

CHAPTER SEVEN

ATOMIC STRUCTURE AND PERIODICITY

Questions

15. Planck's discovery that heated bodies give off only certain frequencies of light and Einstein's study of the photoelectric effect.
16. When something is quantized, it can only have certain discrete values. In the Bohr model of the H-atom, the energy of the electron is quantized.
17. Only very small particles with a tiny mass exhibit wave and particle properties, e.g., an electron. Some evidence supporting the wave properties of matter are:
 - 1) Electrons can be diffracted like light.
 - 2) The electron microscope uses electrons in a fashion similar to the way in which light is used in a light microscope.
18.
 - a. A discrete bundle of light energy.
 - b. A number describing a discrete energy state of an electron.
 - c. The lowest energy state of the electron(s) in an atom or ion.
 - d. An allowed energy state that is higher in energy than the ground state.
19.
 - n : Gives the energy (it completely specifies the energy only for the H-atom or ions with one electron) and the relative size of the orbitals.
 - ℓ : Gives the type (shape) of orbital.
 - m_ℓ : Gives information about the direction in which the orbital is pointing.
20. The 2p orbitals differ from each other in the direction in which they point in space. The 2p and 3p orbitals differ from each other in their size, energy and number of nodes.
21. A nodal surface in an atomic orbital is a surface in which the probability of finding an electron is zero.
22. The electrostatic energy of repulsion, from Coulomb's Law, will be of the form Q^2/r where Q is the

charge of the electron and r is the distance between the two electrons. From the Heisenberg uncertainty principle, we cannot know precisely the position of each electron. Thus, we cannot know precisely the distance between the electrons nor the value of the electrostatic repulsions.

23. No, the spin is a convenient model. Since we cannot locate or "see" the electron, we cannot see if it is spinning.
24. There is a higher probability of finding the 4s electron very close to the nucleus than the 3d electron.
25. The outermost electrons are the valence electrons. When atoms interact with each other, it will be the outermost electrons that are involved in these interactions. In addition, how tightly the nucleus holds these outermost electrons determines atomic size, ionization energy and other properties of atoms.

Elements in the same group have similar valence electron configurations and, as a result, have similar chemical properties.

26. If one more electron is added to a half-filled subshell, electron-electron repulsions will increase since two electrons must now occupy the same atomic orbital. This may slightly decrease the stability of the atom. Hence, half-filled subshells minimize electron-electron repulsions.
27. Across a period, the positive charge from the nucleus increases as protons are added. The number of electrons also increase, but these outer electrons do not completely shield the increasing nuclear charge from each other. The general result is that the outer electrons are more strongly bound as one goes across a period which results in larger ionization energies (and smaller size).

Aluminum is out of order because the electrons in the filled 3s orbital shield some of the nuclear charge from the 3p electron. Hence, the 3p electron is less tightly bound than a 3s electron resulting in a lower ionization energy for aluminum as compared to magnesium. The ionization energy of sulfur is lower than phosphorus because of the extra electron-electron repulsions in the doubly occupied sulfur 3p orbital. These added repulsions, which are not present in phosphorus, make it slightly easier to remove an electron from sulfur as compared to phosphorus.

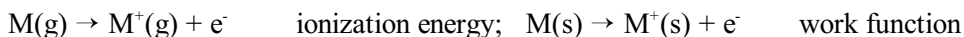
28. As successive electrons are removed, the net positive charge on the resultant ion increases. This increase in positive charge binds the remaining electrons more firmly, and the ionization energy increases.

The electron configuration for Si is $1s^2 2s^2 2p^6 3s^2 3p^2$. There is a large jump in ionization energy when going from the removal of valence electrons to the removal of core electrons. For silicon, this occurs when the fifth electron is removed since we go from the valence electrons in $n = 3$ to the core electrons in $n = 2$. There should be another big jump when the thirteenth electron is removed, i.e., when the 1s electrons are removed.

29. Ionization energy: $P(g) \rightarrow P^+(g) + e^-$; electron affinity: $P(g) + e^- \rightarrow P^-(g)$
30. Size decreases from left to right and increases going down the periodic table. So, going one element right and one element down would result in a similar size for the two elements diagonal to each other.

The ionization energies will be similar for the diagonal elements since the periodic trends also oppose each other. Electron affinities are harder to predict, but atoms with similar size and ionization energy should also have similar electron affinities.

31. The valence electrons are strongly attracted to the nucleus for elements with large ionization energies. One would expect these species to readily accept another electron and have very exothermic electron affinities. The noble gases are an exception; they have a large IE but have an endothermic EA. Noble gases have a stable arrangement of electrons. Adding an electron disrupts this stable arrangement, resulting in unfavorable electron affinities.
32. Electron-electron repulsions become more important when we try to add electrons to an atom. From the standpoint of electron-electron repulsions, larger atoms would have more favorable (more exothermic) electron affinities. Considering only electron-nucleus attractions, smaller atoms would be expected to have the more favorable (more exothermic) EA's. These trends are exactly the opposite of each other. Thus, the overall variation in EA is not as great as ionization energy in which attractions to the nucleus dominate.
33. For hydrogen and one-electron ions (hydrogenlike ions), all atomic orbitals with the same n value have the same energy. For polyatomic atoms/ions, the energy of the atomic orbitals also depends on ℓ . Since there are more nondegenerate energy levels for polyatomic atoms/ions as compared to hydrogen, there are many more possible electronic transitions resulting in more complicated line spectra.
34. Each element has a characteristic spectrum. Thus, the presence of the characteristic spectral lines of an element confirms its presence in any particular sample.
35. Yes, the maximum number of unpaired electrons in any configuration corresponds to a minimum in electron-electron repulsions.
36. The electron is no longer part of that atom. The proton and electron are completely separated.
37. Ionization energy is for removal of the electron from the atom in the gas phase. The work function is for the removal of an electron from the solid.



38. Li^+ ions will be the smallest of the alkali metal cations and will be most strongly attracted to the water molecules.

Exercises

Light and Matter

39. $1 \times 10^{-9} \text{ m} = 1 \text{ nm}; \quad v = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{780. \times 10^{-9} \text{ m}} = 3.84 \times 10^{14} \text{ s}^{-1}$

$$40. \quad 99.5 \text{ MHz} = 99.5 \times 10^6 \text{ Hz} = 99.5 \times 10^6 \text{ s}^{-1}; \quad \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{99.5 \times 10^6 \text{ s}^{-1}} = 3.01 \text{ m}$$

$$41. \quad \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.0 \times 10^{-2} \text{ m}} = 3.0 \times 10^{10} \text{ s}^{-1}$$

$$E = h\nu = 6.63 \times 10^{-34} \text{ J s} \times 3.0 \times 10^{10} \text{ s}^{-1} = 2.0 \times 10^{-23} \text{ J/photon}$$

$$\frac{2.0 \times 10^{-23} \text{ J}}{\text{photon}} \times \frac{6.02 \times 10^{23} \text{ photons}}{\text{mol}} = 12 \text{ J/mol}$$

$$42. \quad E = h\nu = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m/s}}{25 \text{ nm} \times \frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}} = 8.0 \times 10^{-18} \text{ J/photon}$$

$$\frac{8.0 \times 10^{-18} \text{ J}}{\text{photon}} \times \frac{6.02 \times 10^{23} \text{ photons}}{\text{mol}} = 4.8 \times 10^6 \text{ J/mol}$$

43. The wavelength is the distance between consecutive wave peaks. Wave a shows 4 wavelengths and wave b shows 8 wavelengths.

$$\text{Wave a: } \lambda = \frac{1.6 \times 10^{-3} \text{ m}}{4} = 4.0 \times 10^{-4} \text{ m}$$

$$\text{Wave b: } \lambda = \frac{1.6 \times 10^{-3} \text{ m}}{8} = 2.0 \times 10^{-4} \text{ m}$$

Wave a has the longer wavelength. Since frequency and photon energy are both inversely proportional to wavelength, then wave b will have the higher frequency and larger photon energy since it has the shorter wavelength.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{2.0 \times 10^{-4} \text{ m}} = 1.5 \times 10^{12} \text{ s}^{-1}$$

$$E = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m/s}}{2.0 \times 10^{-4} \text{ m}} = 9.9 \times 10^{-22} \text{ J}$$

Since both waves are examples of electromagnetic radiation, then both waves travel at the same speed, c , the speed of light. From Figure 7.2 of the text, both of these waves represent infrared electromagnetic radiation.

44. Referencing figure 7.2 of the text, $2.12 \times 10^{-10} \text{ m}$ electromagnetic radiation is X-rays.

$$\lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m/s}}{107.1 \times 10^6 \text{ s}^{-1}} = 2.799 \text{ m}$$

From the wavelength calculated above, 107.1 MHz electromagnetic radiation is FM radiowaves.

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{3.97 \times 10^{-19} \text{ J}} = 5.00 \times 10^{-7} \text{ m}$$

The 3.97×10^{-19} J/photon electromagnetic radiation is visible (green) light.

The photon energy and frequency order will be the exact opposite of the wavelength ordering because E and ν are both inversely related to λ . From the calculated wavelengths above, the order of photon energy and frequency is:

FM radiowaves	<	visible (green) light	<	X-rays
longest λ				shortest λ
lowest ν				highest ν
smallest E				largest E

45. The energy needed to remove a single electron is:

$$\frac{279.7 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.0221 \times 10^{23}} = 4.645 \times 10^{-22} \text{ kJ} = 4.645 \times 10^{-19} \text{ J}$$

$$E = \frac{hc}{\lambda}, \lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.645 \times 10^{-19} \text{ J}} = 4.277 \times 10^{-7} \text{ m} = 427.7 \text{ nm}$$

46. $\frac{208.4 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.0221 \times 10^{23}} = 3.461 \times 10^{-22} \text{ kJ} = 3.461 \times 10^{-19} \text{ J}$ to remove one electron

$$E = \frac{hc}{\lambda}, \lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{3.461 \times 10^{-19} \text{ J}} = 5.739 \times 10^{-7} \text{ m} = 573.9 \text{ nm}$$

47. a. 90.% of speed of light = $0.90 \times 3.00 \times 10^8 \text{ m/s} = 2.7 \times 10^8 \text{ m/s}$

$$\lambda = \frac{h}{mv}, \lambda = \frac{6.63 \times 10^{-34} \text{ J s}}{1.67 \times 10^{-27} \text{ kg} \times 2.7 \times 10^8 \text{ m/s}} = 1.5 \times 10^{-15} \text{ m} = 1.5 \times 10^{-6} \text{ nm}$$

Note: For units to come out, the mass must be in kg since $1 \text{ J} = \frac{1 \text{ kg m}^2}{\text{s}^2}$.

b. $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{0.15 \text{ kg} \times 10.0 \text{ m/s}} = 4.4 \times 10^{-34} \text{ m} = 4.4 \times 10^{-25} \text{ nm}$

This number is so small that it is essentially zero. We cannot detect a wavelength this small. The meaning of this number is that we do not have to consider the wave properties of large objects.

48. a. $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J s}}{1.675 \times 10^{-27} \text{ kg} \times (0.0100 \times 2.998 \times 10^8 \text{ m/s})} = 1.32 \times 10^{-13} \text{ m}$

b. $\lambda = \frac{h}{mv}, \nu = \frac{h}{\lambda m} = \frac{6.626 \times 10^{-34} \text{ J s}}{75 \times 10^{-12} \text{ m} \times 1.675 \times 10^{-27} \text{ kg}} = 5.3 \times 10^3 \text{ m/s}$

49. $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31} \text{ kg} \times (1.0 \times 10^{-3} \times 3.00 \times 10^8 \text{ m/s})} = 2.4 \times 10^{-9} \text{ m} = 2.4 \text{ nm}$

50. $\lambda = \frac{h}{mv}$, $v = \frac{h}{\lambda m}$; For $\lambda = 1.0 \times 10^2 \text{ nm} = 1.0 \times 10^{-7} \text{ m}$:

$$v = \frac{6.63 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31} \text{ kg} \times 1.0 \times 10^{-7} \text{ m}} = 7.3 \times 10^3 \text{ m/s}$$

For $\lambda = 1.0 \text{ nm} = 1.0 \times 10^{-9} \text{ m}$: $v = \frac{6.63 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31} \text{ kg} \times 1.0 \times 10^{-9} \text{ m}} = 7.3 \times 10^5 \text{ m/s}$

Hydrogen Atom: The Bohr Model

51. For the H atom ($Z = 1$): $E_n = -2.178 \times 10^{-18} \text{ J/n}^2$; For a spectral transition, $\Delta E = E_f - E_i$:

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_i and n_f are the levels of the initial and final states, respectively. A positive value of ΔE always corresponds to an absorption of light, and a negative value of ΔE always corresponds to an emission of light.

a. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{4} - \frac{1}{9} \right)$

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \times (0.2500 - 0.1111) = -3.025 \times 10^{-19} \text{ J}$$

The photon of light must have precisely this energy ($3.025 \times 10^{-19} \text{ J}$).

$$|\Delta E| = E_{\text{photon}} = h\nu = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{3.025 \times 10^{-19} \text{ J}}$$

$$= 6.567 \times 10^{-7} \text{ m} = 656.7 \text{ nm}$$

From Figure 7.2, this is visible electromagnetic radiation (red light).

b. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = -4.084 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.084 \times 10^{-19} \text{ J}} = 4.864 \times 10^{-7} \text{ m} = 486.4 \text{ nm}$$

This is visible electromagnetic radiation (green-blue light).

c. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = -1.634 \times 10^{-18} \text{ J}$

$$\lambda = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.634 \times 10^{-18} \text{ J}} = 1.216 \times 10^{-7} \text{ m} = 121.6 \text{ nm}$$

This is ultraviolet electromagnetic radiation.

52. a. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{3^2} - \frac{1}{4^2} \right) = -1.059 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.059 \times 10^{-19} \text{ J}} = 1.876 \times 10^{-6} \text{ m} = 1876 \text{ nm}$$

From Figure 7.2, this is infrared electromagnetic radiation.

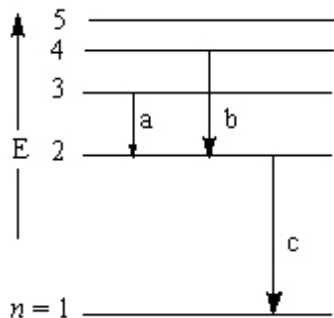
b. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{4^2} - \frac{1}{5^2} \right) = -4.901 \times 10^{-20} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.901 \times 10^{-20} \text{ J}} = \lambda = 4.053 \times 10^{-6} \text{ m} = 4053 \text{ nm (infrared)}$$

c. $\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{3^2} - \frac{1}{5^2} \right) = -1.549 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.549 \times 10^{-19} \text{ J}} = 1.282 \times 10^{-6} \text{ m} = 1282 \text{ nm (infrared)}$$

53.



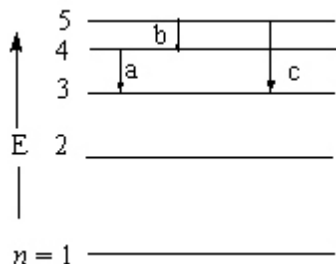
a. $3 \rightarrow 2$

b. $4 \rightarrow 2$

c. $2 \rightarrow 1$

Energy levels are not to scale.

54.



a. $4 \rightarrow 3$

b. $5 \rightarrow 4$

c. $5 \rightarrow 3$; Energy levels are not to scale.

$$55. \quad \Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{5^2} - \frac{1}{1^2} \right) = 2.091 \times 10^{-18} \text{ J} = E_{\text{photon}}$$

$$\lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.091 \times 10^{-18} \text{ J}} = 9.500 \times 10^{-8} \text{ m} = 95.00 \text{ nm}$$

Since wavelength and energy are inversely related, visible light ($\lambda \approx 400 - 700 \text{ nm}$) is not energetic enough to excite an electron in hydrogen from $n = 1$ to $n = 5$.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{6^2} - \frac{1}{2^2} \right) = 4.840 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.840 \times 10^{-19} \text{ J}} = 4.104 \times 10^{-7} \text{ m} = 410.4 \text{ nm}$$

Visible light with $\lambda = 410.4 \text{ nm}$ will excite an electron from the $n = 2$ to the $n = 6$ energy level.

56. Ionization from $n = 1$ corresponds to the transition $n_i = 1 \rightarrow n_f = \infty$ where $E_\infty = 0$.

$$\Delta E = E_\infty - E_1 = -E_1 = 2.178 \times 10^{-18} \left(\frac{1}{1^2} \right) = 2.178 \times 10^{-18} \text{ J} = E_{\text{photon}}$$

$$\lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.178 \times 10^{-18} \text{ J}} = 9.120 \times 10^{-8} \text{ m} = 91.20 \text{ nm}$$

$$\text{To ionize from } n = 2, \Delta E = E_\infty - E_2 = -E_2 = 2.178 \times 10^{-18} \left(\frac{1}{2^2} \right) = 5.445 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{5.445 \times 10^{-19} \text{ J}} = 3.648 \times 10^{-7} \text{ m} = 364.8 \text{ nm}$$

$$57. \quad \Delta E = h\nu = 6.6261 \times 10^{-34} \text{ J s} \times 1.141 \times 10^{14} \text{ s}^{-1} = 7.560 \times 10^{-20} \text{ J}$$

$\Delta E = -7.560 \times 10^{-20} \text{ J}$ since light is emitted.

$$\Delta E = E_4 - E_n, -7.560 \times 10^{-20} \text{ J} = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{4^2} - \frac{1}{n^2} \right)$$

$$3.471 \times 10^{-2} = 6.250 \times 10^{-2} - \frac{1}{n^2}, \quad \frac{1}{n^2} = 2.779 \times 10^{-2}, \quad n^2 = 35.98, \quad n = 6$$

$$58. \quad |\Delta E| = E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{397.2 \times 10^{-9} \text{ m}} = 5.001 \times 10^{-19} \text{ J}$$

$\Delta E = -5.001 \times 10^{-19} \text{ J}$ since we have an emission.

$$-5.001 \times 10^{-19} \text{ J} = E_2 - E_n = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

$$0.2296 = \frac{1}{4} - \frac{1}{n^2}, \quad \frac{1}{n^2} = 0.0204, \quad n = 7$$

Quantum Mechanics, Quantum Numbers, and Orbitals

59. a. $\Delta(mv) = m\Delta v = 9.11 \times 10^{-31} \text{ kg} \times 0.100 \text{ m/s} = \frac{9.11 \times 10^{-32} \text{ kg m}}{\text{s}}$
- $$\Delta(mv) \cdot \Delta x \geq \frac{h}{4\pi}, \Delta x = \frac{h}{4\pi\Delta(mv)} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.142 \times (9.11 \times 10^{-32} \text{ kg m/s})} = 5.79 \times 10^{-4} \text{ m}$$
- b. $\Delta x = \frac{h}{4\pi m\Delta v} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.142 \times 0.145 \text{ kg} \times 0.100 \text{ m/s}} = 3.64 \times 10^{-33} \text{ m}$
- c. The diameter of an H atom is roughly $1.0 \times 10^{-8} \text{ cm}$. The uncertainty in position is much larger than the size of the atom.
- d. The uncertainty is insignificant compared to the size of a baseball.
60. Units of $\Delta E \cdot \Delta t = \text{J} \times \text{s}$, the same as the units of Planck's constant.
- $$\text{Units of } \Delta(mv) \cdot \Delta x = \text{kg} \times \frac{\text{m}}{\text{s}} \times \text{m} = \frac{\text{kg m}^2}{\text{s}} = \frac{\text{kg m}^2}{\text{s}^2} \times \text{s} = \text{J} \times \text{s}$$
61. $n = 1, 2, 3, \dots$; $\ell = 0, 1, 2, \dots (n - 1)$; $m_\ell = -\ell \dots -2, -1, 0, 1, 2, \dots +\ell$
62. 1p: $n = 1, \ell = 1$ is not possible; 3f: $n = 3, \ell = 3$ is not possible; 2d: $n = 2, \ell = 2$ is not possible; In all three incorrect cases, $n = \ell$. The maximum value ℓ can have is $n - 1$, not n .
63. b. ℓ must be smaller than n . d. For $\ell = 0, m_\ell = 0$ is the only allowed value.
64. b. For $\ell = 3, m_\ell$ can range from -3 to +3; thus +4 is not allowed.
- c. n cannot equal zero. d. ℓ cannot be a negative number.
65. Ψ^2 gives the probability of finding the electron at that point.
66. The diagrams of the orbitals in the text give only 90% probabilities of where the electron may reside. We can never be 100% certain of the location of the electrons due to Heisenburg's uncertainty principle.

Polyelectronic Atoms

67. 5p: three orbitals; $3d_{z^2}$: one orbital; 4d: five orbitals
- $n = 5$: $\ell = 0$ (1 orbital), $\ell = 1$ (3 orbitals), $\ell = 2$ (5 orbitals), $\ell = 3$ (7 orbitals), $\ell = 4$ (9 orbitals)
- Total for $n = 5$ is 25 orbitals.
- $n = 4$: $\ell = 0$ (1), $\ell = 1$ (3), $\ell = 2$ (5), $\ell = 3$ (7); Total for $n = 4$ is 16 orbitals.
68. 1p, 0 electrons ($\ell \neq 1$ when $n = 1$); $6d_{x^2-y^2}$, 2 electrons (specifies one atomic orbital); 4f,

- 14 electrons (7 orbitals have 4f designation); 7p, 2 electrons (specifies one atomic orbital); 2s, 2 electrons (specifies one atomic orbital); $n = 3$, 18 electrons (3s, 3p and 3d orbitals are possible; there are one 3s orbital, three 3p orbitals and five 3d orbitals).
69. a. $n = 4$: ℓ can be 0, 1, 2, or 3. Thus we have s (2 e^-), p (6 e^-), d (10 e^-) and f (14 e^-) orbitals present. Total number of electrons to fill these orbitals is 32.
- b. $n = 5$, $m_\ell = +1$: For $n = 5$, $\ell = 0, 1, 2, 3, 4$. For $\ell = 1, 2, 3, 4$, all can have $m_\ell = +1$. Four distinct orbitals, thus 8 electrons.
- c. $n = 5$, $m_s = +1/2$: For $n = 5$, $\ell = 0, 1, 2, 3, 4$. Number of orbitals = 1, 3, 5, 7, 9 for each value of ℓ , respectively. There are 25 orbitals with $n = 5$. They can hold 50 electrons and 25 of these electrons can have $m_s = +1/2$.
- d. $n = 3$, $\ell = 2$: These quantum numbers define a set of 3d orbitals. There are 5 degenerate 3d orbitals which can hold a total of 10 electrons.
- e. $n = 2$, $\ell = 1$: These define a set of 2p orbitals. There are 3 degenerate 2p orbitals which can hold a total of 6 electrons.
70. a. It is impossible for $n = 0$. Thus, no electrons can have this set of quantum numbers.
- b. The four quantum numbers completely specify a single electron.
- c. $n = 3$: 3s, 3p and 3d orbitals all have $n = 3$. These orbitals can hold up to 18 electrons.
- d. $n = 2$, $\ell = 2$: This combination is not possible ($\ell \neq 2$ for $n = 2$). Zero electrons in an atom can have these quantum numbers.
- e. $n = 1$, $\ell = 0$, $m_\ell = 0$: These define a 1s orbital which can hold 2 electrons.
71. Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ or [Ne] $3s^2 3p^2$; Ga: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ or [Ar] $4s^2 3d^{10} 4p^1$
 As: [Ar] $4s^2 3d^{10} 4p^3$; Ge: [Ar] $4s^2 3d^{10} 4p^2$; Al: [Ne] $3s^2 3p^1$; Cd: [Kr] $5s^2 4d^{10}$
 S: [Ne] $3s^2 3p^4$; Se: [Ar] $4s^2 3d^{10} 4p^4$
72. Cu: [Ar] $4s^2 3d^9$ (using periodic table), [Ar] $4s^1 3d^{10}$ (actual)
 O: $1s^2 2s^2 2p^4$; La: [Xe] $6s^2 5d^1$; Y: [Kr] $5s^2 4d^1$; Ba: [Xe] $6s^2$
 Tl: [Xe] $6s^2 4f^{14} 5d^{10} 6p^1$; Bi: [Xe] $6s^2 4f^{14} 5d^{10} 6p^3$
73. The following are complete electron configurations. Noble gas shorthand notation could also be used.
 Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$; Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
 P: $1s^2 2s^2 2p^6 3s^2 3p^3$; Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$
 Eu: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 5d^1$ *

Pt: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^8$ *

Xe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$; Br: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

*Note: These electron configurations were predicted using only the periodic table.

Actual electron configurations are: Eu: $[Xe]6s^2 4f^7$ and Pt: $[Xe]6s^1 4f^{14} 5d^9$

74. Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$ or $[Ne]3s^2 3p^5$ As: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$ or $[Ar]4s^2 3d^{10} 4p^3$

Sr: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$ or $[Kr]5s^2$ W: $[Xe]6s^2 4f^{14} 5d^4$

Pb: $[Xe]6s^2 4f^{14} 5d^{10} 6p^2$

Cf: $[Rn]7s^2 5f^{10}$

Predicting electron configurations for lanthanide and actinide elements is difficult since they have 0, 1 or 2 electrons in d orbitals.

75. Exceptions: Cr, Cu, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Pt, Au; Tc, Ru, Rh, Pd and Pt do not correspond to the supposed extra stability of half-filled and filled subshells.

76. No, in the solid and liquid state the electrons may interact (bonding occurs), and the experimental configuration will not be valid. That is, the experimental electron configurations are for isolated atoms; in condensed phases, the atoms are no longer isolated.

77. a. Both In and I have one unpaired 5p electron, but only the nonmetal I would be expected to form a covalent compound with the nonmetal F. One would predict an ionic compound to form between the metal In and the nonmetal F.

I: $[Kr]5s^2 4d^{10} 5p^5$ $\begin{array}{ccc} \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ 5p & & \end{array}$

b. From the periodic table, this will be element 120. Element 120: $[Rn]7s^2 5f^{14} 6d^{10} 7p^6 8s^2$

c. Rn: $[Xe]6s^2 4f^{14} 5d^{10} 6p^6$; Note that the next discovered noble gas will also have 4f electrons (as well as 5f electrons).

d. This is chromium, which is an exception to the predicted filling order. Cr has 6 unpaired electrons and the next most is 5 unpaired electrons for Mn.

Cr: $[Ar]4s^1 3d^5$ $\begin{array}{ccccc} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ 4s & 3d & & & \end{array}$

78. a. As: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

b. Element 116 will be below Po in the periodic table: $[Rn]7s^2 5f^{14} 6d^{10} 7p^4$

c. Ta: $[Xe]6s^2 4f^{14} 5d^3$ or Ir: $[Xe]6s^2 4f^{14} 5d^7$

- d. At: $[\text{Xe}]6s^24f^45d^{10}6p^5$. Note that element 117 (when it is discovered) will also have electrons in the 6p atomic orbitals (as well as electrons in the 7p atomic orbitals).

79. B : $1s^22s^22p^1$

	n	ℓ	m_ℓ	m_s
1s	1	0	0	+1/2
1s	1	0	0	-1/2
2s	2	0	0	+1/2
2s	2	0	0	-1/2
2p*	2	1	-1	+1/2

*This is only one of several possibilities for the 2p electron. The 2p electron in B could have $m_\ell = -1, 0$ or $+1$, and $m_s = +1/2$ or $-1/2$, a total of six possibilities.

N : $1s^22s^22p^3$

	n	ℓ	m_ℓ	m_s	
1s	1	0	0	+1/2	
1s	1	0	0	-1/2	
2s	2	0	0	+1/2	
2s	2	0	0	-1/2	
2p	2	1	-1	+1/2	} (Or all 2p electrons could have $m_s = -1/2$.)
2p	2	1	0	+1/2	
2p	2	1	+1	+1/2	

80. Ti : $[\text{Ar}]4s^23d^2$

	n	ℓ	m_ℓ	m_s
4s	4	0	0	+1/2
4s	4	0	0	-1/2

3d 3 2 -2 +1/2 Only one of 10 possible combinations of m_ℓ and m_s for the first d electron. For the ground state, the second d electron should be in a different orbital with spin parallel; 4 possibilities.

3d 3 2 -1 +1/2

81. O: $1s^22s^22p_x^22p_y^2$ ($\uparrow\downarrow \uparrow\downarrow \underline{\quad}$); There are no unpaired electrons in this oxygen atom. This configuration would be an excited state, and in going to the more stable ground state ($\uparrow\downarrow \uparrow \underline{\quad} \underline{\quad}$), energy would be released.

82. The number of unpaired electrons is in parentheses.

a. excited state of boron (1) b. ground state of neon (0)

B ground state: $1s^2 2s^2 2p^1$ (1)

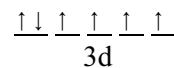
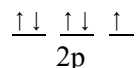
Ne ground state: $1s^2 2s^2 2p^6$

c. excited state of fluorine (3)

d. excited state of iron (6)

F ground state: $1s^2 2s^2 2p^5$ (1)

Fe ground state: $[\text{Ar}] 4s^2 3d^6$ (4)



83. We get the number of unpaired electrons by examining the incompletely filled subshells. The paramagnetic substances have unpaired electrons, and the ones with no unpaired electrons are not paramagnetic (they are called diamagnetic).

Li: $1s^2 2s^1$ $\begin{array}{c} \uparrow \\ 2s \end{array}$; Paramagnetic with 1 unpaired electron.

N: $1s^2 2s^2 2p^3$ $\begin{array}{c} \uparrow \quad \uparrow \quad \uparrow \\ 2p \end{array}$; Paramagnetic with 3 unpaired electrons.

Ni: $[\text{Ar}] 4s^2 3d^8$ $\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow \quad \uparrow \\ 3d \end{array}$; Paramagnetic with 2 unpaired electrons.

Te: $[\text{Kr}] 5s^2 4d^{10} 5p^4$ $\begin{array}{c} \uparrow\downarrow \quad \uparrow \quad \uparrow \\ 5p \end{array}$; Paramagnetic with 2 unpaired electrons.

Ba: $[\text{Xe}] 6s^2$ $\begin{array}{c} \uparrow\downarrow \\ 6s \end{array}$; Not paramagnetic since no unpaired electrons.

Hg: $[\text{Xe}] 6s^2 4f^{14} 5d^{10}$ $\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \\ 5d \end{array}$; Not paramagnetic since no unpaired electrons.

84. We get the number of unpaired electrons by examining the incompletely filled subshells.

O: $[\text{He}] 2s^2 2p^4$ $2p^4$: $\begin{array}{c} \uparrow\downarrow \quad \uparrow \quad \uparrow \end{array}$ two unpaired e^-

O^+ : $[\text{He}] 2s^2 2p^3$ $2p^3$: $\begin{array}{c} \uparrow \quad \uparrow \quad \uparrow \end{array}$ three unpaired e^-

O^- : $[\text{He}] 2s^2 2p^5$ $2p^5$: $\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow \end{array}$ one unpaired e^-

Os: $[\text{Xe}] 6s^2 4f^{14} 5d^6$ $5d^6$: $\begin{array}{c} \uparrow\downarrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \end{array}$ four unpaired e^-

Zr: $[\text{Kr}] 5s^2 4d^2$ $4d^2$: $\begin{array}{c} \uparrow \quad \uparrow \end{array}$ two unpaired e^-

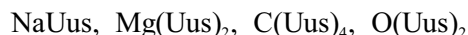
S: $[\text{Ne}] 3s^2 3p^4$ $3p^4$: $\begin{array}{c} \uparrow\downarrow \quad \uparrow \quad \uparrow \end{array}$ two unpaired e^-

F: $[\text{He}] 2s^2 2p^5$ $2p^5$: $\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow \end{array}$ one unpaired e^-

Ar: $[\text{Ne}] 3s^2 3p^6$ $3p^6$ $\begin{array}{c} \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \end{array}$ zero unpaired e^-

The Periodic Table and Periodic Properties

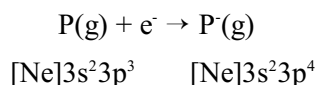
85. Size (radii) decreases left to right across the periodic table, and size increases from top to bottom of the periodic table.
- a. $\text{Be} < \text{Mg} < \text{Ca}$ b. $\text{Xe} < \text{I} < \text{Te}$ c. $\text{Ge} < \text{Ga} < \text{In}$
86. a. $\text{Be} < \text{Na} < \text{Rb}$ b. $\text{Ne} < \text{Se} < \text{Sr}$ c. $\text{O} < \text{P} < \text{Fe}$
(All follow the general radii trend.)
87. The ionization energy trend is the opposite of the radii trend; ionization energy (IE), in general, increases left to right across the periodic table and decreases from top to bottom of the periodic table.
- a. $\text{Ca} < \text{Mg} < \text{Be}$ b. $\text{Te} < \text{I} < \text{Xe}$ c. $\text{In} < \text{Ga} < \text{Ge}$
88. a. $\text{Rb} < \text{Na} < \text{Be}$ b. $\text{Sr} < \text{Se} < \text{Ne}$ c. $\text{Fe} < \text{P} < \text{O}$ (All follow the general IE trend.)
89. a. Li b. P
- c. O^+ . This ion has the fewest electrons as compared to the other oxygen species present. O^+ has the smallest amount of electron-electron repulsions, which makes it the smallest ion with the largest ionization energy.
- d. From the radii trend, $\text{Ar} < \text{Cl} < \text{S}$ and $\text{Kr} > \text{Ar}$. Since variation in size down a family is greater than the variation across a period, we would predict Cl to be the smallest of the three.
- e. Cu
90. a. Ba b. K
- c. O ; In general, group 6A elements have a lower ionization energy than neighboring group 5A elements. This is an exception to the general ionization energy trend across the periodic table.
- d. S^{2-} ; This ion has the most electrons as compared to the other sulfur species present. S^{2-} has the largest amount of electron-electron repulsions which leads to S^{2-} having the largest size and smallest ionization energy.
- e. Cs ; This follows the general ionization energy trend.
91. a. 106: $[\text{Rn}]7s^25f^{14}6d^4$ b. W c. SgO_3 or Sg_2O_3 and SgO_4^{2-} or $\text{Sg}_2\text{O}_7^{2-}$
(similar to Cr; $\text{Sg} = 106$)
92. a. Uus will have 117 electrons. $[\text{Rn}]7s^25f^{14}6d^{10}7p^5$
- b. It will be in the halogen family and most similar to astatine, At.
- c. Uus should form -1 charged anions like the other halogens.



d. Assuming Uus is like the other halogens: UusO^- , UusO_2^- , UusO_3^- , UusO_4^-

93. As: $[\text{Ar}]4s^23d^{10}4p^3$; Se: $[\text{Ar}]4s^23d^{10}4p^4$; The general ionization energy trend predicts that Se should have a higher ionization energy than As. Se is an exception to the general ionization energy trend. There are extra electron-electron repulsions in Se because two electrons are in the same 4p orbital, resulting in a lower ionization energy for Se than predicted.

94. Al (-44), Si(-120), P (-74), S (-200.4), Cl (-348.7); Based on the increasing nuclear charge, we would expect the electron affinity (EA) values to become more exothermic as we go from left to right in the period. Phosphorus is out of line. The reaction for the EA of P is:



The additional electron in P^- will have to go into an orbital that already has one electron. There will be greater repulsions between the paired electrons in P^- , causing the EA of P to be less favorable than predicted based solely on attractions to the nucleus.

95. a. More favorable EA: C and Br; The electron affinity trend is very erratic. Both N and Ar have positive EA values (unfavorable) due to their electron configurations (see text for detailed explanation).

b. Higher IE: N and Ar (follows the IE trend)

c. Larger size: C and Br (follows the radii trend)

96. a. More favorable EA: K and Cl; Mg has a positive EA value, and F has a more positive EA value than expected from its position relative to Cl.

b. Higher IE: Mg and F

c. Larger radius: K and Cl

97. The electron affinity trend is very erratic. In general, EA decreases down the periodic table, and the trend across the table is too erratic to be of much use.

a. $\text{Se} < \text{S}$; S is more exothermic.

b. $\text{I} < \text{Br} < \text{F} < \text{Cl}$; Cl is most exothermic (F is an exception).

98. a. $\text{N} < \text{O} < \text{F}$; F is most exothermic.

b. $\text{Al} < \text{P} < \text{Si}$; Si is most exothermic.

99. Electron-electron repulsions are much greater in O^- than in S^- because the electron goes into a smaller 2p orbital vs. the larger 3p orbital in sulfur. This results in a more favorable (more exothermic) EA for sulfur.

100. O; The electron-electron repulsions will be much more severe for $\text{O}^- + \text{e}^- \rightarrow \text{O}^{2-}$ than for $\text{O} + \text{e}^- \rightarrow \text{O}^-$.

101. a. The electron affinity of Mg^{2+} is ΔH for $\text{Mg}^{2+}(\text{g}) + \text{e}^- \rightarrow \text{Mg}^+(\text{g})$. This is just the reverse of the

second ionization energy, or $EA(Mg^{2+}) = -IE_2(Mg) = -1445 \text{ kJ/mol}$ (Table 7.5).

- b. EA of Al^+ is ΔH for $Al^+(g) + e^- \rightarrow Al(g)$. $EA(Al^+) = -IE_1(Al) = -580 \text{ kJ/mol}$ (Table 7.5)
102. a. IE of Cl^- is ΔH for $Cl^-(g) \rightarrow Cl(g) + e^-$. $IE(Cl^-) = -EA(Cl) = 348.7 \text{ kJ/mol}$ (Table 7.7)
- b. $Cl(g) \rightarrow Cl^+(g) + e^-$ $IE = 1255 \text{ kJ/mol}$ (Table 7.5)
- c. $Cl^+(g) + e^- \rightarrow Cl(g)$ $\Delta H = -IE_1 = -1255 \text{ kJ/mol} = EA(Cl^+)$

Alkali Metals

103. It should be potassium peroxide, K_2O_2 , since K^+ ions are much more stable than K^{2+} ions. The second ionization energy of K is very large as compared to the first ionization energy.
104. a. Li_3N ; lithium nitride b. $NaBr$; sodium bromide c. K_2S ; potassium sulfide
105.
$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{455.5 \times 10^{-9} \text{ m}} = 6.582 \times 10^{14} \text{ s}^{-1}$$

$$E = h\nu = 6.6261 \times 10^{-34} \text{ J s} \times 6.582 \times 10^{14} \text{ s}^{-1} = 4.361 \times 10^{-19} \text{ J}$$

106. For 589.0 nm:
$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{589.0 \times 10^{-9} \text{ m}} = 5.090 \times 10^{14} \text{ s}^{-1}$$

$$E = h\nu = 6.6261 \times 10^{-34} \text{ J s} \times 5.090 \times 10^{14} \text{ s}^{-1} = 3.373 \times 10^{-19} \text{ J}$$

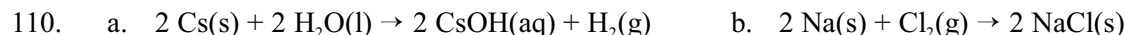
$$\text{For } 589.6 \text{ nm: } \nu = c/\lambda = 5.085 \times 10^{14} \text{ s}^{-1}; \quad E = h\nu = 3.369 \times 10^{-19} \text{ J}$$

The energies in kJ/mol are:

$$3.373 \times 10^{-19} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.0221 \times 10^{23}}{\text{mol}} = 203.1 \text{ kJ/mol}$$

$$3.369 \times 10^{-19} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.0221 \times 10^{23}}{\text{mol}} = 202.9 \text{ kJ/mol}$$

107. Yes; the ionization energy general trend is to decrease down a group, and the atomic radius trend is to increase down a group. The data in Table 7.8 confirm both of these general trends.
108. It should be element #119 with the ground state electron configuration: $[Rn]7s^25f^{14}6d^{10}7p^68s^1$
109. a. $4 \text{ Li(s)} + \text{O}_2(\text{g}) \rightarrow 2 \text{ Li}_2\text{O(s)}$ b. $2 \text{ K(s)} + \text{S(s)} \rightarrow \text{K}_2\text{S(s)}$



Additional Exercises

111. $E = \frac{310. \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 5.15 \times 10^{-22} \text{ kJ} = 5.15 \times 10^{-19} \text{ J}$

$$E = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{5.15 \times 10^{-19}} = 3.86 \times 10^{-7} \text{ m} = 386 \text{ nm}$$

112. Energy to make water boil = $s \times m \times \Delta T = \frac{4.18 \text{ J}}{\text{g } ^\circ\text{C}} \times 50.0 \text{ g} \times 75.0^\circ\text{C} = 1.57 \times 10^4 \text{ J}$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{9.75 \times 10^{-2} \text{ m}} = 2.04 \times 10^{-24} \text{ J}$$

$$1.57 \times 10^4 \text{ J} \times \frac{1 \text{ sec}}{750. \text{ J}} = 20.9 \text{ sec}; \quad 1.57 \times 10^4 \text{ J} \times \frac{1 \text{ photon}}{2.04 \times 10^{-24} \text{ J}} = 7.70 \times 10^{27} \text{ photons}$$

113. $60 \times 10^6 \text{ km} \times \frac{1000 \text{ m}}{\text{km}} \times \frac{1 \text{ s}}{3.00 \times 10^8 \text{ m}} = 200 \text{ s}$ (about 3 minutes)

114. $\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{3.90 \times 10^{-19} \text{ J}} = 5.09 \times 10^{-7} \text{ m} \times \frac{100 \text{ cm}}{\text{m}} = 5.09 \times 10^{-5} \text{ cm}$

From the spectrum, $\lambda = 5.09 \times 10^{-5} \text{ cm}$ is green light.

115. $\Delta E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -2.178 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{6^2} \right) = -4.840 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.840 \times 10^{-19} \text{ J}} = 4.104 \times 10^{-7} \text{ m} \times \frac{100 \text{ cm}}{\text{m}} = 4.104 \times 10^{-5} \text{ cm}$$

From the spectrum, $\lambda = 4.104 \times 10^{-5} \text{ cm}$ is violet light, so the $n = 6$ to $n = 2$ visible spectrum line is violet.

116. a. False; It takes less energy to ionize an electron from $n = 3$ than from the ground state.

b. True

- c. False; The energy difference from $n = 3 \rightarrow n = 2$ is less than the energy difference from $n = 3 \rightarrow n = 1$, thus, the wavelength is larger for $n = 3 \rightarrow n = 2$ than for $n = 3 \rightarrow n = 1$.
- d. True
- e. False; $n = 2$ is the first excited state and $n = 3$ is the second excited state.
117. a. True for H only. b. True for all atoms. c. True for all atoms.
118. $n = 5$; $m_\ell = -4, -3, -2, -1, 0, 1, 2, 3, 4$; 18 electrons
119. Cd: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$
- a. $\ell = 2$ are d orbitals. There are 20 electrons in d orbitals ($3d^{10}$ and $4d^{10}$).
- b. For $n = 4$, there are 4s, 4p, 4d and 4f orbitals. Cd only uses the 4s, 4p and 4d orbitals. Since all are filled with electrons, then Cd has $2 + 6 + 10 = 18$ electrons with $n = 4$.
- c. All p, d and f orbitals have one orbital which has $m_\ell = -1$. So each of the 2p, 3p, 4p, 3d and 4d orbitals (which are filled) have an orbital with $m_\ell = -1$; $5(2) = 10$ electrons with $m_\ell = -1$.
- d. Each orbital used has one of the two paired electrons with $m_s = -1/2$. Therefore, one-half of the total electrons in Cd have $m_s = -1/2$; $(48/2) = 24$ electrons with $m_s = -1/2$.
120. He: $1s^2$; Ne: $1s^2 2s^2 2p^6$; Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$; Each peak in the diagram corresponds to a subshell with different values of n . Corresponding subshells are closer to the nucleus for heavier elements because of the increased nuclear charge.
121. The general ionization energy trend says that ionization energy increases going left to right across the periodic table. However, one of the exceptions to this trend occurs between groups 2A and 3A. Between these two groups, group 3A elements usually have a lower ionization energy than group 2A elements. Therefore, Al should have the lowest first ionization energy value, followed by Mg, with Si having the largest ionization energy. Looking at the values for the first ionization energy in the graph, the green plot is Al, the blue plot is Mg, and the red plot is Si.
- Mg (the blue plot) is the element with the huge jump between I_2 and I_3 . Mg has two valence electrons, so the third electron removed is an inner core electron. Inner core electrons are always much more difficult to remove compared to valence electrons since they are closer to the nucleus, on average, than the valence electrons.
122. a. The $4+$ ion contains 20 electrons. Thus, the electrically neutral atom will contain 24 electrons. The atomic number is 24.
- b. The ground state electron configuration of the ion must be: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^2$; There are 6 electrons in s orbitals.
- c. 12 d. 2

- e. Because of the mass, this is an isotope of $^{50}_{24}\text{Cr}$. There are 26 neutrons in the nucleus.
- f. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ is the ground state electron configuration for Cr. Cr is an exception to the normal filling order.
123. Valence electrons are easier to remove than inner core electrons. The large difference in energy between I_2 and I_3 indicates that this element has two valence electrons. This element is most likely an alkaline earth metal since alkaline earth metal elements all have two valence electrons.
124. Since all oxygen family elements have $ns^2 np^4$ valence electron configurations, this nonmetal is from the oxygen family.
- a. $2 + 4 = 6$ valence electrons
- b. O, S, Se and Te are the nonmetals from the oxygen family (Po is a metal).
- c. Since oxygen family nonmetals form -2 charged ions in ionic compounds, K_2X would be the predicted formula where X is the unknown nonmetal.
- d. From the size trend, this element would have a smaller radius than barium.
- e. From the ionization energy trend, this element would have a smaller ionization energy than fluorine.
125. a.
- | | |
|---|---------------------------------|
| $\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$ | $I_1 = 495 \text{ kJ}$ |
| $\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$ | $\text{EA} = -348.7 \text{ kJ}$ |
| <div style="display: flex; justify-content: space-between;"> $\text{Na(g)} + \text{Cl(g)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$ $\Delta H = 146 \text{ kJ}$ </div> | |
- b.
- | | |
|---|---------------------------------|
| $\text{Mg(g)} \rightarrow \text{Mg}^+(\text{g}) + \text{e}^-$ | $I_1 = 735 \text{ kJ}$ |
| $\text{F(g)} + \text{e}^- \rightarrow \text{F}^-(\text{g})$ | $\text{EA} = -327.8 \text{ kJ}$ |
| <div style="display: flex; justify-content: space-between;"> $\text{Mg(g)} + \text{F(g)} \rightarrow \text{Mg}^+(\text{g}) + \text{F}^-(\text{g})$ $\Delta H = 407 \text{ kJ}$ </div> | |
- c.
- | | |
|--|---------------------------------|
| $\text{Mg}^+(\text{g}) \rightarrow \text{Mg}^{2+}(\text{g}) + \text{e}^-$ | $I_2 = 1445 \text{ kJ}$ |
| $\text{F(g)} + \text{e}^- \rightarrow \text{F}^-(\text{g})$ | $\text{EA} = -327.8 \text{ kJ}$ |
| <div style="display: flex; justify-content: space-between;"> $\text{Mg}^+(\text{g}) + \text{F(g)} \rightarrow \text{Mg}^{2+}(\text{g}) + \text{F}^-(\text{g})$ $\Delta H = 1117 \text{ kJ}$ </div> | |
- d. From parts b and c we get:
- | | |
|---|------------------------------|
| $\text{Mg(g)} + \text{F(g)} \rightarrow \text{Mg}^+(\text{g}) + \text{F}^-(\text{g})$ | $\Delta H = 407 \text{ kJ}$ |
| $\text{Mg}^+(\text{g}) + \text{F(g)} \rightarrow \text{Mg}^{2+}(\text{g}) + \text{F}^-(\text{g})$ | $\Delta H = 1117 \text{ kJ}$ |
| <div style="display: flex; justify-content: space-between;"> $\text{Mg(g)} + 2 \text{ F(g)} \rightarrow \text{Mg}^{2+}(\text{g}) + 2 \text{ F}^-(\text{g})$ $\Delta H = 1524 \text{ kJ}$ </div> | |
126. a. $\text{Se}^{3+}(\text{g}) \rightarrow \text{Se}^{4+}(\text{g}) + \text{e}^-$
- b. $\text{S}^-(\text{g}) + \text{e}^- \rightarrow \text{S}^{2-}(\text{g})$
- c. $\text{Fe}^{3+}(\text{g}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{g})$
- d. $\text{Mg(g)} \rightarrow \text{Mg}^+(\text{g}) + \text{e}^-$

Challenge Problems

$$127. \quad E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{253.4 \times 10^{-9} \text{ m}} = 7.839 \times 10^{-19} \text{ J}; \quad \Delta E = -7.839 \times 10^{-19} \text{ J}$$

The general energy equation for one-electron ions is $E_n = -2.178 \times 10^{-18} \text{ J } (Z^2/n^2)$ where Z = atomic number.

$$\Delta E = -2.178 \times 10^{-18} \text{ J } (Z)^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \quad Z = 4 \text{ for } \text{Be}^{3+}$$

$$-7.839 \times 10^{-19} \text{ J} = -2.178 \times 10^{-18} (4)^2 \left(\frac{1}{n_f^2} - \frac{1}{5^2} \right)$$

$$\frac{7.839 \times 10^{-19}}{2.178 \times 10^{-18} \times 16} + \frac{1}{25} = \frac{1}{n_f^2}, \quad \frac{1}{n_f^2} = 0.06249, \quad n_f = 4$$

This emission line corresponds to the $n = 5 \rightarrow n = 4$ electronic transition.

128. a. Since wavelength is inversely proportional to energy, the spectral line to the right of B (at a larger wavelength) represents the lowest possible energy transition; this is $n = 4$ to $n = 3$. The B line represents the next lowest energy transition, which is $n = 5$ to $n = 3$ and the A line corresponds to the $n = 6$ to $n = 3$ electronic transition.
- b. Since this spectrum is for a one-electron ion, then $E_n = -2.178 \times 10^{-18} \text{ J } (Z^2/n^2)$. To determine ΔE and, in turn, the wavelength of spectral line A, we must determine Z , the atomic number of the one-electron species. Use spectral line B data to determine Z .

$$\Delta E_{5 \rightarrow 3} = -2.178 \times 10^{-18} \text{ J } (Z^2) \left(\frac{1}{3^2} - \frac{1}{5^2} \right) = -2.178 \times 10^{-18} \left(\frac{Z^2}{3^2} - \frac{Z^2}{5^2} \right)$$

$$\Delta E_{5 \rightarrow 3} = -2.178 \times 10^{-18} \left(\frac{16 Z^2}{9 \times 25} \right)$$

$$E = \frac{hc}{\lambda} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{142.5 \times 10^{-9} \text{ m}} = 1.394 \times 10^{-18} \text{ J}$$

Since an emission occurs, $\Delta E_{5 \rightarrow 3} = -1.394 \times 10^{-18} \text{ J}$.

$$\Delta E = -1.394 \times 10^{-18} \text{ J} = -2.178 \times 10^{-18} \text{ J } \left(\frac{16 Z^2}{9 \times 25} \right), \quad Z^2 = 9.001, \quad Z = 3; \quad \text{The ion is } \text{Li}^{2+}.$$

Solving for the wavelength of line A:

$$\Delta E_{6 \rightarrow 3} = -2.178 \times 10^{-18} (3)^2 \left(\frac{1}{3^2} - \frac{1}{6^2} \right) = -1.634 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.634 \times 10^{-18} \text{ J}} = 1.216 \times 10^{-7} \text{ m} = 121.6 \text{ nm}$$

129. For $r = a_0$ and $\theta = 0^\circ$ ($Z = 1$ for H):

$$\psi_{2p_z} = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{5.29 \times 10^{-11}} \right)^{3/2} (1) e^{-1/2} \cos 0 = 1.57 \times 10^{14}; \quad \psi^2 = 2.46 \times 10^{28}$$

For $r = a_0$ and $\theta = 90^\circ$, $\psi_{2p_z} = 0$ since $\cos 90^\circ = 0$; $\psi^2 = 0$

There is no probability of finding an electron in the $2p_z$ orbital with $\theta = 0^\circ$. As expected, the xy plane, which corresponds to $\theta = 0^\circ$, is a node for the $2p_z$ atomic orbital.

130. a. Each orbital could hold 3 electrons.

b. The first period corresponds to $n = 1$ which can only have 1s orbitals. The 1s orbital could hold 3 electrons, hence the first period would have three elements. The second period corresponds to $n = 2$, which has 2s and 2p orbitals. These four orbitals can each hold three electrons. A total of 12 elements would be in the second period.

c. 15

d. 21

131. a. 1st period: $p = 1, q = 1, r = 0, s = \pm 1/2$ (2 elements)

2nd period: $p = 2, q = 1, r = 0, s = \pm 1/2$ (2 elements)

3rd period: $p = 3, q = 1, r = 0, s = \pm 1/2$ (2 elements)

$p = 3, q = 3, r = -2, s = \pm 1/2$ (2 elements)

$p = 3, q = 3, r = 0, s = \pm 1/2$ (2 elements)

$p = 3, q = 3, r = +2, s = \pm 1/2$ (2 elements)

4th period: $p = 4$; q and r values are the same as with $p = 3$ (8 total elements)

1							2
3							4
5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20

- b. Elements 2, 4, 12 and 20 all have filled shells and will be least reactive.
- c. Draw similarities to the modern periodic table.

XY could be X^+Y^- , $X^{2+}Y^{2-}$ or $X^{3+}Y^{3-}$. Possible ions for each are:

X^+ could be elements 1, 3, 5 or 13; Y^- could be 11 or 19.

X^{2+} could be 6 or 14; Y^{2-} could be 10 or 18.

X^{3+} could be 7 or 15; Y^{3-} could be 9 or 17.

Note: X^{4+} and Y^{4-} ions probably won't form.

XY_2 will be $X^{2+}(Y^-)_2$; See above for possible ions.

X_2Y will be $(X^+)_2Y^{2-}$; See above for possible ions.

XY_3 will be $X^{3+}(Y^-)_3$; See above for possible ions.

X_2Y_3 will be $(X^{3+})_2(Y^{2-})_3$; See above for possible ions.

- d. $p = 4$, $q = 3$, $r = -2$, $s = \pm 1/2$ (2)

$$p = 4, q = 3, r = 0, s = \pm 1/2 \text{ (2)}$$

$$p = 4, q = 3, r = +2, s = \pm 1/2 \text{ (2)}$$

A total of 6 electrons can have $p = 4$ and $q = 3$.

- e. $p = 3$, $q = 0$, $r = 0$: This is not allowed; q must be odd. Zero electrons can have these quantum numbers.

- f. $p = 6$, $q = 1$, $r = 0$, $s = \pm 1/2$ (2)

$$p = 6, q = 3, r = -2, 0, +2; s = \pm 1/2 \text{ (6)}$$

$$p = 6, q = 5, r = -4, -2, 0, +2, +4; s = \pm 1/2 \text{ (10)}$$

Eighteen electrons can have $p = 6$.

132. Size also decreases going across a period. Sc & Ti and Y & Zr are adjacent elements. There are 14 elements (the lanthanides) between La and Hf, making Hf considerably smaller.
133. a. As we remove succeeding electrons, the electron being removed is closer to the nucleus, and there are fewer electrons left repelling it. The remaining electrons are more strongly attracted to the nucleus, and it takes more energy to remove these electrons.
- b. Al : $1s^2 2s^2 2p^6 3s^2 3p^1$; For I_4 , we begin by removing an electron with $n = 2$. For I_3 , we remove an electron with $n = 3$. In going from $n = 3$ to $n = 2$, there is a big jump in ionization energy

because the $n = 2$ electrons (inner core electrons) are much closer to the nucleus on average than $n = 3$ electrons (valence electrons). Since the $n = 2$ electrons are closer to the nucleus, they are held more tightly and require a much larger amount of energy to remove them compared to the $n = 3$ electrons.

- c. Al^{4+} ; The electron affinity for Al^{4+} is ΔH for the reaction:



- d. The greater the number of electrons, the greater the size.

Size trend: $\text{Al}^{4+} < \text{Al}^{3+} < \text{Al}^{2+} < \text{Al}^+ < \text{Al}$

134. None of the noble gases and no subatomic particles had been discovered when Mendeleev published his periodic table. Thus, there was not an element out of place in terms of reactivity. There was no reason to predict an entire family of elements. Mendeleev ordered his table by mass; he had no way of knowing there were gaps in atomic numbers (they hadn't been discovered yet).