6 Electronic Structure of Atoms

Visualizing Concepts

6.1 (a) Speed is distance traveled per unit time. Measure the distance between the center point and a second reference point, possibly the edge of the container. Using a stop watch, measure the elapsed time between when a wave forms at the center and when it reaches the second reference point. Find the ratio of distance to time.

(b) Measure the distance between two wave crests (or troughs or any analogous points on two adjacent waves). Better yet, measure the distance between two crests (or analogous points) that are several waves apart and divide by the number of waves that separate them.

(c) Since speed is distance/time, and wavelength is distance, we can calculate frequency by dividing speed by wavelength, $\nu = c/\lambda$.

(d) We can measure frequency of the wave by dropping an object such as a cork in the water and counting the number of times per second it moves through a complete cycle of motion.

6.2 Given: 2450 MHz radiation. $\text{Hz} = \text{s}^{-1}$, unit of frequency. $\text{M} = 1 \times 10^6$; $2450 \times 10^6\ \text{Hz} = 2.45 \times 10^9\ \text{Hz} = 2.45 \times 10^9\ \text{s}^{-1}$.

(a) Find $2.45 \times 10^9\ \text{s}^{-1}$ on the frequency axis of Figure 6.4. The wavelength that corresponds to this frequency is approximately $1 \times 10^{-1} = 0.1$ m or 10 cm.

(b) No, visible radiation has wavelengths of 4×10^{-7} to 7×10^{-7} m, much shorter than 0.1 m.

(c) Energy and wavelength are inversely proportional. Photons of the longer 0.1 m radiation have less energy than visible photons.

(d) Radiation of 0.1 m is in the low energy portion of the microwave region. The appliance is probably a microwave oven. (The highest FM radio frequency is 108 MHz, so the device is not an FM radio.)

6.3 Wave (a) corresponds to higher energy radiation. The energy of electromagnetic radiation is directly proportional to frequency and inversely proportional to wavelength. Wave (a) has the shorter wavelength and thus the higher energy.

6.4 (a) The glowing stove burner is an example of black body radiation, the observational basis for Planck's quantum theory. The wavelengths emitted are related to temperature, with cooler temperatures emitting longer wavelengths and hotter temperatures emitting shorter wavelengths. At the hottest setting, the burner emits orange visible light. At the cooler low setting, the burner emits longer wavelengths out of the visible region, and the burner appears black.

(b) If the burner had a super high setting, the emitted wavelengths would be shorter than those of orange light and the glow color would be more yellowish, progressing to white. (See Figure 6.5.)

6.5 (a) Increase. The rainbow has shorter wavelength blue light on the inside and longer wavelength red light on the outside. (See Figure 6.4.)

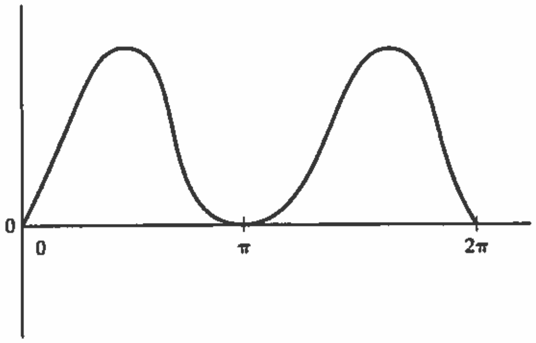
(b) Decrease. Wavelength and frequency are inversely related. Wavelength increases so frequency decreases going from the inside to the outside of the rainbow.

(c) The light from the hydrogen discharge tube is not a continuous spectrum, so not all visible wavelengths will be in our "hydrogen discharge rainbow." Starting with the shortest wavelengths, it will be violet followed by blue-violet and blue-green on the inside. Then there will be a gap, and finally a red band. (See the H spectrum in Figure 6.11.)

6.6 (a) $n = 1, n = 4$ (b) $n = 1, n = 2$

(c) Wavelength and energy are inversely proportional; the smaller the energy, the longer the wavelength. In order of increasing wavelength (and decreasing energy): (iii) $n = 2$ to $n = 4$ < (iv) $n = 3$ to $n = 1$ < (ii) $n = 3$ to $n = 2$ < (i) $n = 1$ to $n = 2$

6.7 (a) $\psi^2(x)$ will be positive or zero at all values of x, and have two maxima with larger magnitudes than the maximum in $\psi(x)$.



(b) The greatest probability of finding the electron is at the two maxima in $\psi^2(x)$ at $x = \pi/2$ and $3\pi/2$.

(c) There is zero probability of finding the electron at $x = \pi$. This value is called a node.

6.8 (a) 1

(b) p (dumbbell shape, node at the nucleus)

(c) The lobes in the contour representation would extend farther along the y axis. A larger principle quantum number (4p vs. 3p) implies a greater average distance from the nucleus for electrons occupying the orbital.

6.9 (a) In the left-most box, the two electrons cannot have the same spin. The *Pauli exclusion principle* states that no two electrons can have the same set of quantum numbers. Since the first three quantum numbers describe an orbital, the fourth quantum number, m_s, must have different values for two electrons in the same orbital; their "spins" must be opposite.

(b) Flip one of the arrows in the left-most box, so that one points up and the other down.

(c) Group 6A. The drawing shows three boxes or orbitals at the same energy, so it must represent p orbitals. Since some of these p orbitals are partially filled, they must be the valence orbitals of the element. Elements with four valence electrons in their p orbitals belong to group 6A.

6.10 (a) Group 7A or 17, the halogens, the column second from the right

(b) Group 5A or 15

(c) Gallium, atomic number 31, at the intersection of row 4 and group 3A or 13

(d) All of the B groups, groups 3-12, in the middle of the major part of the table, not including the two rows of *f*-block elements

The Wave Nature of Light (section 6.1)

6.11 (a) Meters (m) (b) 1/seconds (s^{-1}) (c) meters/second ($m{\cdot}s^{-1}$ or m/s)

6.12 (a) Wavelength (λ) and frequency (ν) are inversely proportional; the proportionality constant is the speed of light (c). $\nu = c/\lambda$.

(b) Light in the 210–230 nm range is in the ultraviolet region of the spectrum. These wavelengths are slightly shorter than the 400 nm short-wavelength boundary of the visible region.

6.13 (a) True.

(b) False. Ultraviolet light has shorter wavelengths than visible light. [See Solution 6.12(b).]

(c) False. X-rays travel at the same speed as microwaves. (X-rays and microwaves are both electromagnetic radiation.)

(d) False. Electromagnetic radiation and sound waves travel at different speeds. (Sound is not a form of electromagnetic radiation.)

6.14 (a) False. The frequency of radiation decreases as the wavelength increases.

(b) True.

(c) False. Infrared light has lower frequencies than visible light.

(d) False. The glow from a fireplace and the energy within a microwave oven are both forms of electromagnetic radiation. (A foghorn blast is a form of sound waves, which are not accompanied by oscillating electric and magnetic fields.)

6.15 *Analyze/Plan.* Use the electromagnetic spectrum in Figure 6.4 to determine the wavelength of each type of radiation; put them in order from shortest to longest wavelength. *Solve.*

Wavelength of X-rays < ultraviolet < green light < red light < infrared < radio waves

Check. These types of radiation should read from left to right on Figure 6.4

6.16 Wavelength of (a) gamma rays < (d) yellow (visible) light < (e) red (visible) light < (b) 93.1 MHz FM (radio) waves < (c) 680 kHz or 0.680 MHz AM (radio) waves

6.17 *Analyze/Plan.* These questions involve relationships between wavelength, frequency, and the speed of light. Manipulate the equation $\nu = c/\lambda$ to obtain the desired quantities, paying attention to units. *Solve.*

(a) $\nu = c/\lambda;\ \dfrac{2.998 \times 10^8\ \text{m}}{\text{s}} \times \dfrac{1}{10\ \mu\text{m}} \times \dfrac{1\ \mu\text{m}}{1 \times 10^{-6}\ \text{m}} = 3.0 \times 10^{13}\ \text{s}^{-1}$

(b) $\lambda = c/\nu;\ \dfrac{2.998 \times 10^8\ \text{m}}{\text{s}} \times \dfrac{1\ \text{s}}{5.50 \times 10^{14}} = 5.45 \times 10^{-7}\ \text{m}\quad (545\ \text{nm})$

(c) The radiation in (b) is in the visible region and is "visible" to humans. The 10 μm (1×10^{-5} m) radiation in (a) is in the infrared region and is not visible.

(d) $50.0\ \mu\text{s} \times \dfrac{1\ \text{s}}{1 \times 10^6\ \mu\text{s}} \times \dfrac{2.998 \times 10^8\ \text{m}}{\text{s}} = 1.50 \times 10^4\ \text{m}$

Check. Confirm that powers of 10 make sense and units are correct.

6.18 (a) $\nu = c/\lambda;\ \dfrac{2.998 \times 10^8\ \text{m}}{\text{s}} \times \dfrac{1}{5.0 \times 10^{-5}\ \text{m}} = 6.0 \times 10^{12}\ \text{s}^{-1}$

(b) $\lambda = c/\nu;\ \dfrac{2.998 \times 10^8\ \text{m}}{\text{s}} \times \dfrac{1\ \text{s}}{2.5 \times 10^8} = 1.2\ \text{m}$

(c) Neither of the radiations in (a) and (b) can be observed by an X-ray detector. Radiation (a) is infrared and radiation (b) is radio frequency.

(d) $10.5\ \text{fs} \times \dfrac{1 \times 10^{-15}\ \text{s}}{1\ \text{fs}} \times \dfrac{2.998 \times 10^8\ \text{m}}{\text{s}} = 3.15 \times 10^{-6}\ \text{m}\ (3.15\ \mu\text{m})$

6.19 *Analyze/Plan.* $\nu = c/\lambda$; change nm → m.

Solve. $\nu = c/\lambda;\ \dfrac{2.998 \times 10^8\ \text{m}}{1\ \text{s}} \times \dfrac{1}{532\ \text{nm}} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 5.64 \times 10^{14}\ \text{s}^{-1}$

The color is green.

Check. $(3000 \times 10^5 / 500 \times 10^{-9}) = 6 \times 10^{14}\ \text{s}^{-1}$; units are correct.

6.20 According to Figure 6.4, ultraviolet radiation has both higher frequency and shorter wavelength than infrared radiation. Looking forward to section 6.2, the energy of a photon is directly proportional to frequency ($E = h\nu$), so ultraviolet radiation yields more energy from a photovoltaic device.

Quantized Energy and Photons (section 6.2)

6.21 Quantization means that energy changes can only happen in certain allowed increments. If the human growth quantum is one-foot, growth occurs instantaneously in one-foot increments. That is, a child experiences growth spurts of one-foot; her height changes by one-foot increments.

6.22 Planck's original hypothesis was that energy could only be gained or lost in discrete amounts (quanta) with a certain minimum size. The size of the minimum energy change is related to the frequency of the radiation absorbed or emitted, $\Delta E = h\nu$, and energy changes occur only in multiples of $h\nu$.

Einstein postulated that light itself is quantized, that the minimum energy of a photon (a quantum of light) is directly proportional to its frequency, $E = h\nu$. If a photon that strikes a metal surface has less than the threshold energy, no electron is emitted from the surface. If the photon has energy equal to or greater than the threshold energy, an electron is emitted and any excess energy becomes the kinetic energy of the electron.

6.23 *Analyze/Plan.* These questions deal with the relationships between energy, wavelength, and frequency. Use the relationships $E = h\nu = hc/\lambda$ to calculate the desired quantities. Pay attention to units. *Solve.*

(a) $E = h\nu = 6.626 \times 10^{-34}\ \text{J-s} \times 6.75 \times 10^{12}\ \text{s}^{-1} = 4.47 \times 10^{-21}\ \text{J}$

(b) $\Delta E = h\nu = \dfrac{hc}{\lambda} = \dfrac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{322\ \text{nm}} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 6.17 \times 10^{-19}\ \text{J}$

(c) $\lambda = hc/\Delta E = \dfrac{6.626 \times 10^{-34}\ \text{J-s}}{2.87 \times 10^{-18}\ \text{J}} \times \dfrac{2.998 \times 10^{8}\ \text{m}}{1\text{s}} = 6.92 \times 10^{-8}\ \text{m} = 69.2\ \text{nm}$

6.24 *Analyze/Plan.* These questions deal with the relationships between energy, wavelength, and frequency. Use the relationships $E = h\nu = hc/\lambda$ to calculate the desired quantities. Pay attention to units. *Solve.*

(a) $\nu = c/\lambda = \dfrac{2.998 \times 10^{8}\ \text{m}}{\text{s}} \times \dfrac{1}{650\ \text{nm}} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 4.6123 \times 10^{14} = 4.61 \times 10^{14}\ \text{s}^{-1}$

(b) $\Delta E = h\nu = 6.626 \times 10^{-34}\ \text{J-s} \times 4.6123 \times 10^{14}\ \text{s}^{-1} = 3.06 \times 10^{-19}\ \text{J}$

(c) The energy gap between the ground and excited states is the energy of a single 650 nm photon emitted when one electron relaxes from the excited to the ground state. $\Delta E = 3.06 \times 10^{-19}\ \text{J}$

6.25 *Analyze/Plan.* Use $E = hc/\lambda$; pay close attention to units. *Solve.*

(a) $E = hc/\lambda = 6.626 \times 10^{-34}\ \text{J-s} \times \dfrac{2.998 \times 10^{8}\ \text{m}}{1\ \text{s}} \times \dfrac{1}{3.3\ \mu\text{m}} \times \dfrac{1\ \mu\text{m}}{1 \times 10^{-6}\ \text{m}}$

$= 6.0 \times 10^{-20}\ \text{J}$

$E = hc/\lambda = 6.626 \times 10^{-34}\ \text{J-s} \times \dfrac{2.998 \times 10^{8}\ \text{m}}{1\ \text{s}} \times \dfrac{1}{0.154\ \text{nm}} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}}$

$= 1.29 \times 10^{-15}\ \text{J}$

Check. $(6.6 \times 3/3.3) \times (10^{-34} \times 10^{8}/10^{-6}) \approx 6 \times 10^{-20}\ \text{J}$

$(6.6 \times 3/0.15) \times (10^{-34} \times 10^{8}/10^{-9}) \approx 120 \times 10^{-17} \approx 1.2 \times 10^{-15}\ \text{J}$

The results are reasonable. We expect the longer wavelength 3.3 μm radiation to have the lower energy.

(b) The 3.3 μm photon is in the infrared and the 0.154 nm (1.54×10^{-10} m) photon is in the X-ray region; the X-ray photon has the greater energy.

6.26 $E = h\nu$

AM: $6.626 \times 10^{-34}\ \text{J-s} \times \dfrac{1010 \times 10^{3}}{1\ \text{s}} = 6.69 \times 10^{-28}\ \text{J}$

$$\text{FM}: 6.626 \times 10^{-34}\ \text{J}\cdot\text{s} \times \frac{98.3 \times 10^{6}}{1\ \text{s}} = 6.51 \times 10^{-26}\ \text{J}$$

The FM photon has about 100 times more energy than the AM photon.

6.27 *Analyze/Plan.* Use $E = hc/\lambda$ to calculate J/photon; Avogadro's number to calculate J/mol; photon/J [the result from part (a)] to calculate photons in 1.00 mJ. Pay attention to units. *Solve.*

(a) $$E_{\text{photon}} = hc/\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{325 \times 10^{-9}\ \text{m}} \times \frac{2.998 \times 10^{8}\ \text{m}}{\text{s}} = 6.1122 \times 10^{-19}$$
$$= 6.11 \times 10^{-19}\ \text{J/photon}$$

(b) $$\frac{6.1122 \times 10^{-19}\ \text{J}}{1\ \text{photon}} \times \frac{6.022 \times 10^{23}\ \text{photons}}{1\ \text{mol}} = 3.68 \times 10^{5}\ \text{J/mol} = 368\ \text{kJ/mol}$$

(c) $$\frac{1\ \text{photon}}{6.1122 \times 10^{-19}\ \text{J}} \times 1.00\ \text{mJ} \times \frac{1 \times 10^{-3}\ \text{J}}{1\ \text{mJ}} = 1.64 \times 10^{15}\ \text{photons}$$

Check. Powers of 10 (orders of magnitude) and units are correct.

(d) If the energy of one 325 nm photon breaks exactly one bond, one mol of photons break 1 mol of bonds. The average bond energy in kJ/mol is the energy of 1 mol of photons (from part b) 368 kJ/mol.

6.28 $$\frac{941 \times 10^{3}\ \text{J}}{\text{mol N}_2} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{photons}} = 1.563 \times 10^{-18} = 1.56 \times 10^{-18}\ \text{J/photon}$$

$$\lambda = hc/E = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{1.563 \times 10^{-18}\ \text{J}} \times \frac{2.998\times10^{8}\ \text{m}}{1\ \text{s}} = 1.27 \times 10^{-7}\ \text{m} = 127\ \text{nm}$$

According to Figure 6.4, this is ultraviolet radiation.

6.29 *Analyze/Plan.* $E = hc/\lambda$ gives J/photon. Use this result with J/s (given) to calculate photons/s. *Solve.*

(a) The ~1×10^{-6} m radiation is infrared but very near the visible edge.

(b) $$E_{\text{photon}} = hc/\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{987 \times 10^{-9}\ \text{m}} \times \frac{2.998 \times 10^{8}\ \text{m}}{1\ \text{s}} = 2.0126 \times 10^{-19}$$
$$= 2.01 \times 10^{-19}\ \text{J/photon}$$

$$\frac{0.52\ \text{J}}{32\ \text{s}} \times \frac{1\ \text{photon}}{2.0126 \times 10^{-19}\ \text{J}} = 8.1 \times 10^{16}\ \text{photons/s}$$

Check. $(7 \times 3/1000) \times (10^{-34} \times 10^{8}/10^{-9}) \approx 21 \times 10^{-20} \approx 2.1 \times 10^{-19}$ J/photon

$(0.5/30/2) \times (1/10^{-19}) = 0.008 \times 10^{19} = 8 \times 10^{16}$ photons/s

Units are correct; powers of 10 are reasonable.

6.30 (a) 3.55 mm = 3.55×10^{-3} m; the radiation is microwave.

(b) $$E_{\text{photon}} = hc/\lambda = \frac{6.626 \times 10^{-34}\ \text{J}\cdot\text{s}}{3.55 \times 10^{-3}\ \text{m}} \times \frac{2.998 \times 10^{8}\ \text{m}}{1\ \text{s}} = 5.5957 \times 10^{-23}$$
$$= 5.60\times10^{-23}\ \text{J/photon}$$

$$\frac{5.5957 \times 10^{-23}\ \text{J}}{1\ \text{photon}} \times \frac{3.2 \times 10^{8}\ \text{photons}}{1\ \text{s}} \times \frac{60\ \text{s}}{1\ \text{min}} \times \frac{60\ \text{min}}{1\ \text{hr}} = 6.4463 \times 10^{-11}$$

$$= 6.4 \times 10^{-11}\ \text{J/hr}$$

6.31 *Analyze/Plan.* Use $E = h\nu$ and $\nu = c/\lambda$. Calculate the desired characteristics of the photons. Assume 1 photon interacts with 1 electron. Compare E_{min} and E_{120} to calculate maximum kinetic energy of the emitted electron. *Solve.*

(a) $E = h\nu = 6.626 \times 10^{-34}\ \text{J-s} \times 1.09 \times 10^{15}\ \text{s}^{-1} = 7.22 \times 10^{-19}\ \text{J}$

(b) $\lambda = c/\nu = \dfrac{2.998 \times 10^{8}\ \text{m}}{1\ \text{s}} \times \dfrac{1\ \text{s}}{1.09 \times 10^{15}} = 2.75 \times 10^{-7}\ \text{m} = 275\ \text{nm}$

(c) $E_{120} = hc/\lambda = 6.626 \times 10^{-34}\ \text{J-s} \times \dfrac{2.998 \times 10^{8}\ \text{m}}{1\ \text{s}} \times \dfrac{1}{120\ \text{nm}} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}}$

$$= 1.655 \times 10^{-18} = 1.66 \times 10^{-18}\ \text{J}$$

The excess energy of the 120 nm photon is converted into the kinetic energy of the emitted electron.

$E_k = E_{120} - E_{min} = 16.55 \times 10^{-19}\ \text{J} - 7.22 \times 10^{-19}\ \text{J} = 9.3 \times 10^{-19}\ \text{J/electron}$

Check. E_{120} must be greater than E_{min} in order for the photon to impart kinetic energy to the emitted electron. Our calculations are consistent with this requirement.

6.32 (a) $\nu = E/h = \dfrac{4.41 \times 10^{-19}\ \text{J}}{6.626 \times 10^{-34}\ \text{J-s}} = 6.6556 \times 10^{14} = 6.66 \times 10^{14}\ \text{s}^{-1}$

(b) $\lambda = hc/E = \dfrac{6.626 \times 10^{-34}\ \text{J-s}}{4.41 \times 10^{-19}\ \text{J}} \times \dfrac{2.998 \times 10^{8}\ \text{m}}{\text{s}} = 4.50 \times 10^{-7}\ \text{m} = 450\ \text{nm}$

(c) $E_{405} = hc/\lambda = \dfrac{6.626 \times 10^{-34}\ \text{J-s}}{405 \times 10^{-9}\ \text{m}} \times \dfrac{2.998 \times 10^{8}\ \text{m}}{\text{s}} = 4.9049 \times 10^{-19} = 4.90 \times 10^{-19}\ \text{J}$

$E_K = E_{405} - E_{min} = 4.9049 \times 10^{-19}\ \text{J} - 4.41 \times 10^{-19}\ \text{J} = 0.4949 \times 10^{-19} = 4.9 \times 10^{-20}\ \text{J}$

(d) One electron is emitted per photon. Calculate the number of 405 nm photons in 1.00 μJ. The excess energy in each photon will become the kinetic energy of the electron; it cannot be "pooled" to emit additional electrons.

$$1.00\ \mu\text{J} \times \frac{1 \times 10^{-6}\ \text{J}}{\mu\text{J}} \times \frac{1\ \text{photon}}{4.9049 \times 10^{-19}\ \text{J}} \times \frac{1\ e^-}{1\ \text{photon}} = 2.04 \times 10^{12}\ \text{electrons}$$

Bohr's Model; Matter Waves (sections 6.3 and 6.4)

6.33 When applied to atoms, the notion of quantized energies means that only certain energies can be gained or lost, only certain values of ΔE are allowed. The allowed values of ΔE are represented by the lines in the emission spectra of excited atoms.

6.34 (a) According to Bohr theory, when hydrogen emits radiant energy, electrons are moving from a higher allowed energy state to a lower one. Since only certain energy states are allowed, only certain energy changes can occur. These allowed energy changes correspond ($\lambda = hc/\Delta E$) to the wavelengths of the lines in the emission spectrum of hydrogen.

(b) When a hydrogen atom changes from the ground state to an excited state, the single electron moves further away from the nucleus, so the atom "expands."

6.35 *Analyze/Plan.* An isolated electron is assigned an energy of zero; the closer the electron comes to the nucleus, the more negative its energy. Thus, as an electron moves closer to the nucleus, the energy of the electron decreases and the excess energy is emitted. Conversely, as an electron moves further from the nucleus, the energy of the electron increases and energy must be absorbed. *Solve.*

(a) As the principle quantum number decreases, the electron moves toward the nucleus and energy is emitted.

(b) An increase in the radius of the orbit means the electron moves away from the nucleus; energy is absorbed.

(c) An isolated electron is assigned an energy of zero. As the electron moves to the $n = 3$ state closer to the H^+ nucleus, its energy becomes more negative (decreases) and energy is emitted.

6.36 (a) Absorbed. (b) Emitted. (c) Absorbed.

6.37 *Analyze/Plan.* Equation 6.5: $E = (-2.18 \times 10^{-18}\ J)(1/n^2)$. *Solve.*

(a) $E_2 = -2.18 \times 10^{-18}\ J/(2)^2 = -5.45 \times 10^{-19}\ J$

$E_6 = -2.18 \times 10^{-18}\ J/(6)^2 = -6.0556 \times 10^{-20} = -0.606 \times 10^{-19}\ J$

$\Delta E = E_2 - E_6 = (-5.45 \times 10^{-19}\ J) - (-0.606 \times 10^{-19}\ J)$

$= -4.844 \times 10^{-19}\ J = -4.84 \times 10^{-19}\ J$

$$\lambda = hc/\Delta E = \frac{6.626 \times 10^{-34}\ J\text{-}s}{4.844 \times 10^{-19}\ J} \times \frac{2.998 \times 10^{8}\ m}{s} = 4.10 \times 10^{-7}\ m = 410\ nm$$

(b) The visible range is 400–700 nm, so this line is visible; the observed color is violet.

Check. We expect E_6 to be a more positive (or less negative) than E_2, and it is. ΔE is negative, which indicates emission. The orders of magnitude make sense and units are correct.

6.38 (a) $E_1 = -2.18 \times 10^{-18}\ J/(1)^2 = -2.18 \times 10^{-18}\ J$

$E_\infty = -2.18 \times 10^{-18}\ J/(\infty)^2 = 0\ J$

$\Delta E = E_\infty - E_1 = 0 - (-2.18 \times 10^{-18}\ J) = 2.18 \times 10^{-18}\ J\ /\text{electron}$

$$\frac{2.18 \times 10^{-18}\ J}{\text{electron}} \times \frac{6.022 \times 10^{23}\ \text{electrons}}{\text{mol}} \times \frac{1\ kJ}{1000\ J} = 1.31 \times 10^{3}\ kJ/mol$$

(b) The result from (a) is 1.31×10^3 kJ/mol = 1, 310 kJ/mol. Ionization energy calculated from the Bohr model agrees with the experimental result to three significant figures.

6.39 (a) Only lines with $n_f = 2$ represent ΔE values and wavelengths that lie in the visible portion of the spectrum. Lines with $n_f = 1$ have larger ΔE values and shorter wavelengths that lie in the ultraviolet. Lines with $n_f > 2$ have smaller ΔE values and lie in the lower energy longer wavelength regions of the electromagnetic spectrum.

(b) *Analyze/Plan.* Use Equation 6.7 to calculate ΔE, then $\lambda = hc/\Delta E$. *Solve.*

$$n_i = 3, n_f = 2; \quad \Delta E = -2.18 \times 10^{-18}\ J\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] = -2.18 \times 10^{-18}\ J\,(1/4 - 1/9)$$

$$\lambda = hc/E = \frac{6.626 \times 10^{-34}\ J\text{-}s \times 2.998 \times 10^{8}\ m/s}{-2.18 \times 10^{-18}\ J\,(1/4 - 1/9)} = 6.56 \times 10^{-7}\ m$$

This is the red line at 656 nm.

$$n_i = 4, n_f = 2; \quad \lambda = hc/E = \frac{6.626 \times 10^{-34}\ J\text{-}s \times 2.998 \times 10^{8}\ m/s}{-2.18 \times 10^{-18}\ J\,(1/4 - 1/16)} = 4.86 \times 10^{-7}\ m$$

This is the blue-green line at 486 nm.

$$n_i = 5, n_f = 2; \quad \lambda = hc/E = \frac{6.626 \times 10^{-34}\ J\text{-}s \times 2.998 \times 10^{8}\ m/s}{-2.18 \times 10^{-18}\ J\,(1/4 - 1/25)} = 4.34 \times 10^{-7}\ m$$

This is the blue-violet line at 434 nm.

Check. The calculated wavelengths correspond well to three lines in the H emission spectrum in Figure 6.11, so the results are sensible.

6.40 (a) Transitions with $n_f = 1$ have larger ΔE values and shorter wavelengths than those with $n_f = 2$. These transitions will lie in the ultraviolet region.

(b)
$$n_i = 2, n_f = 1; \quad \lambda = hc/E = \frac{6.626 \times 10^{-34}\ J\text{-}s \times 2.998 \times 10^{8}\ m/s}{-2.18 \times 10^{-18}\ J\,(1/1 - 1/4)} = 1.21 \times 10^{-7}\ m$$

$$n_i = 3, n_f = 1; \quad \lambda = hc/E = \frac{6.626 \times 10^{-34}\ J\text{-}s \times 2.998 \times 10^{8}\ m/s}{-2.18 \times 10^{-18}\ J\,(1/1 - 1/9)} = 1.03 \times 10^{-7}\ m$$

$$n_i = 4, n_f = 1; \quad \lambda = hc/E = \frac{6.626 \times 10^{-34}\ J\text{-}s \times 2.998 \times 10^{8}\ m/s}{-2.18 \times 10^{-18}\ J\,(1/1 - 1/16)} = 0.972 \times 10^{-7}\ m$$

6.41 (a) $93.8\ nm \times \frac{1 \times 10^{-9}\ m}{1\ nm} = 9.38 \times 10^{-8}\ m$; this line is in the ultraviolet region.

(b) *Analyze/Plan.* Only lines with $n_f = 1$ have a large enough ΔE to lie in the ultraviolet region (see Solutions 6.39 and 6.40). Solve Equation 6.7 for n_i, recalling that ΔE is negative for emission. *Solve.*

$$\frac{-hc}{\lambda} = -2.18 \times 10^{-18}\ J\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]; \quad \frac{hc}{\lambda(2.18 \times 10^{-18}\ J)} = \left[1 - \frac{1}{n_i^2}\right]$$

$$-\frac{1}{n_i^2} = \left[\frac{hc}{\lambda(2.18 \times 10^{-18}\ J)} - 1\right]; \quad \frac{1}{n_i^2} = \left[1 - \frac{hc}{\lambda(2.18 \times 10^{-18}\ J)}\right]$$

$$n_i^2 = \left[1 - \frac{hc}{\lambda(2.18 \times 10^{-18}\ J)}\right]^{-1}; \quad n_i = \left[1 - \frac{hc}{\lambda(2.18 \times 10^{-18}\ J)}\right]^{-1/2}$$

$$n_i = \left(1 - \frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{9.38 \times 10^{-8}\ \text{m} \times 2.18 \times 10^{-18}\ \text{J}}\right)^{-1/2} = 6 \text{ (n values must be integers)}$$

$n_i = 6$, $n_f = 1$

Check. From Solution 6.40, we know that $n_i > 4$ for $\lambda = 93.8$ nm. The calculated result is close to 6, so the answer is reasonable.

6.42 (a) $2626\ \text{nm} \times \dfrac{1 \times 10^{-9}\ \text{m}}{1\ \text{nm}} = 2.626 \times 10^{-6}\ \text{m}$; this line is in the infrared.

(b) Absorption lines with $n_i = 1$ are in the ultraviolet and with $n_i = 2$ are in the visible. Thus, $n_i \geq 3$, but we do not know the exact value of n_i. Calculate the longest wavelength with $n_i = 3$ ($n_f = 4$). If this is less than 2626 nm, $n_i > 3$.

$$\lambda = hc/E = \frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{-2.18 \times 10^{-18}\ \text{J}\,(1/16 - 1/9)} = 1.875 \times 10^{-6}\ \text{m}$$

This wavelength is shorter than 2.626×10^{-6} m, so $n_i > 3$; try $n_i = 4$ and solve for n_f as in Solution 6.41. Note that ΔE is positive because we are dealing with absorption.

$$n_f = \left(\frac{1}{n_i^2} - \frac{hc}{\lambda(2.18 \times 10^{-18}\ \text{J})}\right)^{-1/2} = \left(1/16 - \frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{2.626 \times 10^{-6}\ \text{m} \times 2.18 \times 10^{-18}\ \text{J}}\right)^{-1/2} = 6$$

$n_f = 6$, $n_i = 4$

6.43 *Analyze/Plan.* $\lambda = \dfrac{h}{mv}$; $1\ \text{J} = \dfrac{1\ \text{kg-m}^2}{\text{s}^2}$;

Change mass to kg and velocity to m/s in each case. *Solve.*

(a) $\dfrac{50\ \text{km}}{1\ \text{hr}} \times \dfrac{1000\ \text{m}}{1\ \text{km}} \times \dfrac{1\ \text{hr}}{60\ \text{min}} \times \dfrac{1\ \text{min}}{60\ \text{s}} = 13.89 = 14\ \text{m/s}$

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg-m}^2\text{-s}}{1\ \text{s}^2} \times \frac{1}{85\ \text{kg}} \times \frac{1\ \text{s}}{13.89\ \text{m}} = 5.6 \times 10^{-37}\ \text{m}$$

(b) $10.0\ \text{g} \times \dfrac{1\ \text{kg}}{1000\ \text{g}} = 0.0100\ \text{kg}$

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg-m}^2\text{-s}}{1\ \text{s}^2} \times \frac{1}{0.0100\ \text{kg}} \times \frac{1\ \text{s}}{250\ \text{m}} = 2.65 \times 10^{-34}\ \text{m}$$

(c) We need to calculate the mass of a single Li atom in kg.

$$\frac{6.94\ \text{g Li}}{1\ \text{mol Li}} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{Li atoms}} = 1.152 \times 10^{-26} = 1.15 \times 10^{-26}\ \text{kg}$$

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg-m}^2\text{-s}}{1\ \text{s}^2} \times \frac{1}{1.152 \times 10^{-26}\ \text{kg}} \times \frac{1\ \text{s}}{2.5 \times 10^{5}\ \text{m}} = 2.3 \times 10^{-13}\ \text{m}$$

(d) Calculate the mass of a single O_3 molecule in kg.

$$\frac{48.00\ \text{g}\ O_3}{1\ \text{mol}\ O_3} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ O_3\ \text{molecules}} = 7.971 \times 10^{-26}$$

$$= 7.97 \times 10^{-26}\ \text{kg}$$

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg-m}^2\text{-s}}{1\ \text{s}^2} \times \frac{1}{7.971 \times 10^{-26}\ \text{kg}} \times \frac{1\ \text{s}}{550\ \text{m}}$$

$$= 1.51 \times 10^{-11}\ \text{m}\ (15\ \text{pm})$$

6.44 $\lambda = h/mv$; change mass to kg and velocity to m/s

$$\text{mass of muon} = 206.8 \times 9.1094 \times 10^{-28}\ \text{g} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 1.8838 \times 10^{-28} = 1.88 \times 10^{-28}\ \text{kg}$$

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg-m}^2\text{-s}}{1\ \text{s}^2} \times \frac{1}{1.8838 \times 10^{-28}\ \text{kg}} \times \frac{1\ \text{s}}{8.85 \times 10^3\ \text{m/s}} = 3.97 \times 10^{-10}\ \text{m}$$

$$= 3.97\ \text{Å}$$

6.45 *Analyze/Plan.* Use $v = h/m\lambda$; change wavelength to meters and mass of neutron (back inside cover) to kg. *Solve.*

$$\lambda = 0.955\ \text{Å} \times \frac{1 \times 10^{-10}\ \text{m}}{1\ \text{Å}} = 0.955 \times 10^{-10}\ \text{m};\ m = 1.6749 \times 10^{-27}\ \text{kg}$$

$$v = \frac{6.626 \times 10^{-34}\ \text{kg-m}^2\text{-s}}{1\ \text{s}^2} \times \frac{1}{1.6749 \times 10^{-27}\ \text{kg}} \times \frac{1}{0.955 \times 10^{-10}\ \text{m}} = 4.14 \times 10^3\ \text{m/s}$$

Check. $(6.6/1.6/1) \times (10^{-34}/10^{-27}/10^{-10}) \approx 4 \times 10^3$ m/s

6.46 $m_e = 9.1094 \times 10^{-31}$ kg (back inside cover of text)

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{kg-m}^2\text{-s}}{1\ \text{s}^2} \times \frac{1}{9.1094 \times 10^{-31}\ \text{kg}} \times \frac{1\ \text{s}}{8.95 \times 10^6\ \text{m}} = 8.13 \times 10^{-11}\ \text{m}$$

$$8.13 \times 10^{-11}\ \text{m} \times \frac{1\ \text{Å}}{1 \times 10^{-10}\ \text{m}} = 0.813\ \text{Å}$$

Since atomic radii and interatomic distances are on the order of 1–5 Å (Section 2.3), the wavelength of this electron is comparable to the size of atoms.

6.47 *Analyze/Plan.* Use $\Delta x \geq h/4\pi\, m\, \Delta v$, paying attention to appropriate units. Note that the uncertainty in speed of the particle (Δv) is important, rather than the speed itself. *Solve.*

(a) $$m = 1.50\ \text{mg} \times \frac{1\ \text{g}}{1000\ \text{mg}} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 1.50 \times 10^{-6}\ \text{kg};\ \Delta v = 0.01\ \text{m/s}$$

$$\Delta x \geq = \frac{6.626 \times 10^{-34}\ \text{J-s}}{4\pi(1.50 \times 10^{-6}\ \text{kg})(0.01\ \text{m/s})} \geq 3.52 \times 10^{-27} = 4 \times 10^{-27}\ \text{m}$$

(b) $$m = 1.673 \times 10^{-24}\ \text{g} = 1.673 \times 10^{-27}\ \text{kg};\ \Delta v = 0.01 \times 10^4\ \text{m/s}$$

$$\Delta x \geq = \frac{6.626 \times 10^{-34}\ \text{J-s}}{4\pi(1.673 \times 10^{-27}\ \text{kg})(0.01 \times 10^4\ \text{m/s})} \geq 3 \times 10^{-10}\ \text{m}$$

Check. The more massive particle in (a) has a much smaller uncertainty in position.

6.48 $\Delta x \geq = h/4\pi m \Delta v$; use masses in kg, Δv in m/s.

(a) $$\frac{6.626 \times 10^{-34}\ \text{J-s}}{4\pi(9.109 \times 10^{-31}\ \text{kg})(0.01 \times 10^{5}\ \text{m/s})} = 6 \times 10^{-8}\ \text{m}$$

(b) $$\frac{6.626 \times 10^{-34}\ \text{J-s}}{4\pi(1.675 \times 10^{-27}\ \text{kg})(0.01 \times 10^{5}\ \text{m/s})} = 3 \times 10^{-11}\ \text{m}$$

(c) For particles moving with the same uncertainty in velocity, the more massive neutron has a much smaller uncertainty in position than the lighter electron. In our model of the atom, we know where the massive particles in the nucleus are located, but we cannot know the location of the electrons with any certainty, if we know their speed.

Quantum Mechanics and Atomic Orbitals (sections 6.5 and 6.6)

6.49 (a) The uncertainty principle states that there is a limit to how precisely we can simultaneously know the position and momentum (related to energy) of an electron. The Bohr model states that electrons move about the nucleus in precisely circular orbits of known radius; each permitted orbit has an allowed energy associated with it. Thus, according to the Bohr model, we can know the exact distance of an electron from the nucleus and its energy. This violates the uncertainty principle.

(b) De Broglie stated that electrons demonstrate the properties of both particles and waves, that each particle has a wave associated with it. A wave function is the mathematical description of the matter wave of an electron.

(c) Although we cannot predict the exact location of an electron in an allowed energy state, we can determine the likelihood or probability of finding an electron at a particular position (or within a particular volume). This statistical knowledge of electron location is called the *probability density* or electron density and is a function of ψ^2, the square of the wave function ψ.

6.50 (a) The Bohr model states with 100% certainty that the electron in hydrogen can be found 0.53 Å from the nucleus. The quantum mechanical model, taking the wave nature of the electron and the uncertainty principle into account, is a statistical model that states the probability of finding the electron in certain regions around the nucleus. While 0.53 Å might be the radius with highest probability, that probability would always be less than 100%.

(b) The equations of classical physics predict the instantaneous position, direction of motion, and speed of a macroscopic particle; they do not take quantum theory or the wave nature of matter into account. For macroscopic particles, these are not significant, but for microscopic particles like electrons, they are crucial. Schrödinger's equation takes these important theories into account to produce a statistical model of electron location given a specific energy.

(c) The square of the wave function has the physical significance of an amplitude, or probability. The quantity ψ^2 at a given point in space is the probability of locating the electron within a small volume element around that point at any given instant. The total probability, that is, the sum of ψ^2 over all the space around the nucleus, must equal 1.

6.51 (a) The possible values of l are $(n - 1)$ to 0. $n = 4$, $l = 3, 2, 1, 0$

(b) The possible values of m_l are $-l$ to $+l$. $l = 2$, $m_l = -2, -1, 0, 1, 2$

(c) Since the value of m_l is less than or equal to the value of l, $m_l = 2$ must have an l-value greater than or equal to 2. In terms of elements that have been observed, the possibilities are 2, 3 and 4.

6.52 (a) For $n = 3$, there are three l values (2, 1, 0) and nine m_l values ($l = 2$; $m_l = -2, -1, 0, 1, 2$; $l = 1$, $m_l = -1, 0, 1$; $l = 0$, $m_l = 0$).

(b) For $n = 5$, there are five l values (4, 3, 2, 1, 0) and twenty-five m_l values ($l = 4$, $m_l = -4$ to $+4$; $l = 3$, $m_l = -3$ to $+3$; $l = 2$, $m_l = -2$ to $+2$; $l = 1$, $m_l = -1$ to $+1$; $l = 0$, $= 0$).

In general, for each principal quantum number n there are n l-values and n^2 m_l-values. For each shell, there are n kinds of orbitals and n^2 total orbitals.

6.53 (a) 3p: $n = 3$, $l = 1$ (b) 2s: $n = 2$, $l = 0$

(c) 4f: $n = 4$, $l = 3$ (d) 5d: $n = 5$, $l = 2$

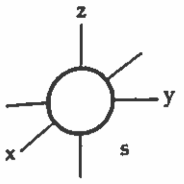
6.54 (a) 2, 1, 1; 2, 1, 0; 2, 1, −1 (b) 5, 2, 2; 5, 2, 1; 5, 2, 0; 5, 2, −1; 5, 2, −2

6.55 Impossible: (a) 1p, only $l = 0$ is possible for $n = 1$; (d) 2d, for $n = 2$, $l = 1$ or 0, but not 2

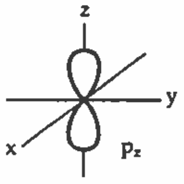
6.56

n	l	m_l	orbital
2	1	−1	2p (example)
1	0	0	1s
3	−3	2	not allowed ($l < n$ and + only)
3	2	−2	3d
2	0	−1	not allowed ($m_l = -l$ to $+l$)
0	0	0	not allowed ($n \neq 0$)
4	2	1	4d
5	3	0	5f

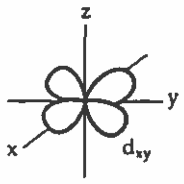
6.57



(a)

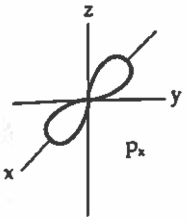


(b)

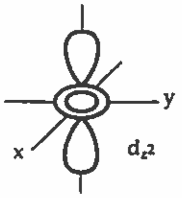


(c)

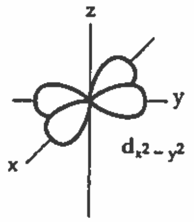
6.58



(a)



(b)



(c)

6.59 (a) The 1s and 2s orbitals of a hydrogen atom have the same overall spherical shape. The 2s orbital has a larger radial extension and one node, while the 1s orbital has continuous electron density. Since the 2s orbital is "larger," there is greater probability of finding an electron further from the nucleus in the 2s orbital.

(b) A single 2p orbital is directional in that its electron density is concentrated along one of the three Cartesian axes of the atom. The $d_{x^2-y^2}$ orbital has electron density along both the x- and y-axes, while the p_x orbital has density only along the x-axis.

(c) The average distance of an electron from the nucleus in a 3s orbital is greater than for an electron in a 2s orbital. In general, for the same kind of orbital, the larger the *n* value, the greater the average distance of an electron from the nucleus of the atom.

(d) 1s < 2p < 3d < 4f < 6s. In the hydrogen atom, orbitals with the same *n* value are degenerate and energy increases with increasing *n* value. Thus, the order of increasing energy is given above.

6.60 (a) In an s orbital, there are $(n - 1)$ nodes.

(b) The $2p_x$ orbital has one node (the yz plane passing through the nucleus of the atom). The 3s orbital has two nodes.

(c) Probability density, $\psi^2(r)$, is the probability of finding an electron at a single point, r. The radial probability function, P(r), is the probability of finding an electron at any point that is distance r from the nucleus. Figure 6.18 contains plots of P(r) vs. r for 1s, 2s, and 3s orbitals. The most obvious features of these plots are the radii of maximum probability for the three orbitals, and the number and location of nodes for the three orbitals.

By comparing plots for the three orbitals, we see that as n increases, the number of nodes increases and the radius of maximum probability (orbital size) increases.

(d) 2s = 2p < 3s < 4d < 5s. In the hydrogen atom, orbitals with the same *n* value are degenerate and energy increases with increasing *n* value.

Many-Electron Atoms and Electron Configurations (sections 6.7 – 6.9)

6.61 (a) In the hydrogen atom, orbitals with the same principle quantum number, *n*, have the same energy; they are degenerate.

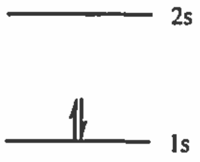
(b) In a many-electron atom, for a given *n*-value, orbital energy increases with increasing *l*-value: s < p < d < f.

6.62 (a) The electron with the greater average distance from the nucleus feels a smaller attraction for the nucleus and is higher in energy. Thus the 3p is higher in energy than 3s.

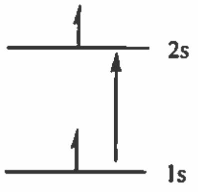
(b) Because it has a larger *n* value, a 3s electron has a greater average distance from the chlorine nucleus than a 2p electron. The 3s electron experiences a smaller attraction for the nucleus and requires less energy to remove from the chlorine atom.

6.63 (a) There are two main pieces of experimental evidence for electron "spin": the Stern-Gerlach experiment and line spectra of multi-electron atoms. The Stern-Gerlach experiment shows that a beam of neutral Ag atoms passed through a nonhomogeneous magnetic field is deflected equally in two directions. This shows that atoms with a single unpaired electron interact differently with the magnetic field and suggests that there are two and only two values for an atom's own magnetic field. Examination of the fine details of emission line-spectra of multi-electron atoms reveals that each line is really a close pair of lines. Both observations can be rationalized if electrons have the property of spin.

(b) Note that 2 electrons in the same orbital have opposite spin; this is called spin-pairing.



(c)



6.64 (a) The Pauli exclusion principle states that no two electrons can have the same four quantum numbers.

(b) An alternate statement of the Pauli exclusion principle is that a single orbital can hold a maximum of two electrons. Thus, the Pauli principle limits the maximum number of electrons in a main shell and its subshells, which determines when a new row of the periodic table begins.

6.65 *Analyze/Plan.* Each subshell has an l-value associated with it. For a particular l-value, permissible m_l-values are $-l$ to $+l$. Each m_l-value represents an orbital, which can hold two electrons. *Solve.*

(a) 6 (b) 10 (c) 2 (d) 14

6.66 (a) 4 (b) 14 (c) 2 (d) 2

6.67 (a) "Valence electrons" are those involved in chemical bonding. They are part (or all) of the outer-shell electrons listed after core electrons in a condensed electron configuration.

(b) "Core electrons" are inner shell electrons that have the electron configuration of the nearest noble-gas element.

(c) Each box represents an orbital.

(d) Each half-arrow in an orbital diagram represents an electron. The direction of the half-arrow represents electron spin.

6.68

Element	(a) C	(b) P	(c) Ne
Electron Configuration	$[He]2s^22p^2$	$[Ne]3s^23p^3$	$[He]2s^22p^6$
Core electrons	2	10	2
Valence electrons	4	5	8
Unpaired electrons	2	3	0

[The concept of "valence electrons" for noble gas elements is problematic, since they are mostly unreactive. We could list the core for neon as [Ne], with no valence or unpaired electrons.]

6.69 *Analyze/Plan.* Follow the logic in Sample Exercise 6.9. *Solve.*

(a) Cs: $[Xe]6s^1$

(b) Ni: $[Ar]4s^23d^8$

(c) Se: $[Ar]4s^23d^{10}4p^4$

(d) Cd: $[Kr]5s^24d^{10}$

(e) U: $[Rn]5f^36d^17s^2$. (Note the U and several other *f*-block elements have irregular *d*- and *f*-electron orders.)

(f) Pb: $[Xe]6s^24f^{14}5d^{10}6p^2$

6.70 (a) Mg: $[Ne]3s^2$, 0 unpaired electrons

(b) Ge: $[Ar]4s^23d^{10}4p^2$, 2 unpaired electrons

(c) Br: $[Ar]4s^23d^{10}4p^5$, 1 unpaired electron

(d) V: $[Ar]4s^23d^3$, 3 unpaired electrons

(e) Y: $[Kr]5s^24d^1$, 1 unpaired electron

(f) Lu: $[Xe]6s^24f^{14}5d^1$, 1 unpaired electron

6.71 (a) Be, 0 unpaired electrons

(b) O, 2 unpaired electrons

(c) Cr, 6 unpaired electrons

(d) Te, 2 unpaired electrons

6.72 (a) 7A (halogens), 1 unpaired electron

(b) 4B, 2 unpaired electrons

(c) 3A (row 4 and below), 1 unpaired electron

(d) the f-block elements Sm and Pu, 6 unpaired electrons

6.73 (a) The fifth electron would fill the 2p subshell (same *n*-value as 2s) before the 3s.

(b) The Ne core has filled 2s and 2p subshells. Either the core is [He] or the outer electron configuration should be $3s^23p^3$.

(c) The 3p subshell would fill before the 3d because it has the lower *l*-value and the same *n*-value. (If there were more electrons, 4s would also fill before 3d.)

6.74 Count the total number of electrons to assign the element.

(a) N: $[He]2s^22p^3$ (b) Se: $[Ar]4s^23d^{10}4p^4$ (c) Rh: $[Kr]5s^24d^7$

Additional Exercises

6.75 (a) $\lambda_A = 1.6 \times 10^{-7}\ \text{m} / 4.5 = 3.56 \times 10^{-8} = 3.6 \times 10^{-8}\ \text{m}$

$\lambda_B = 1.6 \times 10^{-7}\ \text{m} / 2 = 8.0 \times 10^{-8}\ \text{m}$

(b) $\nu = c/\lambda;\ \nu_A = \dfrac{2.998 \times 10^8\ \text{m}}{1\ \text{s}} \times \dfrac{1}{3.56 \times 10^{-8}\ \text{m}} = 8.4 \times 10^{15}\ \text{s}^{-1}$

$\nu_B = \dfrac{2.998 \times 10^8\ \text{m}}{1\ \text{s}} \times \dfrac{1}{8.0 \times 10^{-8}\ \text{m}} = 3.7 \times 10^{15}\ \text{s}^{-1}$

(c) A: ultraviolet, B: ultraviolet

6.76 (a) $\nu = c/\lambda = \dfrac{2.998 \times 10^8\ \text{m}}{\text{s}} \times \dfrac{1}{589\ \text{nm}} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 5.0900 \times 10^{14}$

$= 5.09 \times 10^{14}\ s^{-1}$

(b) $E = h\nu = 6.626 \times 10^{-34}\ \text{J-s} \times 5.0900 \times 10^{14}\ s^{-1} \times \dfrac{6.022 \times 10^{23}\ \textit{photons}}{\text{mol}}$

$\times\ 0.1\ \text{mol} = 2.03 \times 10^4\ \text{J} = 20.3\ \text{kJ}$

(c) $\Delta E = h\nu = \dfrac{hc}{\lambda} = \dfrac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^8\ \text{m/s}}{589\ nm} \times \dfrac{1\ nm}{1 \times 10^{-9}\ m}$

$= 3.37 \times 10^{-19}\ \text{J}$

(d) The 589 nm light emission is characteristic of Na^+. If the pickle is soaked in a different salt long enough to remove all Na^+, the 589 nm light would not be observed. Emission at a different wavelength, characteristic of the new salt, would be observed.

6.77 (a) Elements that emit in the visible: Ba (blue), Ca (violet-blue), K (violet), Na (yellow/orange). (The other wavelengths are in the ultraviolet.)

(b) Au: shortest wavelength, highest energy

Na: longest wavelength, lowest energy

(c) $\lambda = c/\nu = \dfrac{2.998 \times 10^8 \text{ m/s}}{6.59 \times 10^{14}\text{/s}} \times \dfrac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = 455 \text{ nm}$, Ba

6.78 All electromagnetic radiation travels at the same speed, 2.998×10^8 m/s. Change miles to meters and seconds to some appropriate unit of time.

$$746 \times 10^6 \text{ mi} \times \frac{1.6093 \text{ km}}{1 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} \times \frac{1 \text{ s}}{2.998 \times 10^8 \text{ m}} \times \frac{1 \text{ min}}{60 \text{ s}} = 66.7 \text{ min}$$

6.79 (a) $\nu = c/\lambda = \dfrac{2.998 \times 10^8 \text{ m/s}}{320 \text{ nm}} \times \dfrac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = 9.37 \times 10^{14} \text{ s}^{-1}$

(b) $E = hc/\lambda = \dfrac{6.626 \times 10^{-34} \text{ J-s} \times 2.998 \times 10^8 \text{ m/s}}{3.20 \times 10^{-7} \text{ m}} \times \dfrac{1 \text{ kJ}}{1000 \text{ J}} \times \dfrac{6.022 \times 10^{23} \text{ photons}}{\text{mole}}$

$= 374$ kJ/mol

(c) UV-B photons have shorter wavelength and higher energy.

(d) Yes. The higher energy UV-B photons would be more likely to cause sunburn.

6.80 $E = hc/\lambda \rightarrow$ J/photon; total energy = power × time; photons = total energy / J / photon

$$E = \frac{6.626 \times 10^{-34} \text{ J-s} \times 2.998 \times 10^8 \text{ m/s}}{780 \times 10^{-9} \text{ m}} = 2.5468 \times 10^{-19} = 2.55 \times 10^{-19} \text{ J/photon}$$

$$0.10 \text{ mW} = \frac{0.10 \times 10^{-3} \text{ J}}{1 \text{ s}} \times 69 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 0.4140 = 0.41 \text{ J}$$

$$0.4140 \text{ J} \times \frac{1 \text{ photon}}{2.5468 \times 10^{-19} \text{ J}} = 1.626 \times 10^{18} = 1.6 \times 10^{18} \text{ photons}$$

6.81 (a) If a plant appears orange, it absorbs the complementary (opposite) color on the color wheel. The plant most strongly absorbs blue light in the range 430-490 nm.

(b) $E = hc/\lambda = \dfrac{6.626 \times 10^{-34} \text{ J-s}}{455 \text{ nm}} \times \dfrac{2.998 \times 10^8 \text{ m}}{1 \text{ s}} \times \dfrac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = 4.37 \times 10^{-19} \text{ J}$

6.82 $\dfrac{2.6 \times 10^{-12} \text{ C}}{1 \text{ s}} \times \dfrac{1 \text{ e}^-}{1.602 \times 10^{-19} \text{ C}} \times \dfrac{1 \text{ photon}}{1 \text{ e}^-} = 1.623 \times 10^7 = 1.6 \times 10^7$ photons/s

$$\frac{E}{\text{photon}} = hc/\lambda = \frac{6.626 \times 10^{-34} \text{ J-s}}{630 \text{ nm}} \times \frac{2.998 \times 10^8 \text{ m}}{1 \text{ s}} \times \frac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} \times \frac{1.623 \times 10^7 \text{ photon}}{\text{s}}$$

$= 5.1 \times 10^{-12}$ J/s

6.83 (a) $\nu = c/\lambda; \quad \dfrac{2.998 \times 10^8 \text{ m}}{\text{s}} \times \dfrac{1}{680 \text{ nm}} \times \dfrac{1 \text{ nm}}{1 \times 10^{-9} \text{ m}} = 4.4088 \times 10^{14} = 4.41 \times 10^{14} \text{ s}^{-1}$

(b) Calculate J/photon using $E = hc/\lambda$; change to kJ/mol.

$$E_{\text{photon}} = \frac{6.626 \times 10^{-34} \text{ J-s}}{680 \times 10^{-9} \text{ m}} \times \frac{2.998 \times 10^8 \text{ m}}{\text{s}} = 2.9213 \times 10^{-19} = 2.92 \times 10^{-19} \text{ J/photon}$$

$$\frac{2.9213 \times 10^{-19} \text{ J}}{\text{photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 175.92 = 176 \text{ kJ/mol}$$

(c) Nothing. The incoming (incident) radiation does not transfer sufficient energy to an electron to overcome the attractive forces holding the electron in the metal.

(d) For frequencies greater than ν_o, any "extra" energy not needed to remove the electron from the metal becomes the kinetic energy of the ejected electron. The kinetic energy of the electron is directly proportional to this extra energy.

(e) Yes. Let E_{total} be the total energy of an incident photon, E_{min} be the minimum energy required to eject an electron, and E_k be the "extra" energy that becomes the kinetic energy of the ejected electron.

$E_{\text{total}} = E_{\text{min}} + E_k$, $E_k = E_{\text{total}} - E_{\text{min}} = h\nu - h\nu_o$, $E_k = h(\nu - \nu_o)$. The slope of the line is the value of h, Planck's constant.

6.84 (a) "blue" cone, $\lambda_{\text{max}} = 450 \text{ nm} = 450 \times 10^{-9} \text{ m}$

$$E = hc/\lambda = \frac{6.626 \times 10^{-34} \text{ J-s}}{450 \times 10^{-9} \text{ m}} \times \frac{2.998 \times 10^8 \text{ m}}{1 \text{ s}} = 4.41 \times 10^{-19} \text{ J}$$

"green" cone, $\lambda_{\text{max}} = 450 \text{ nm} = 450 \times 10^{-9} \text{ m}$

$$E = hc/\lambda = \frac{6.626 \times 10^{-34} \text{ J-s}}{545 \times 10^{-9} \text{ m}} \times \frac{2.998 \times 10^8 \text{ m}}{1 \text{ s}} = 3.64 \times 10^{-19} \text{ J}$$

"red" cone, $\lambda_{\text{max}} = 585 \text{ nm} = 585 \times 10^{-9} \text{ m}$

$$E = hc/\lambda = \frac{6.626 \times 10^{-34} \text{ J-s}}{585 \times 10^{-9} \text{ m}} \times \frac{2.998 \times 10^8 \text{ m}}{1 \text{ s}} = 3.40 \times 10^{-19} \text{ J}$$

(b) $\text{"blue" scattering efficiency} = \left(\dfrac{1}{450}\right)^4; \quad \text{"green" scattering efficiency} = \left(\dfrac{1}{545}\right)^4$

$$\text{ratio of "blue" to "green"} = \frac{\left(\dfrac{1}{450 \text{ nm}}\right)^4}{\left(\dfrac{1}{545 \text{ nm}}\right)^4} \times \left(\frac{545}{450}\right)^4 = 2.15$$

(c) Mainly, the shorter wavelengths perceived by the "blue" cone are scattered more efficiently, so there is more of the blue light to see. Also, the amplitude of the absorption curve for the "blue" cone is greater than the amplitudes of the other two curves. This indicates that our eyes are more sensitive to blue light than the other wavelengths. (It is also true that the intensities of the different wavelengths reaching Earth are not the same, but this information is not conveyed in the exercise.)

6.85 (a) Lines with $n_f = 1$ lie in the ultraviolet (see Solution 6.40) and with $n_f = 2$ lie in the visible (see Solution 6.39). Lines with $n_f = 3$ will have smaller ΔE and longer wavelengths and lie in the infrared.

(b) Use Equation 6.7 to calculate ΔE, then $\lambda = hc/\Delta E$.

$$n_i = 4, n_f = 3; \Delta E = -2.18 \times 10^{-18}\ \text{J}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] = -2.18 \times 10^{-18}\ \text{J}\ (1/9 - 1/16)$$

$$\lambda = hc/E = \frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{-2.18 \times 10^{-18}\ (1/9 - 1/16)} = 1.87 \times 10^{-6}\ \text{m}$$

$$n_i = 5, n_f = 3; \lambda = hc/E = \frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{-2.18 \times 10^{-18}\ (1/9 - 1/25)} = 1.28 \times 10^{-6}\ \text{m}$$

$$n_i = 6, n_f = 3; \lambda = hc/E = \frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{-2.18 \times 10^{-18}\ (1/9 - 1/36)} = 1.09 \times 10^{-6}\ \text{m}$$

These three wavelengths are all greater than 1 μm or 1×10^{-6} m. They are in the infrared, close to the visible edge (0.7×10^{-6} m).

6.86 (a) Gaseous atoms of various elements in the sun's atmosphere typically have ground state electron configurations. When these atoms are exposed to radiation from the sun, the electrons change from the ground state to one of several allowed excited states. Atoms absorb the wavelengths of light which correspond to these allowed energy changes. All other wavelengths of solar radiation pass through the atmosphere unchanged. Thus, the dark lines are the wavelengths that correspond to allowed energy changes in atoms of the solar atmosphere. The continuous background is all other wavelengths of solar radiation.

(b) The scientist should record the absorption spectrum of pure neon or other elements of interest. The Fraunhofer lines that belong to a particular element will appear at the same wavelength as the lines in the absorption spectrum of that element.

6.87 (a) He^+ is hydrogen-like because it is a one-electron particle. An He atom has two electrons. The Bohr model is based on the interaction of a single electron with the nucleus, but does not accurately account for additional interactions when two or more electrons are present.

(b) Divide each energy by the smallest value to find the integer relationship.

H: $-2.18 \times 10^{-18} / -2.18 \times 10^{-18} = 1;\ Z = 1$

He^+: $-8.72 \times 10^{-18} / -2.18 \times 10^{-18} = 4;\ Z = 2$

Li^{2+}: $-1.96 \times 10^{-17} / -2.18 \times 10^{-18} = 9;\ Z = 3$

The ground-state energies are in the ratio of 1:4:9, which is also the ratio Z^2, the square of the nuclear charge for each particle.

The ground state energy for hydrogen-like particles is:

$E = R_H Z^2$. (By definition, n = 1 for the ground state of a one-electron particle.)

(c) $Z = 6$ for C^{5+}. $E = -2.18 \times 10^{-18}\ \text{J}\ (6)^2 = -7.85 \times 10^{-17}\ \text{J}$

6.88 *Plan.* Change keV to J/electron. Calculate v from kinetic energy. $\lambda = h/mv$. *Solve.*

$$18.6\ \text{keV} \times \frac{1000\ \text{eV}}{\text{keV}} \times \frac{96.485\ \text{kJ}}{1\ \text{eV}\cdot\text{mol}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{electrons}}$$
$$= 2.980 \times 10^{-15} = 2.98 \times 10^{-15}\ \text{J/electron}$$

$$E_k = mv^2/2;\ v^2 = 2E_k/m;\ v = \sqrt{2E_k/m}$$

$$v = \left(\frac{2 \times 2.980 \times 10^{-15}\ \text{kg}\cdot\text{m}^2/\text{s}^2}{9.1094 \times 10^{-31}\ \text{kg}}\right)^{1/2} = 8.089 \times 10^7 = 8.09 \times 10^7\ \text{m/s}$$

$$\lambda = h/mv = \frac{6.626 \times 10^{-34}\ \text{J-s}}{9.1094 \times 10^{-31}\ \text{kg} \times 8.089 \times 10^7\ \text{m/s}} \times \frac{1\ \text{kg}\cdot\text{m}^2/\text{s}^2}{1\ \text{J}} = 8.99 \times 10^{-12}\ \text{m} = 8.99\ \text{pm}$$

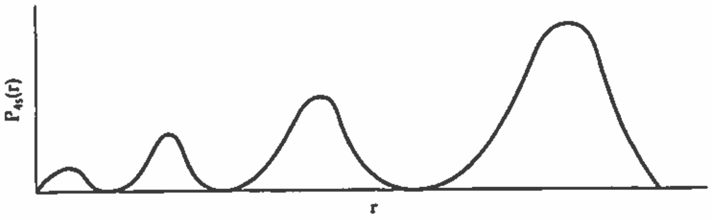
6.89 Heisenberg postulated that the dual nature of matter places a limitation on how precisely we can know both the position and momentum of an object. This limitation is significant at the subatomic particle level. The *Star Trek* transporter (presumably) disassembles humans into their protons, neutrons and electrons, moves the particles at high speed (possibly the speed of light) to a new location, and reassembles the particles into the human. Heisenberg's uncertainty principle indicates that if we know the momentum (*mv*) of the moving particles, we can't precisely know their position (*x*). If a few of the subatomic particles don't arrive in exactly the correct location, the human would not be reassembled in their original form. So, the "Heisenberg compensator" is necessary to make sure that the transported human arrives at the new location intact.

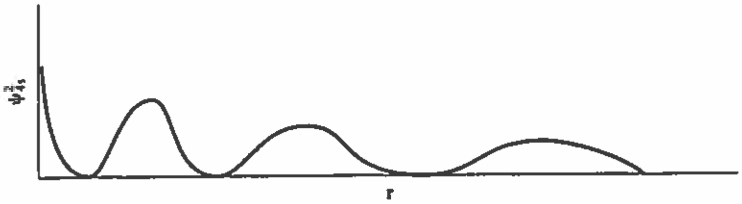
6.90 (a) l (b) n and l (c) m_s (d) m_l

6.91 (a) Probability density, $[\psi(r)]^2$, is the probability of finding an electron at a single point at distance r from the nucleus. The radial probability function, $4\pi r^2$, is the probability of finding an electron at any point on the sphere defined by radius r. $P(r) = 4\pi r^2[\psi(r)]^2$.

(b) The term $4\pi r^2$ explains the differences in plots of the two functions. Plots of the probability density, $[\psi(r)^2]$ for s orbitals shown in Figure 6.21 each have their maximum value at $r = 0$, with $(n - 1)$ smaller maxima at greater values of r. The plots of radial probability, P(r), for the same s orbitals shown in Figure 6.18 have values of zero at $r = 0$ and the size of the maxima increases. P(r) is the product of $[\psi(r)]^2$ and $4\pi r^2$. At $r = 0$, the value of $[\psi(r)]^2$ is finite and large, but the value of $4\pi r^2$ is zero, so the value of P(r) is zero. As r increases, the values of $[\psi(r)]^2$ vary as shown in Figure 6.21, but the values of $4\pi r^2$ increase continuously, leading to the increasing size of P(r) maxima as r increases.

(c)





6.92 (a) The p_z orbital has a nodal plane where $z = 0$. This is the xy plane.

(b) The d_{xy} orbital has four lobes and two nodal planes, the two planes where $x = 0$ and $y = 0$. These are the yz and xz planes.

(c) The $d_{x^2-y^2}$ has four lobes and two nodal planes, the planes where $x^2 - y^2 = 0$. These are the planes that bisect the x and y axes and contain the z axis.

6.93 (a) This is the frequency of radiowaves that excite the nuclei from one spin state to the other.

(b) $\Delta E = h\nu = 6.626 \times 10^{-34}\ \text{J-s} \times \dfrac{450 \times 10^6}{\text{s}} = 2.98 \times 10^{-25}\ \text{J}$

(c) Since $\Delta E = 0$ in the absence of a magnetic field, it is reasonable to assume that the stronger the external field, the greater ΔE. (In fact, ΔE is directly proportional to field strength). Because ΔE is relatively small [see part (b)], the two spin states are almost equally populated, with a very slight excess in the lower energy state. The stronger the magnetic field, the larger ΔE, the greater number of nuclei in the lower energy spin state. With more nuclei in the lower energy state, more are able to absorb the appropriate radio wave photons and reach the higher energy state. This increases the intensity of the NMR signal, which provides more information and more reliable information than a weak absorption signal.

6.94 If m_s had three allowed values instead of two, each orbital would hold three electrons instead of two. Assuming that the same orbitals are available (that there is no change in the n, l, and m_l values), the number of elements in each of the first four rows would be:

1st row:	1 orbital × 3 = 3 elements
2nd row:	4 orbitals × 3 = 12 elements
3rd row:	4 orbitals × 3 = 12 elements
4th row:	9 orbitals × 3 = 27 elements

The s-block would be 3 columns wide, the p-block 9 columns wide and the d-block 15 columns wide.

6.95 (a) Si: [Ne]$3s^2 3p^2$, 2 unpaired electrons

(b) Zn: [Ar]$4s^2 3d^{10}$, 0 unpaired electrons

(c) Zr: [Kr]$5s^2 4d^2$, 2 unpaired electrons

(d) Sn: [Kr]$5s^2 4d^{10} 5p^2$, 2 unpaired electrons

(e) Ba: [Xe]$6s^2$, 0 unpaired electrons

(f) Tl: [Xe]$6s^2 4f^{14} 5d^{10} 6p^1$, 1 unpaired electrons

6.96 The core would be the electron configuration of element 118. If no new subshell begins to fill, the condensed electron configuration of element 126 would be similar to those of elements vertically above it on the periodic chart, Pu and Sm. The condensed configuration would be [118]$8s^2 6f^6$. On the other hand, the 5g subshell could begin to fill after 8s, resulting in the condensed configuration [118]$8s^2 5g^6$. Exceptions are also possible (likely).

Integrative Exercises

6.97 (a) We know the wavelength of microwave radiation, the volume of coffee to be heated, and the desired temperature change. Assume the density and heat capacity of coffee are the same as pure water. We need to calculate: (i) the total energy required to heat the coffee and (ii) the energy of a single photon in order to find (iii) the number of photons required.

(i) From Chapter 5, the heat capacity of liquid water is 4.184 J/g°C.

To find the mass of 200 mL of coffee at 23°C, use the density of water given in Appendix B.

$$200 \text{ mL} \times \frac{0.997 \text{ g}}{1 \text{ mL}} = 199.4 = 199 \text{ g coffee}$$

$$\frac{4.184 \text{ J}}{1 \text{ g °C}} \times 199.4 \text{ g} \times (60°\text{C} - 23°\text{C}) = 3.087 \times 10^4 \text{ J} = 31 \text{ kJ}$$

(ii) $$E = hc/\lambda = 6.626 \times 10^{-34} \text{ J-s} \times \frac{2.998 \times 10^8 \text{ m}}{1 \text{ s}} \times \frac{1}{0.112 \text{ m}}$$

$$= \frac{1.77 \times 10^{-24} \text{ J}}{1 \text{ photon}}$$

(iii) $$3.087 \times 10^4 \text{ J} \times \frac{1 \text{ photon}}{1.774 \times 10^{-24} \text{ J}} = 1.7 \times 10^{28} \text{ photons}$$

(The answer has 2 sig figs because the temperature change, 37°C, has 2 sig figs.)

(b) 1 W = 1 J/s. 900 W = 900 J/s. From part (a), 31 kJ are required to heat the coffee.

$$3.087 \times 10^4 \text{ J} \times \frac{1 \text{ s}}{900 \text{ J}} = 34.30 = 34 \text{ s}$$

6.98 $$\Delta H^\circ_{rxn} = \Delta H^\circ_f\ O_2(g) + \Delta H^\circ_f\ O(g) - \Delta H^\circ_f\ O_3(g)$$

$$\Delta H^\circ_{rxn} = 0 + 247.5\ \text{kJ} - 142.3\ \text{kJ} = +105.2\ \text{kJ}$$

$$\frac{105.2\ \text{kJ}}{\text{mol}\ O_3} \times \frac{1\ \text{mol}\ O_3}{6.022 \times 10^{23}\ \text{molecules}} \times \frac{1000\ \text{J}}{1\ \text{kJ}} = \frac{1.747 \times 10^{-19}\ \text{J}}{O_3\ \text{molecule}}$$

$$\Delta E = hc/\lambda;\ \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34}\ \text{J-s} \times 2.998 \times 10^{8}\ \text{m/s}}{1.747 \times 10^{-19}\ \text{J}} = 1.137 \times 10^{-6}\ \text{m}$$

Radiation with this wavelength is in the infrared portion of the spectrum. (Clearly, processes other than simple photodissociation cause O_3 to absorb ultraviolet radiation.)

6.99 (a) The electron configuration of Zr is $[Kr]5s^2 4d^2$ and that of Hf is $[Xe]6s^2 4f^{14} 5d^2$. Although Hf has electrons in f orbitals as the rare earth elements do, the 4f subshell in Hf is filled, and the 5d electrons primarily determine the chemical properties of the element. Thus, Hf should be chemically similar to Zr rather than the rare earth elements.

(b) $ZrCl_4(s) + 4Na(l) \rightarrow Zr(s) + 4NaCl(s)$

This is an oxidation-reduction reaction; Na is oxidized and Zr is reduced.

(c) $2ZrO_2(s) + 4Cl_2(g) + 3C(s) \rightarrow 2ZrCl_4\ (s) + CO_2(g) + 2CO(g)$

$$55.4\ \text{g}\ ZrO_2 \times \frac{1\ \text{mol}\ ZrO_2}{123.2\ \text{g}\ ZrO_2} \times \frac{2\ \text{mol}\ ZrCl_4}{2\ \text{mol}\ ZrO_2} \times \frac{233.0\ \text{g}\ ZrCl_4}{1\ \text{mol}\ ZrCl_4} = 105\ \text{g}\ ZrCl_4$$

(d) In ionic compounds of the type MCl_4 and MO_2, the metal ions have a 4+ charge, indicating that the neutral atoms have lost four electrons. Zr, $[Kr]5s^2 4d^2$, loses the four electrons beyond its Kr core configuration. Hf, $[Xe]6s^2 4f^{14} 5d^2$, similarly loses its four 6s and 5d electrons, but not electrons from the "complete" 4f subshell.

6.100 (a) Each oxide ion, O^{2-}, carries a 2- charge. Each metal oxide is a neutral compound, so the metal ion or ions must adopt a total positive charge equal to the total negative charge of the oxide ions in the compound. The table below lists the electron configuration of the neutral metal atom, the positive charge of each metal ion in the oxide, and the corresponding electron configuration of the metal ion.

i.	K:	$[Ar]\,4s^1$	1+	[Ar]
ii.	Ca:	$[Ar]\,4s^2$	2+	[Ar]
iii.	Sc:	$[Ar]\,4s^2 3d^1$	3+	[Ar]
iv.	Ti:	$[Ar]\,4s^2 3d^2$	4+	[Ar]
v.	V:	$[Ar]\,4s^2 3d^3$	5+	[Ar]
vi.	Cr:	$[Ar]\,4s^1 3d^5$	6+	[Ar]

Each metal atom loses all (valence) electrons beyond the Ar core configuration. In K_2O, Sc_2O_3 and V_2O_5, where the metal ions have odd charges, two metal ions are required to produce a neutral oxide.

(b) i. potassium oxide
ii. calcium oxide
iii. scandium(III) oxide
iv. titanium (IV) oxide
v. vanadium (V) oxide
vi. chromium (VI) oxide

(Roman numerals are required to specify the charges on the transition metal ions, because more than one stable ion may exist.)

(c) Recall that $\Delta H^\circ_f = 0$ for elements in their standard states. In these reactions, M(s) and $H_2(g)$ are elements in their standard states.

i. $K_2O(s) + H_2(g) \rightarrow 2K(s) + H_2O(g)$

$$\Delta H^\circ = \Delta H^\circ_f\ H_2O(g) + 2\Delta H^\circ_f\ K(s) - \Delta H\ K_2O(s) - \Delta H^\circ_f\ H_2(g)$$

$$\Delta H^\circ = -241.82\ kJ + 2(0) - (-363.2\ kJ) - 0 = 121.4\ kJ$$

ii. $CaO(s) + H_2(g) \rightarrow Ca(s) + H_2O(g)$

$$\Delta H^\circ = \Delta H^\circ_f\ H_2O(g) + \Delta H^\circ_f\ Ca(s) - \Delta H^\circ_f\ CaO(s) - \Delta H^\circ_f\ H_2(g)$$

$$\Delta H^\circ = -241.82\ kJ + 0 - (-635.1\ kJ) - 0 = 393.3\ kJ$$

iii. $TiO_2(s) + 2H_2(g) \rightarrow Ti(s) + 2H_2O(g)$

$$\Delta H^\circ = 2\Delta H^\circ_f\ H_2O(g) + \Delta H^\circ_f\ Ti(s) - \Delta H^\circ_f\ TiO_2(s) - 2\Delta H^\circ_f\ H_2(g)$$

$$= 2(-241.82) + 0 - (-938.7) - 2(0) = 455.1\ kJ$$

iv. $V_2O_5(s) + 5H_2(g) \rightarrow 2V(s) + 5H_2O(g)$

$$\Delta H^\circ = 5\Delta H^\circ_f\ H_2O(g) + 2\Delta H^\circ_f\ V(s) - \Delta H^\circ_f\ V_2O_5(s) - 5\Delta H^\circ_f\ H_2(g)$$

$$= 5(-241.82) + 2(0) - (-1550.6) - 5(0) = 341.5\ kJ$$

(d) ΔH°_f becomes more negative moving from left to right across this row of the periodic chart. Since Sc lies between Ca and Ti, the median of the two ΔH°_f values is approximately -785 kJ/mol. However, the trend is clearly not linear. Dividing the ΔH°_f values by the positive charge on the pertinent metal ion produces the values -363, -318, -235, and -310. The value between Ca^{2+} (-318) and Ti^{4+} (-235) is Sc^{3+} (-277). Multiplying (-277) by 3, a value of approximately -830 kJ results. A reasonable range of values for ΔH°_f of $Sc_2O_3(s)$ is then -785 to -830 kJ/mol.

6.101 (a) Bohr's theory was based on the Rutherford "nuclear" model of the atom. That is, Bohr theory assumed a dense positive charge at the center of the atom and a diffuse negative charge (electrons) surrounding it. Bohr's theory then specified the nature of the diffuse negative charge. The prevailing theory before the nuclear model was Thomson's plum pudding or watermelon model, with discrete electrons scattered about a diffuse positive charge cloud. Bohr's theory could not have been based on the Thomson model of the atom.

(b) De Broglie's hypothesis is that electrons exhibit both particle and wave properties. Thomson's conclusion that electrons have mass is a particle property, while the nature of cathode rays is a wave property. De Broglie's hypothesis actually rationalizes these two seemingly contradictory observations about the properties of electrons.

6.102 (a) ^{238}U: 92 p, 146 n, 92 e; ^{235}U: 92 p, 143 n, 92 e

In keeping with the definition isotopes, only the number of neutrons is different in the two nuclides. Since the two isotopes have the same number of electrons, they will have the same electron configuration.

(b) U: [Rn]$7s^25f^4$

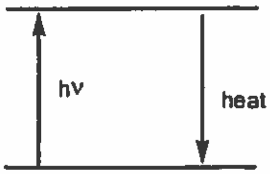
(c) From Figure 6.31, the actual electron configuration is [Rn]$7s^25f^36d^1$. The energies of the 6d and 5f orbitals are very close, and electron configurations of many actinides include 6d electrons.

(d) $^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$ ^{234}Th has 90 p, 144 n, 90 e. ^{238}U has lost 2 p, 2 n, 2 e.

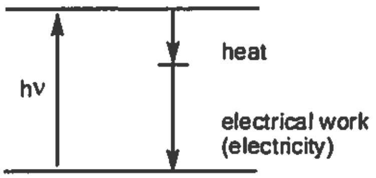
These are organized into $^{4}_{2}\text{He}$ shown in the nuclear reaction above.

(e) From Figure 6.31, the electron configuration of Th is [Rn]$7s^26d^2$. This is not really surprising because there are so many rare earth electron configurations that are exceptions to the expected orbital filling order. However, Th is the only rare earth that has two d valence electrons. Furthermore, the configuration of Th is different than that of Ce, the element above it on the periodic chart, so the electron configuration is at least interesting.

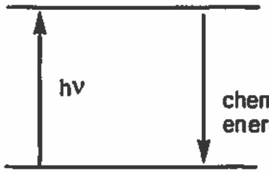
6.103 In each case, radiant energy from the sun in shown as hν.



inert black material



photovoltaic cell



green leaf

Energy from the sun irradiates the earth without external intervention. In the absence of an appropriate receiver, the energy is dissipated as heat, as the diagram for the inert black material shows. When sunlight hits a material that can convert the energy to a useable form, such as a leaf or a photovoltaic cell, the sun becomes a sustainable energy source.