space provided.

Table 6.5 shows photoelectron spectra values of orbital ionization energies in kJ/mol for elements 11–21.

**Table 6.5** Photoelectron spectra values of orbital ionization energies for elements 11–21.

	Na	Mg	Al	Si	P	S	CI	Ar	K	Ca	Sc
2s	6840	9070							1		
2 <i>p</i>	3670	5310	7790						1	1	+
3 <i>s</i>	500	740	1090	1460	1950	2050	2440	2820	3930	4650	5440
3 <i>p</i>			580	790	1010	1000	1250	1520	2380	2900	3240
3 <i>d</i>											770
4s									420	590	630

#### Your Turn 6.8

- a. Why are the values for the 1s electrons missing?
- b. Why are the values for the 2s electrons from aluminum through scandium missing, whereas they exist for sodium and magnesium?
- c. Use Coulomb's law to explain why sodium's 3s energy value is lower than its 2s sublevel.
- d. How do the values listed for magnesium give evidence for the shell model of the atom?
- e. Predict the relative intensities of the three peaks corresponding to the energy values given for the aluminum atom. Justify your answer.
- f. Determine the trend in energy values from left to right along the row corresponding to the 3s sublevel.
- g. Suggest a plausible reason for your answer to part f.

h. Why does only scandium show an energy value for the 3d sublevel?

Write your answers in the space provided.

**Spectroscopy** is the study of the interaction of light with matter. Matter interacts differently with light of different energies. Thus, various methods of spectroscopy use different wavelengths of light to study different properties of matter. We have already seen applications of the following forms of spectroscopy.

Mass spectrometry uses high-energy electrons, rather than light, to knock electrons from atoms and molecules producing positive ions that separate in a magnetic field according to their masses. Mass spectrometry is useful in determining atomic and molar masses and studying isotope ratios.

**Atomic emission spectroscopy** uses high-energy photons, usually in the ultraviolet range, to excite electrons into higher atomic energy states. When an electron returns to a lower atomic energy state, it gives off a photon of light corresponding to the difference in energy between the states. Hydrogen and all other elements exhibit characteristic fingerprints: their unique atomic emission spectra. These spectra provide a basis for identifying elements. A practical use of atomic emission spectra is in fluorescent lighting. Fluorescent tubes, containing gases such as mercury vapor, neon, and argon, become excited by a high-voltage electrical discharge. As the excited electrons return to the ground state, they emit light that is absorbed and reemitted by a phosphorescent coating on the inside of the tube.

**Photoelectron spectroscopy** uses ultraviolet photons to ionize atoms. The measured energy of the ejected electron is used to calculate its ionization energy.

**Infrared spectroscopy** probes the vibrations of molecules and gives evidence for various types of covalent bonds (discussed in Topics 8 and 9, respectively). Bonds in molecules vibrate with energies that correspond to the energies of infrared light, making infrared spectroscopy a valuable tool for determining the types of bonds in molecules.

**Ultraviolet and visible** radiation promote electronic transitions within atoms and molecules and give information about atomic and molecular structure. As the electrons vibrate with near ultraviolet and visible energies, they absorb light. By measuring light absorption, we can deduce molecular structure and measure the concentrations of the absorbing molecules.

### **Multiple Choice Questions**

1. Gaseous atoms of which of the following elements have electron configurations that are paramagnetic in their ground states?

- I. Na
- II. Mg
- III. Al
- IV. P

A) I, II, III, and IV

- B) I, II, and III only
- C) I, III, and IV only
- D) II only
- E) III and IV only

2. What is the wavelength of light that has a frequency of  $6.0 \times 10^{14}$ Hz?

- A)  $2.0 \times 10^6 nm$
- B) 2000 nm
- C) 500 nm
- D) 200 nm
- E)  $5.0 \times 10^{-7} nm$

3. What is the maximum number of electrons that can occupy the 5f sublevel?

- A) 2
- B) 5
- C) 10
- D) 14
- E) 18

4. What is the maximum number of orbitals in a 4d sublevel?

- A) 2
- B) 5
- C) 10
- D) 14
- E) 18

5.  $X:1s^22s^22p^3$   $Y:1s^22s^1$ 

Atoms X and Y have the ground state electronic configuration shown above. The formula for the compound most likely formed from X and Y is

- A) YX.
- B)  $Y_2X$ .
- C)  $Y_3X$ .
- D)  $YX_3$ .
- E)  $Y_2X$ .
- 6. A blue line in the atomic emission spectrum of hydrogen has a wavelength of 434 nm. Which of the following calculates the energy of this light per mole of photons?
  - A)  $(10^6)(6.63)(3.00)(6.02)(434) kJ/mol$
  - B)  $(10^3)(6.63)(3.00)(6.02)(434) kJ/mol$
  - C)  $(10^6)(6.63)(3.00)(6.02)(434) J/mol$
  - D)  $(10^3)(6.63)(3.00)(6.02)(434) J/mol$
  - E)  $(10^3)(434)(6.02)/(6.63)(3.00) kJ/mol$
- 7. The wavelength of electromagnetic radiation is longer when
  - A) its energy is small and its frequency is large.
  - B) its energy is small and its frequency is small.
  - C) its energy is large and its frequency is large.
  - D) its energy is large and its frequency is small.
  - E) its energy is large and its amplitude is high.

## Free Response Questions

- A line having a wavelength of 656 nm exists in the atomic emission spectrum of hydrogen.
  - a. For the line, calculate the following values and specify their units:
    - i. frequency
    - ii. energy of a photon
    - iii. energy of a mole of photons
  - b. What color is the line? Explain your reasoning.
  - c. Discuss the origin of the line, citing the Bohr theory of the atom. Specify any energy transitions that are applicable.

## 112 TOPIC 6

- 2. Molecules of oxygen are converted to atomic oxygen in the upper atmosphere by absorbing photons having wavelengths of 240 nm and shorter.
  - a. Write the electron configuration of oxygen and tell why atomic oxygen is diamagnetic or paramagnetic.
  - b. Write the electron configuration of the oxide ion.
  - c. Calculate the energy equivalent of a photon of wavelength 240 nm in units of kJ/mol.