

## BEING AN EFFECTIVE TEACHING ASSISTANT

by Steven Zumdahl

In large general chemistry programs, teaching assistants typically play a crucial role. Their attitudes and levels of preparation greatly affect the quality of education that the students receive. Following is an excerpt from the TA manual used at the University of Illinois. We hope these comments will also be helpful to TAs at other institutions.

### INTRODUCTION

Teaching assistants form the heart of any large general chemistry program. The quality of the instruction is highly dependent on your attitude and your teaching skills. You have most of the close contacts with the students and thus can most directly influence their performance. It is very important that you take this responsibility seriously and do the best job possible. Following are some specific suggestions that you should find helpful.

### GENERAL COMMENTS

1. **Spend some time thinking about the learning process.** Although you may never have taken a course in the psychology of education, you have a great deal of experience in the field—you have been a student for over 15 years. Think about your experience as a student. Figure out why some teachers were very effective and others very ineffective. Your long experience as a student is excellent preparation for your teaching career.

2. **Your attitude is crucial** in setting the correct tone for your class.

**Be enthusiastic.** Project a positive attitude toward your students and the subject. Presumably you are excited about chemistry or you wouldn't be pursuing a graduate degree in the subject. Let this enthusiasm shine through.

**Avoid being cynical and negative.** Poor attitudes will rub off on your students. If you have a criticism of the way the course is being run, see the professor for the course—do not gripe to the students. Your attitude has a very important effect on the attitudes of your students. Setting a good example is one of the most important things a good teacher does for his/her students.

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might mean a molecule such as N or O or we might mean a large sample such as a bar of aluminum or the graphite (“lead”) in a pencil. Be sure to help students realize that chemists use terms in many ways and they need to look at the context of the word to be sure that they understand what is intended. Chemists are accustomed to thinking about things at the macroscopic and microscopic level simultaneously. Encourage students to think about what they read and to consider how the terms are being used.

- Sections 1.3 and 1.4 provide another opportunity to discuss the difference between laws and theories. Dalton’s atomic theory is relatively simple in scope, and this is as it should be. John Dalton was trying to explain laws such as the law of constant composition. The success of this makes the model successful, but not absolutely correct (a model is always a simplification). For example, Dalton’s theory does not explain questions such as “Why/how do atoms stick together to form molecules?”, and “Why/how do molecules stick together to form liquids and solids?”. But no model answers all questions.
- The discovery of the proton leads to an excellent example of how and why models change. Dalton’s model of the atom did not account for isotopes since he assumed that all atoms of an element are exactly alike. As knowledge expands models change to accommodate the new information

## CHAPTER TWO: ATOMIC STRUCTURE AND PERIODICITY

### Chapter Learning Goals:

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|----------------|--|
| Section One:   | To characterize electromagnetic radiation in terms of wavelength, frequency, and speed.  |
| Section Two:   | To introduce the concept of quantized energy.<br>To show that light has both wave and particulate properties.<br>To describe how diffraction experiments were used to demonstrate the dual nature of all matter. |
| Section Three: | To show that the line spectrum of hydrogen demonstrates the quantized nature of the energy of its electron.  |
| Section Four:  | To describe the development of the Bohr model for the hydrogen atom.   |
| Section Five:  | To show how standing waves can be used to describe electrons in atoms.<br>To describe the Heisenberg uncertainty principle.<br>To explain the significance of electron probability distributions.                |
| Section Six:   | To explain the quantum numbers $n$ , $l$ , and $m_l$ .   |
| Section Seven: | To describe the shapes of orbitals designated by s, p, d, and f and to discuss orbital energies.   |
| Section Eight: | To define electron spin and the electron spin quantum number.  |

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- To explain the Pauli exclusion principle.
- Section Nine: To show how the quantum mechanical model can be applied to atoms besides hydrogen.
- Section Ten: To trace the development of the periodic table.
- Section Eleven: To explain the Aufbau principle.
- Section Twelve: To show general trends in ionization energy, electron affinity, and atomic radius in the periodic table.
- Section Thirteen: To show what types of information can be obtained from the periodic table.

This chapter combines into one what many texts do in two. Particular attention is paid to the relationship between models and facts. The order of topics is very similar to texts that treat electronic structure and the periodic table separately. The nature of light and the quantum mechanical model of the hydrogen atom are discussed. Then the historical development of the periodic table is followed by a discussion of the quantum mechanical model of polyelectronic atoms and how the model fits the periodic table. In discussing polyelectronic atoms, observation and the periodic table are emphasized. The concept of shielding is used to rationalize the periodic trends in size, ionization energy, and electron affinity. At first this may seem to be too sophisticated and abstract an approach for first-year chemistry students. However, the approach is very pictorial and easy to comprehend. We have found this approach to work well in our classes. Emphasis can be shifted at the instructor's option between models and the experimental facts. Combining the atomic theory with the periodic table makes this easier.

The last part of the chapter discusses the periodic trends and properties of the alkali metals. This presents the instructor with another opportunity to integrate more descriptive chemistry in with the chemical principles. Chapter 19 is organized to discuss the elements by periodic group. Instructors may choose other groups from these chapters to illustrate chemical periodicity.

A further point should be made concerning atomic radii. The volumes given in Chapter 2 are for covalent radii. The covalent radii of He, Ne, and Ar are estimates. All comparisons of atomic sizes to each other can be done consistently with this set of radii.

In Chapter 3, instructors may want to compare the sizes of a series of ions to the isoelectronic noble gases. The radii of the noble gases for this comparison should be the univalent crystal radii. These values are: He = 93 pm, Ne = 112 pm, Ar = 154 pm, Kr = 169 pm, and Xe = 190 pm. Huheey<sup>1</sup> and Pauling<sup>2</sup> provide detailed information on uses of ionic radii and tables of their values.

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<sup>1</sup>James E. Huheey, *Inorganic Chemistry; Principles of Structure and Reactivity*, 3rd ed., Harper and Row (1983).

<sup>2</sup>Linus Pauling, *The Nature of The Chemical Bond*, Cornell University Press (1960), pp. 511-519.

### Teaching Tips

- Students often consider the forms of electromagnetic radiation outside the visible range (radio, X-rays, infrared, microwaves) to be entirely different from light. Use Figure 2.2 (the electromagnetic spectrum) to show the range of frequencies for each type of radiation.
- A commonly used analogy for the energy levels within an atom is the staircase. A person can move from one step to another or even move up 2 or 3 steps and down a similar number. It is not possible however to move up or down a part of a step. Within atoms electron energies are quantized – the energy levels are like stairsteps. Electrons can change only between established energy levels, not in between. Compare this to using a ramp which is like continuous energies.
- Be sure to discuss how hydrogen can have multiple lines even though it has only one electron. Students often forget that they are observing multiple atoms simultaneously when observing a line emission spectrum.
- Point out that the quantized nature of atoms is a surprise and non-intuitive. It is comforting to students to realize that this topic is complicated even to people who have been studying it for awhile.
- This is an excellent time to discuss the colors of streetlights. The mercury vapor lights have a blue cast, while the sodium lights are yellow and neon lights are more orange. You may also want to discuss the difference between an incandescent light and a vapor light. Many students think all lights are the same. They may not realize that an incandescent lamp produces a continuous spectrum since the tiny filament is radiating all wavelengths of visible light while vapor lamps (like many street lights) are more like gas discharge tubes in their operation.
- It is a good idea to emphasize that although the Bohr model of the atoms is important historically, it does not represent an accurate model for the atom. Bohr's model is no longer accepted because it is considered fundamentally incorrect (this is why the section is so short). A discussion of this model is useful in discussing the nature of science. The Bohr model is a relatively simple model with the sole intent of explaining the results of the hydrogen emission spectrum. It succeeded in doing so and this is why it was considered powerful. However, this model does not fit polyelectronic atoms and electrons do not move in fixed orbits.
- In this section the idea of probability as a model for understanding nature is introduced. This will be new to all students and most will find it confusing. It is a fundamental change from determinism in looking at the world and it is understandable that students will have difficulty with it. For example, students

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will tend to think of orbitals as physical structures and will find it difficult to think of them as probability distributions. In Section 2.5 we describe the orbital as a *potential space* for an electron. This is a good way for the students to think about it initially.

- Many students confuse orbitals and orbits. An orbit describes a particular path an object follows as it travels around another. For example, the moon has an orbit about the earth. Electrons do not follow a particular path around the nucleus. An orbital describes the volume around the nucleus where an electron is likely to be found. The exact path of an electron in this area is not known.
- For polyelectronic atoms the third electron goes to the 2s orbital. In the hydrogen atom the 2s and 2p orbitals have the same energy. However, multiple electrons change this. With multiple electrons, in a given energy level the s orbitals are lower in energy (and thus filled first) than the p orbitals, which in turn are lower in energy than the d orbitals.
- Encourage the students to use the periodic table to assist them in figuring out electron configurations. Once they see that they can just move across the rows, filling electrons into the s and p orbitals, electron configurations become much easier to write. This should be used to emphasize the periodicity of the periodic table (even though the table was invented before the discovery of electrons). Thus, the students should realize that with an understanding of how the periodic table is put together, the students can figure out the expected electron configuration of any element. They need not memorize these. See Figures 2.27 and 2.28 in the text.
- Make sure students understand the trends for atomic size across rows and down groups in the periodic table. If they understand these trends, the trends for ionization energy are much easier to grasp. The students should be able to see that the trends for atomic size and ionization energy are consistent with one another.
- Many students believe that alkali metals “want” to lose an electron; that is, the potassium atom, for example, will release energy to become an ion. Or they believe that less energy is required to remove the second electron from calcium, for example, than the first because calcium “wants” to lose two electrons. Energy is always required to remove an electron, and successive electrons can only be removed with an increasing amount of energy.

## CHAPTER THREE: BONDING: GENERAL CONCEPTS

### Chapter Learning Goals:

## Discussion of Active Learning Questions

important here is to stress that the answers are more contingent on their support than on absolute “correctness.” However, most students will probably claim in part a that electrons are the most important for the formation of compounds (especially due to Thomson's findings that the electrons are so easily removed). In the case of part c, it is most important to stress that any model that explains Thomson's findings is reasonable, and that this endeavor is what developing models is about; that is, matching observations, not reality. This emphasis on models is extremely important in chemistry and will be further stressed in Chapter 7.

5. When several hundred incoming UIUC students were asked what happens to the size of molecules and to the mass of a sample as ice is heated (until it is steam), about one-third of the students believed that the mass and molecular size varies. Most of these students believed that the mass of the ice is greater than that of the steam, and that the size of the “steam molecules” is greater than that of the “ice molecules.” The drawings in conjunction with the explanations can reveal quite a bit about the students' ideas.
6. When several hundred incoming UIUC students were asked this question, almost 40% of the students responded that the mass of this system would decrease, presumably because the chemical has either “disappeared” or has been converted into a gas (which many believed has less mass than the solid). Most of the rest correctly believe that the system ends up with the same mass, although it again is interesting to ask them explain why (especially without using the phrase “law of conservation of mass”).
7. Many students will choose “b”. The correct answer is “d” (although there can be air bubbles as well initially when water begins to boil).
8. Yes, many questions are raised from Dalton's theory. For example: What are the masses of the atoms? Are atoms really structureless? What forces hold atoms together in compounds?
9. We now know that some atoms of the same element have different masses. We have had to include the existence of isotopes in our models.
10. Students should realize that it is the number of protons that “define” an element. Thus, choices b and c are correct.

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1. The purpose of this question is to prompt students to think about the difference between wavelike and particulate properties. It is important for the students to realize that the properties describe the same electron, and perhaps even to realize that the concept of an electron is a model we use.

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- This question is primarily to get the students thinking about what it means for something to be a model, why a model is said to work, and why one would want to abandon an existing model in favor of a new model. In this case, Bohr's model works with hydrogen (and with any one-electron species). In the one-electron cases, it is quite a good model that can predict behavior (although models do not describe reality). Because of the complexities of electron-electron repulsion, however, the model fails to account for other elements.
- In this problem the students should note that there is a great change between the second and third ionization energies for both elements X and Y. This could indicate that the elements are alkaline earth metals. Because the ionization energies of Y are greater than those of X, element Y should be above X in the periodic table (so, for example, Y could be Mg and X could be Ca). The purpose here is to have the students think about what these numbers mean and how to use the learned trends.
- Many students think of the first ionization energy for a noble gas as being higher than the second ionization energy because of a memorized rule such as "All elements want to be like noble gases." While this statement is true to an extent, many students misuse it to mean that an atom such as He "really does not want to" lose an electron; however, if it already has, then it is not so difficult to lose the next one. Using this logic, students will also claim that the second ionization energy for an atom such as Mg will actually be negative so that it can be like Ne. Again, the goal here is to prompt the students to elaborate on their ideas.
- Many students realize that taking a second electron from lithium will be difficult (take quite a bit of energy) because after losing the first electron, the ion will have the same configuration as He. However, as mentioned above, many students will also claim that the second ionization energy for beryllium will be negative (exothermic) because the beryllium ion will "want" to lose another electron to be like He. Do not allow the students to look up the numbers before answering this question (although it might be a good idea to do so after a lengthy discussion) and make sure that the students do not just provide a quick answer (such as "The second IE for Li is greater") but rather explain their reasoning.
- This question is meant to stress exceptions. Even though these exceptions are explained at length in the book, many time students tend not to give graphs and figures their full attention; whenever you can ask them to explain a figure or graph, it is probably a good idea. This will be especially true in later chapters when some Active Learning Questions explicitly ask students to explain figures.
- This question is intended to get the students to think about how to use the trends they have learned. Also, you can get a better idea about what they are thinking in terms of atoms "wanting" to be like noble gases as in questions 4 and 5. Having the students compare their answers to those in the book and then trying

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to understand the differences can also be enlightening.

8. Students have noticed this trend and are not sure why it exists. In fact, some students have just accepted it as “the way that it is,” which is an attitude that should be dispelled as soon as possible. Questions such as this one, which ask the students to explain something that they may have been merely accepting, are therefore quite educational. Even if we are not sure of the answer, it is a good idea for the students to see that we can make educated hypotheses based on previous information. Students may equate metallic behavior with atomic size and answer accordingly, or you may have to lead them through this concept a bit; whatever the case, allow the students time to discuss their ideas.
9. This question is intended to get the students thinking about the vagueness inherent in the concept of an electron, away from a negatively charged particle with a known orbit.
10. Again, one of the best aspects of a question like this one is that the students are required to explain why they did not choose four of the choices, and, of course, why they did choose a specific answer (not just to choose it but to explain it). In this case, the answer is c, but what is more important at this point is to allow the students the chance to elaborate on their ideas. Once a considerable discussion has taken place, and after choice c is considered as the best answer, this situation serves as another example of Hess' law (depending on when it is covered).
11. As with other questions for this chapter, the goal here is to get to students' ideas about ionization energy when an atom losing an electron is isoelectronic with a noble gas. The most important issue here (as with the other questions) is not to just allow students to answer either “true” or “false” but to explain their ideas. In this case, energy is still required for a potassium atom to lose an electron even though many students will claim that a potassium atom “wants to do this,” and will therefore lose an electron spontaneously (sometimes even claiming that energy is given off).
12. The main reason for this question stems from the observation that many times students merely memorize trends across and down the periodic table or, at best, use a memorized rule as an explanation (such as “there is an increase in electrons”). Thus this question provides a discrepant situation -- if a student uses the “increase in electron” rule as an explanation, this question serves to show the students that this rule has the opposite effects intended. Have the students explain the trends instead of just memorizing them.
13. Students have a notion that we know exactly where the electrons are and that they move in predictable orbits. We need to help them accept the idea that our models are based on probability.



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14. The term “orbital” is unfortunate in that many students infer a circular orbit from it. However, it represents a region of probability in which one is likely to find an electron. This distinction is crucial.
15. These concepts are discussed in section 2.5, but the subtleties can be missed without an “active” read of this section.
16. This is true although some students will say it is false and claim that the hydrogen atom only has a 1s orbital. This question can be followed by a discussion of the concept of orbitals.
17. This 2s and 2p orbitals are degenerate for hydrogen because there is only one electron. For helium, the 2s orbital is lower in energy than the 2p. If one electron of the helium atom is excited, it has a greater probability of being in the 2s orbital because of the so-called “penetration effect” discussed in section 2.9.
18. The students should be able to do this with data given in Chapter 2, providing they understand the concepts of ionization energy and electron affinity. The data needed are: ionization energy of Na (495 kJ/mol), ionization energy of F (about 1750 kJ/mol), and electron affinity of F (-327.8 kJ/mol). Thus, to take an electron from Na, and then have the F take it in, would require 167.2 kJ/mol (495-327.8), while taking from one F and giving to another would require about 1422.2 kJ/mol (1750-327.8). While both are energetically unfavorable, it is “less unfavorable” for the reaction between Na and F than F and F. This is a good lead into a discussion of lattice energy for Chapter 3.

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1. It would be best to have the students answer this question only using a periodic table (without the textbook). Having them understand how these properties are related will decrease the likelihood that students merely memorize the trends.
2. This question allows the students to discuss lattice energy and ionization energy, and to try to understand how to achieve a lowest possible energy state. A discussion of this question may also shed some light on how an alkali metal can “want” to lose an electron, even though the IE is endothermic. Students may be able to do quantitative problems with lattice energy, but they are not always sure what lattice energy means; this problem is meant to get them to apply their definition.
3. As with question 1, have the students answer this question without using the textbook. The goal here is for students to explain their reasoning rather than simply use a catch-phrase. Allow the students to discuss their predictions once they have looked up the answers in the text, as this discussion could provide you with more insight into their ideas.

## CHAPTER 2

### ATOMIC STRUCTURE AND PERIODICITY

#### Questions

19. The equations relating the terms are  $v\lambda = c$ ,  $E = hv$ , and  $E = hc/\lambda$ . From the equations, wavelength and frequency are inversely related, photon energy and frequency are directly related, and photon energy and wavelength are inversely related. The unit of 1 Joule (J) = 1 kg m<sup>2</sup>/s<sup>2</sup>. This is why you must change mass units to kg when using the deBroglie equation.
20. Frequency is the number of waves (cycles) of electromagnetic radiation per second that pass a given point in space. Speed refers to the distance a wave travels per unit time. All electromagnetic radiation (EMR) travels at the same speed (c, the speed of light =  $2.998 \times 10^8$  m/s). However, each wavelength of EMR has its own unique frequency.
21. The photoelectric effect refers to the phenomenon in which electrons are emitted from the surface of a metal when light strikes it. The light must have a certain minimum frequency (energy) in order to remove electrons from the surface of a metal. Light having a frequency below the minimum results in no electrons being emitted, whereas light at or higher than the minimum frequency does cause electrons to be emitted. For light having a frequency higher than the minimum frequency, the excess energy is transferred into kinetic energy for the emitted electron. Albert Einstein explained the photoelectric effect by applying quantum theory.
22. The emission of light by excited atoms has been the key interconnection between the macroscopic world we can observe and measure, and what is happening on a microscopic basis within an atom. Excited atoms emit light (which we can observe and measure) because of changes in the microscopic structure of the atom. By studying the emissions of atoms, we can trace back to what happened inside the atom. Specifically, our current model of the atom relates the energy of light emitted to electrons in the atom moving from higher allowed energy states to lower allowed energy states.
23. Example 2-3 calculates the de Broglie wavelength of a ball and of an electron. The ball has a wavelength on the order of  $10^{-34}$  m. This is incredibly short and, as far as the wave-particle duality is concerned, the wave properties of large objects are insignificant. The electron, with its tiny mass, also has a short wavelength; on the order of  $10^{-10}$  m. However, this wavelength is significant because it is on the same order as the spacing between atoms in a typical crystal. For very tiny objects like electrons, the wave properties are important. The wave properties must be considered, along with the particle properties, when hypothesizing about the electron motion in an atom.

24. a. For hydrogen ( $Z = 1$ ), the energy levels in units of Joules are given by the equation  $E_n = -2.178 \times 10^{-18}(1/n^2)$ . As  $n$  increases, the differences between  $1/n^2$  for consecutive energy levels becomes smaller and smaller. Consider the difference between  $1/n^2$  values for  $n = 1$  and  $n = 2$  as compared to  $n = 3$  and  $n = 4$ .

For  $n = 1$  and  $n = 2$ :

$$\frac{1}{1^2} - \frac{1}{2^2} = 1 - 0.25 = 0.75$$

For  $n = 3$  and  $n = 4$ :

$$\frac{1}{3^2} - \frac{1}{4^2} = 0.1111 - 0.0625 = 0.0486$$

So because the differences between  $1/n^2$  values for consecutive energy levels decrease as  $n$  increases, the energy levels get closer together as  $n$  increases.

- b. For a spectral transition for hydrogen,  $\Delta E = E_f - E_i$ :

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

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

In the diagram, the red line is for the  $n_i = 3$  to  $n_f = 2$  transition.

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

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

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

$$|\Delta E| = E_{\text{photon}} = h\nu = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{3.025 \times 10^{-19} \text{ J}} \\ = 6.567 \times 10^{-7} \text{ m} = 656.7 \text{ nm}$$

From Figure 2-2,  $\lambda = 656.7 \text{ nm}$  is red light so the diagram is correct for the red line.

In the diagram, the green line is for the  $n_i = 4$  to  $n_f = 2$  transition.

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

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

From Figure 2-2,  $\lambda = 486.4 \text{ nm}$  is green-blue light. So the diagram is ok with this line.

In the diagram, the blue line is for the  $n_i = 5$  to  $n_f = 2$  transition.

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = -4.574 \times 10^{-19} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{4.574 \times 10^{-19} \text{ J}} = 4.343 \times 10^{-7} \text{ m} = 434.3 \text{ nm}$$

From Figure 2-2,  $\lambda = 434.3 \text{ nm}$  is blue or blue-violet light. So the diagram is ok with this line also.

25. The Bohr model was an important step in the development of the current quantum mechanical model of the atom. The idea that electrons can only occupy certain, allowed energy levels is illustrated nicely (and relatively easily). We talk about the Bohr model to present the idea of quantized energy levels.

26. The figure on the left tells us that the probability of finding the electron in the 1s orbital at points along a line drawn outward in any direction. This probability is greatest close to the nucleus and drops off rapidly as the distance from the nucleus increases.

The figure on the right represents the total probability of finding the electron at a particular distance from the nucleus for a 1s hydrogen orbital. For this distribution, the hydrogen 1s orbital is divided into successive thin spherical shells and the total probability of finding the electron in each spherical shell is plotted versus distance from the nucleus. This graph is called the radial probability distribution.

27. When the p and d orbital functions are evaluated at various points in space, the results sometimes have positive values and sometimes have negative values. The term phase is often associated with the + and - signs. For example, a sine wave has alternating positive and negative phases. This is analogous to the positive and negative values (phases) in the p and d orbitals.

28. The widths of the various blocks in the periodic table are determined by the number of electrons that can occupy the specific orbital(s). In the s block, we have one orbital ( $\ell = 0$ ,  $m_\ell = 0$ ) that can hold two electrons; the s block is two elements wide. For the f block, there are 7 degenerate f orbitals ( $\ell = 3$ ,  $m_\ell = -3, -2, -1, 0, 1, 2, 3$ ), so the f block is 14 elements wide. The g block corresponds to  $\ell = 4$ . The number of degenerate g orbitals is 9. This comes from the 9 possible  $m_\ell$  values when  $\ell = 4$  ( $m_\ell = -4, -3, -2, -1, 0, 1, 2, 3, 4$ ). With 9 orbitals, each orbital holding two electrons, the g block would be 18 elements wide. The h block has  $\ell = 5$ ,  $m_\ell = -5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5$ . With 11 degenerate h orbitals, the h block would be 22 elements wide.

29. If one more electron is added to a half-filled subshell, electron-electron repulsions will increase because two electrons must now occupy the same atomic orbital. This may slightly decrease the stability of the atom.

30. Size decreases from left to right and increases going down the periodic table. Thus, 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 sizes and ionization energies 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 negative (favorable) electron affinities. The noble gases are an exception; they have large ionization energy values but have positive (unfavorable) electron affinity values. Noble gases have a filled valence shell of electrons. The added electron in a noble gas must go into a higher  $n$  value atomic orbital, having a significantly higher energy, and this is very unfavorable.
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 negative) electron affinities. Considering only electron-nucleus attractions, smaller atoms would be expected to have the more favorable (more negative) electron affinity values. These trends are exactly the opposite of each other. Thus the overall variation in electron affinity is not as great as ionization energy in which attractions to the nucleus dominate.
33. For hydrogen and one-electron ions (hydrogen-like 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  $\ell$ . Because 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 because each element has unique energy levels. 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 applies to the removal of the electron from an atom in the gas phase. The work function applies to the removal of an electron from the solid element.
- Ionization energy:  $M(g) \rightarrow M^+(g) + e^-$ ; work function:  $M(s) \rightarrow M^+(s) + e^-$
38.  $Li^+$  ions are the smallest of the alkali metal cations and will be most strongly attracted to the water molecules.

## Exercises

### Light and Matter

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

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

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

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

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

$$\frac{8.0 \times 10^{-18} \text{ J}}{\text{photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} = 4.8 \times 10^6 \text{ J/mol}$$

$$43. \quad 280 \text{ nm: } \nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{280 \text{ nm} \times \frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}} = 1.1 \times 10^{15} \text{ s}^{-1}$$

$$320 \text{ nm: } \nu = \frac{3.00 \times 10^8 \text{ m/s}}{320 \times 10^{-9} \text{ nm}} = 9.4 \times 10^{14} \text{ s}^{-1}$$

The compounds in the sunscreen absorb ultraviolet B (UVB) electromagnetic radiation having a frequency from  $9.4 \times 10^{14} \text{ s}^{-1}$  to  $1.1 \times 10^{15} \text{ s}^{-1}$ .

$$44. \quad \text{S-type cone receptors: } \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{6.00 \times 10^{14} \text{ s}^{-1}} = 5.00 \times 10^{-7} \text{ m} = 500. \text{ nm}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{7.49 \times 10^{14} \text{ s}^{-1}} = 4.00 \times 10^{-7} \text{ m} = 400. \text{ nm}$$

S-type cone receptors detect 400-500 nm light. From Figure 2-2 in the text, this is violet to green light.

$$\text{M-type cone receptors: } \lambda = \frac{2.998 \times 10^8 \text{ m/s}}{4.76 \times 10^{14} \text{ s}^{-1}} = 6.30 \times 10^{-7} \text{ m} = 630. \text{ nm}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{6.62 \times 10^{14} \text{ s}^{-1}} = 4.53 \times 10^{-7} \text{ m} = 453 \text{ nm}$$

M-type cone receptors detect 450-630 nm light. From Figure 2-2 in the text, this is blue to orange light.

$$\text{L-type cone receptors: } \lambda = \frac{2.998 \times 10^8 \text{ m/s}}{4.28 \times 10^{14} \text{ s}^{-1}} = 7.00 \times 10^{-7} \text{ m} = 700. \text{ nm}$$

$$\lambda = \frac{2.998 \times 10^8 \text{ m/s}}{6.00 \times 10^{14} \text{ s}^{-1}} = 5.00 \times 10^{-7} \text{ m} = 500. \text{ nm}$$

L-type cone receptors detect 500-700 nm light. This represents green to red light.

45. 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. Because frequency and photon energy are both inversely proportional to wavelength, wave *b* will have the higher frequency and larger photon energy since it has the shorter wavelength.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{2.0 \times 10^{-4} \text{ m}} = 1.5 \times 10^{12} \text{ s}^{-1}$$

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{2.0 \times 10^{-4} \text{ m}} = 9.9 \times 10^{-22} \text{ J}$$

Because both waves are examples of electromagnetic radiation, both waves travel at the same speed, *c*, the speed of light. From Figure 2-2 of the text, both of these waves represent infrared electromagnetic radiation.

46. Referencing Figure 2-2 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 radio-waves.

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

The  $3.97 \times 10^{-19} \text{ J}$ /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  $\nu$  are both inversely related to  $\lambda$ . From the previously calculated wavelengths, the order of photon energy and frequency is:

FM radiowaves	<	visible (green) light	<	X rays
longest $\lambda$				shortest $\lambda$
lowest $\nu$				highest $\nu$
smallest <i>E</i>				largest <i>E</i>

47. 
$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{150. \text{ nm} \times \frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}} = 1.32 \times 10^{-18} \text{ J}$$

$$1.98 \times 10^5 \text{ J} \times \frac{1 \text{ photon}}{1.32 \times 10^{-18} \text{ J}} \times \frac{1 \text{ atom C}}{\text{photon}} = 1.50 \times 10^{23} \text{ atoms C}$$

$$48. \quad E_{\text{photon}} = h\nu = \frac{hc}{\lambda}, \quad E_{\text{photon}} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{1.0 \times 10^{-10} \text{ m}} = 2.0 \times 10^{-15} \text{ J}$$

$$\frac{2.0 \times 10^{-15} \text{ J}}{\text{photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.2 \times 10^6 \text{ kJ/mol}$$

$$E_{\text{photon}} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{1.0 \times 10^4 \text{ m}} = 2.0 \times 10^{-29} \text{ J}$$

$$\frac{2.0 \times 10^{-29} \text{ J}}{\text{photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 1.2 \times 10^{-8} \text{ kJ/mol}$$

X rays do have an energy greater than the carbon-carbon bond energy. Therefore, X rays could conceivably break carbon-carbon bonds in organic compounds and thereby disrupt the function of an organic molecule. Radio waves, however, do not have sufficient energy to break carbon-carbon bonds and are therefore relatively harmless.

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

$$\frac{279.7 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 4.645 \times 10^{-22} \text{ kJ} = 4.645 \times 10^{-19} \text{ J}$$

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

$$50. \quad \frac{208.4 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 3.461 \times 10^{-22} \text{ kJ} = 3.461 \times 10^{-19} \text{ J to remove one electron}$$

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

51. Ionization energy = energy to remove an electron =  $7.21 \times 10^{-19} \text{ J} = E_{\text{photon}}$

$$E_{\text{photon}} = h\nu \text{ and } \lambda\nu = c. \text{ So } \nu = \frac{c}{\lambda} \text{ and } E = \frac{hc}{\lambda}.$$

$$\lambda = \frac{hc}{E_{\text{photon}}} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m/s}}{7.21 \times 10^{-19} \text{ J}} = 2.76 \times 10^{-7} \text{ m} = 276 \text{ nm}$$

$$52. \quad \frac{890.1 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = \frac{1.478 \times 10^{-21} \text{ kJ}}{\text{atom}} = \frac{1.478 \times 10^{-18} \text{ J}}{\text{atom}}$$

= ionization energy per atom



$$E = \frac{hc}{\lambda}, \lambda = \frac{hc}{E} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1.478 \times 10^{-18} \text{ J}} = 1.344 \times 10^{-7} \text{ m} = 134.4 \text{ nm}$$

No, it will take light having a wavelength of 134.4 nm or less to ionize gold. A photon of light having a wavelength of 225 nm is longer wavelength and thus lower energy than 134.4 nm light.

53. a. 10.0% of speed of light =  $0.10 \times 3.00 \times 10^8 \text{ m/s} = 3.0 \times 10^7 \text{ m/s}$

$$\lambda = \frac{h}{mv}, \lambda = \frac{6.63 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31} \text{ kg} \times 3.0 \times 10^7 \text{ m/s}} = 2.4 \times 10^{-11} \text{ m} = 2.4 \times 10^{-2} \text{ nm}$$

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

b.  $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J s}}{0.055 \text{ kg} \times 35 \text{ m/s}} = 3.4 \times 10^{-34} \text{ m} = 3.4 \times 10^{-25} \text{ nm}$

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

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

55.  $\lambda = \frac{h}{mv}, m = \frac{h}{\lambda v} = \frac{6.63 \times 10^{-34} \text{ J s}}{1.5 \times 10^{-15} \text{ m} \times (0.90 \times 3.00 \times 10^8 \text{ m/s})} = 1.6 \times 10^{-27} \text{ kg}$

This particle is probably a proton or a neutron.

56.  $\lambda = \frac{h}{mv}, v = \frac{h}{\lambda m}$ ; 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**

57. 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  $\Delta E$  always corresponds to an absorption of light, and a negative value of  $\Delta E$  always corresponds to an emission of light.

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

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

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

$$|\Delta E| = E_{\text{photon}} = h\nu = \frac{hc}{\lambda}, \quad \lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{3.025 \times 10^{-19} \text{ J}} \\ = 6.567 \times 10^{-7} \text{ m} = 656.7 \text{ nm}$$

From Figure 2-2, this is visible electromagnetic radiation (red light).

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

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

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

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

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

This is ultraviolet electromagnetic radiation.

$$\text{58. a. } \Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{3^2} - \frac{1}{4^2} \right) = -1.059 \times 10^{-19} \text{ J}$$

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

From Figure 2-2, this is infrared electromagnetic radiation.

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

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

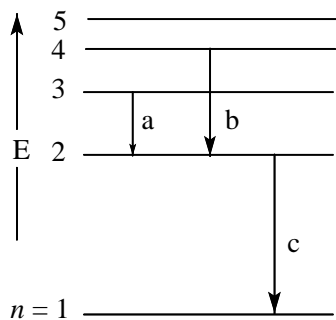
= 4053 nm (infrared)

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

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

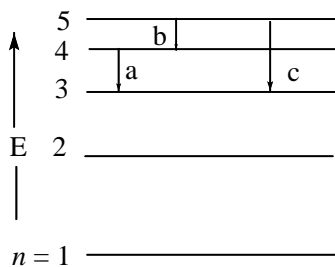
= 1282 nm (infrared)

59.

a.  $3 \rightarrow 2$ b.  $4 \rightarrow 2$ c.  $2 \rightarrow 1$ 

Energy levels are not to scale.

60.

a.  $4 \rightarrow 3$ b.  $5 \rightarrow 4$ c.  $5 \rightarrow 3$ 

Energy levels are not to scale.

61. The longest wavelength light emitted will correspond to the transition with the smallest energy change (smallest  $\Delta E$ ). This is the transition from  $n = 6$  to  $n = 5$ .

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{5^2} - \frac{1}{6^2} \right) = -2.662 \times 10^{-20} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.662 \times 10^{-20} \text{ J}} = 7.462 \times 10^{-6} \text{ m} = 7462 \text{ nm}$$

The shortest wavelength emitted will correspond to the largest  $\Delta E$ ; this is  $n = 6 \rightarrow n = 1$ .

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{1^2} - \frac{1}{6^2} \right) = -2.118 \times 10^{-18} \text{ J}$$

$$\lambda = \frac{hc}{|\Delta E|} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{2.118 \times 10^{-18} \text{ J}} = 9.379 \times 10^{-8} \text{ m} = 93.79 \text{ nm}$$

62. There are 4 possible transitions for an electron in the  $n = 5$  level ( $5 \rightarrow 4$ ,  $5 \rightarrow 3$ ,  $5 \rightarrow 2$ , and  $5 \rightarrow 1$ ). If an electron initially drops to the  $n = 4$  level, three additional transitions can occur ( $4 \rightarrow 3$ ,  $4 \rightarrow 2$ , and  $4 \rightarrow 1$ ). Similarly, there are two more transitions from the  $n = 3$  level ( $3 \rightarrow 2$ ,  $3 \rightarrow 1$ ) and one more transition for the  $n = 2$  level ( $2 \rightarrow 1$ ). There are a total of 10 possible transitions for an electron in the  $n = 5$  level for a possible total of 10 different wavelength emissions.

$$63. \quad \Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{5^2} - \frac{1}{1^2} \right) = 2.091 \times 10^{-18} \text{ J} = E_{\text{photon}}$$

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

Because wavelength and energy are inversely related, visible light ( $\lambda \approx 400\text{--}700 \text{ nm}$ ) 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.

64. 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 between  $n = 3$  and  $n = 2$  is smaller than the energy difference between  $n = 3$  and  $n = 1$ ; thus the wavelength is larger for the  $n = 3 \rightarrow n = 2$  electronic transition than for the  $n = 3 \rightarrow n = 1$  transition.  $E$  and  $\lambda$  are inversely proportional to each other ( $E = hc/\lambda$ ).  
 d. True  
 e. False;  $n = 2$  is the first excited state, and  $n = 3$  is the second excited state.
65. Ionization from  $n = 1$  corresponds to the transition  $n_i = 1 \rightarrow n_f = \infty$ , where  $E_\infty = 0$ .

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

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

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

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

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

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{1460 \times 10^{-9} \text{ m}} = 1.36 \times 10^{-19} \text{ J}$$

$$E_{\text{photon}} = \Delta E = 1.36 \times 10^{-19} \text{ J} = 2.178 \times 10^{-18} \left( \frac{1}{n^2} \right), \quad n^2 = 16.0, \quad n = 4$$

67.  $|\Delta E| = E_{\text{photon}} = h\nu = 6.662 \times 10^{-34} \text{ J s} \times 6.90 \times 10^{14} \text{ s}^{-1} = 4.57 \times 10^{-19} \text{ J}$

$\Delta E = -4.57 \times 10^{-19} \text{ J}$  because we have an emission.

$$-4.57 \times 10^{-19} \text{ J} = E_n - E_5 = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{n^2} - \frac{1}{5^2} \right)$$

$$\frac{1}{n^2} - \frac{1}{25} = 0.210, \quad \frac{1}{n^2} = 0.250, \quad n^2 = 4, \quad n = 2$$

The electronic transition is from  $n = 5$  to  $n = 2$ .

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

$\Delta E = -5.001 \times 10^{-19} \text{ J}$  because 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

69. a.  $\Delta p = m\Delta v = 9.11 \times 10^{-31} \text{ kg} \times 0.100 \text{ m/s} = \frac{9.11 \times 10^{-32} \text{ kg m}}{\text{s}}$

$$\Delta p \Delta x \geq \frac{h}{4\pi}, \Delta x = \frac{h}{4\pi \Delta p} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.142 \times (9.11 \times 10^{-32} \text{ kg m/s})} = 5.79 \times 10^{-4} \text{ m}$$

$$\text{b. } \Delta x = \frac{h}{4\pi \Delta p} = \frac{6.626 \times 10^{-34} \text{ J s}}{4 \times 3.142 \times 0.145 \text{ kg} \times 0.100 \text{ m/s}} = 3.64 \times 10^{-33} \text{ m}$$

The diameter of an H atom is roughly  $2 \times 10^{-8}$  cm. The uncertainty in the position of the electron is much larger than the size of the atom, whereas, the uncertainty in the position of the baseball is insignificant as compared to the size of a baseball.

70. Units of  $\Delta E \cdot \Delta t = \text{J} \times \text{s}$ , the same as the units of Planck's constant.

$$\text{Units of } \Delta(mv) \cdot \Delta x = \text{kg} \times \frac{\text{m}}{\text{s}} \times \text{m} = \frac{\text{kg m}^2}{\text{s}} = \frac{\text{kg m}^2}{\text{s}^2} \times \text{s} = \text{J} \times \text{s}$$

71.  $n = 1, 2, 3, \dots$ ;  $\ell = 0, 1, 2, \dots (n - 1)$ ;  $m_\ell = -\ell \dots -2, -1, 0, 1, 2, \dots +\ell$

72. a. This general shape represents a p orbital ( $\ell = 1$ ) and because there is a node in each of the lobes, this figure represents a 3p orbital ( $n = 3, \ell = 1$ )

b. This is an s orbital ( $\ell = 0$ ). And because there is one node present, this is a 2s orbital ( $n = 2, \ell = 0$ ).

c. This is the shape of a specific d oriented orbital ( $\ell = 2$ ). This orbital is designated as a  $d_{z^2}$ . Because no additional nodes are present inside any of the boundary surfaces, this is a  $3d_{z^2}$  orbital ( $n = 3, \ell = 2$ ).

73. b. For  $\ell = 3$ ,  $m_\ell$  can range from  $-3$  to  $+3$ ; thus  $+4$  is not allowed.

c.  $n$  cannot equal zero.

d.  $\ell$  cannot be a negative number.

74. a. For  $n = 3$ ,  $\ell = 3$  is not possible.

d.  $m_s$  cannot equal  $-1$ .

e.  $\ell$  cannot be a negative number.

f. For  $\ell = 1$ ,  $m_\ell$  cannot equal 2.

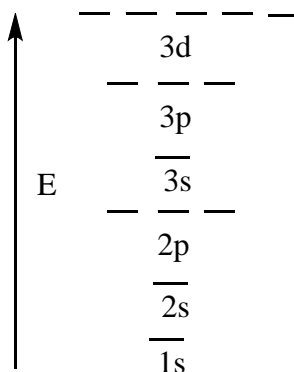
The quantum numbers in parts b and c are allowed.

75.  $\psi^2$  gives the probability of finding the electron at that point.

76. 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 Heisenberg's uncertainty principle.

**Polyelectronic Atoms**

77. 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.
78. In polyelectronic atoms, the orbitals of a given principal quantum level are not degenerate. In polyelectronic atoms, the energy order of the  $n = 1, 2,$  and  $3$  orbitals are (not to scale):



In general, the lower the  $n$  value for an orbital, the closer on average the electron can be to the nucleus, and the lower the energy. Within a specific  $n$  value orbital (like  $2s$  vs.  $2p$  or  $3s$  vs.  $3p$  vs.  $3d$ ), it is generally true that  $E_{ns} < E_{np} < E_{nd} < E_{nf}$ .

To rationalize this order, we utilize the radial probability distributions. In the  $2s$  and  $2p$  distribution, notice that the  $2s$  orbital has a small hump of electron density very near the nucleus. This indicates that an electron in the  $2s$  orbital can be very close to the nucleus some of the time. The  $2s$  electron penetrates to the nucleus more than a  $2p$  electron, and with this penetration comes a lower overall energy for the  $2s$  orbital as compared to the  $2p$  orbital.

In the  $n = 3$  radial probability distribution, the  $3s$  electron has two humps of electron density very close to the nucleus, and the  $3p$  orbital has one hump very close to the nucleus. The  $3s$  orbital electron is most penetrating, with the  $3p$  orbital electron the next most penetrating, followed by the least penetrating  $3d$  orbital electron. The more penetrating the electron, the lower the overall energy. Hence the  $3s$  orbital is lower energy than the  $3p$  orbitals which is lower energy than the  $3d$  orbitals.

79.  $5p$ : 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.

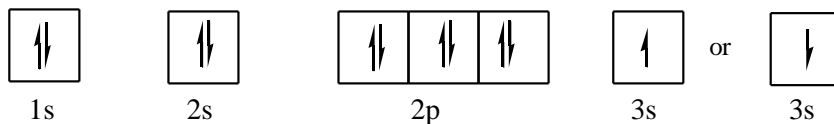
$n = 4$ :  $\ell = 0$  (1),  $\ell = 1$  (3),  $\ell = 2$  (5),  $\ell = 3$  (7); total for  $n = 4$  is 16 orbitals.

80.  $1p$ , 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);  $7p_y$ , 2 electrons (specifies one atomic orbital);  $2s$ ,

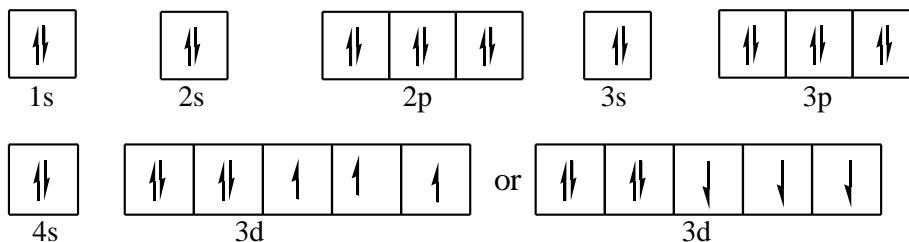
2 electrons (specifies one atomic orbital);  $n = 3$ , 18 electrons (3s, 3p, and 3d orbitals are possible; there are one 3s orbital, three 3p orbitals, and five 3d orbitals).

81. a.  $n = 4$ :  $\ell$  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  $\ell$ , 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 that 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 that can hold a total of 6 electrons.
82. a. It is impossible to have  $n = 0$ . Thus no electrons can have this set of quantum numbers.
- b. The four quantum numbers completely specify a single electron in a 2p orbital.
- c.  $n = 3$ ,  $m_s = +1/2$ : 3s, 3p, and 3d orbitals all have  $n = 3$ . These nine orbitals can each hold one electron with  $m_s = +1/2$ ; 9 electrons can have these quantum numbers
- 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 that can hold 2 electrons.

83. a. Na:  $1s^2 2s^2 2p^6 3s^1$ ; Na has 1 unpaired electron.

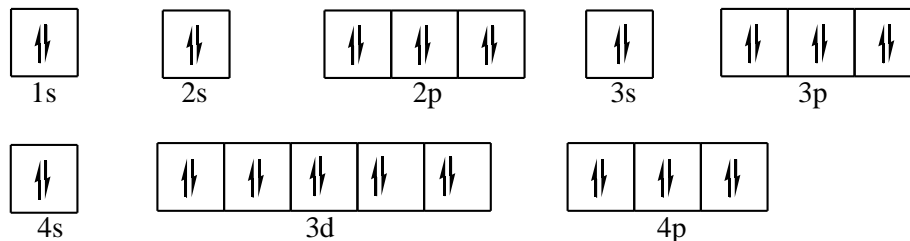


- b. Co:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ ; Co has 3 unpaired electrons.



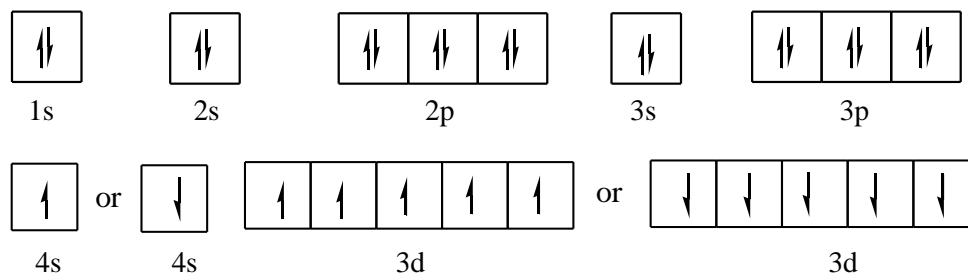


c. Kr:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ ; Kr has 0 unpaired electrons.

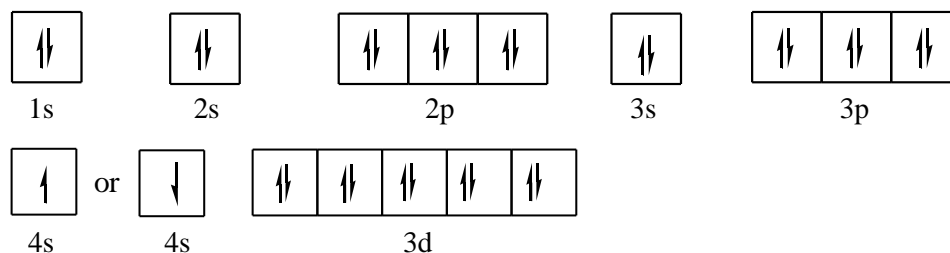


84. The two exceptions are Cr and Cu.

Cr:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ ; Cr has 6 unpaired electrons.



Cu:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ ; Cu has 1 unpaired electron.



85. Si:  $1s^2 2s^2 2p^6 3s^2 3p^2$  or  $[\text{Ne}]3s^2 3p^2$ ; Ga:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$  or  $[\text{Ar}]4s^2 3d^{10} 4p^1$

As:  $[\text{Ar}]4s^2 3d^{10} 4p^3$ ; Ge:  $[\text{Ar}]4s^2 3d^{10} 4p^2$ ; Al:  $[\text{Ne}]3s^2 3p^1$ ; Cd:  $[\text{Kr}]5s^2 4d^{10}$

S:  $[\text{Ne}]3s^2 3p^4$ ; Se:  $[\text{Ar}]4s^2 3d^{10} 4p^4$

86. Cu:  $[\text{Ar}]4s^2 3d^9$  (using periodic table),  $[\text{Ar}]4s^1 3d^{10}$  (actual)

O:  $1s^2 2s^2 2p^4$ ; La:  $[\text{Xe}]6s^2 5d^1$ ; Y:  $[\text{Kr}]5s^2 4d^1$ ; Ba:  $[\text{Xe}]6s^2$

Tl:  $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^1$ ; Bi:  $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^3$

87. 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.

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

88. Cl:  $1s^2 2s^2 2p^6 3s^2 3p^5$  or  $[\text{Ne}]3s^2 3p^5$  Sb:  $[\text{Kr}]5s^2 4d^{10} 5p^3$

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

Pb:  $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^2$  Cf:  $[\text{Rn}]7s^2 5f^{10}$ \*

\*Note: Predicting electron configurations for lanthanide and actinide elements is difficult since they have 0, 1, or 2 electrons in d orbitals. This is the actual Cf electron configuration.

89. O:  $1s^2 2s^2 2p^4$ ; C:  $1s^2 2s^2 2p^2$ ; H:  $1s^1$ ; N:  $1s^2 2s^2 2p^3$ ; Ca:  $[\text{Ar}]4s^2$ ; P:  $[\text{Ne}]3s^2 3p^3$ ;  
Mg:  $[\text{Ne}]3s^2$ ; K:  $[\text{Ar}]4s^1$

90. Cr:  $[\text{Ar}]4s^1 3d^5$ , 6 unpaired electrons (Cr is an exception to the normal filling order);  
Mn:  $[\text{Ar}]4s^2 3d^5$ , 5 unpaired  $e^-$ ; Fe:  $[\text{Ar}]4s^2 3d^6$ , 4 unpaired  $e^-$ ; Co:  $[\text{Ar}]4s^2 3d^7$ , 3 unpaired  $e^-$ ;  
Ni:  $[\text{Ar}]4s^2 3d^8$ , 2 unpaired  $e^-$ ; Cu:  $[\text{Ar}]4s^1 3d^{10}$ , 1 unpaired  $e^-$  (Cu is also an exception to the normal filling order); Zn:  $[\text{Ar}]4s^2 3d^{10}$ , 0 unpaired  $e^-$ .

91. 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:  $[\text{Kr}]5s^2 4d^{10} 5p^5$   $\uparrow\downarrow \uparrow\downarrow \uparrow$   
5p

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

c. Rn:  $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^6$ ; 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:  $[\text{Ar}]4s^1 3d^5$   $\uparrow$   $\uparrow \uparrow \uparrow \uparrow \uparrow$   
4s 3d

92. 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:  $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^4$

- c. Ta:  $[\text{Xe}]6s^24f^{14}5d^3$  or Ir:  $[\text{Xe}]6s^24f^{14}5d^7$
- d. At:  $[\text{Xe}]6s^24f^{14}5d^{10}6p^5$ . 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).
93. a. The complete ground state electron for this neutral atom is  $1s^22s^22p^63s^23p^4$ . This atom has  $2 + 2 + 6 + 2 + 4 = 16$  electrons. Because the atom is neutral, it also has 16 protons, making the atom sulfur, S.
- b. Complete excited state electron configuration:  $1s^22s^12p^4$ ; this neutral atom has  $2 + 1 + 4 = 7$  electrons, which means it has 7 protons, which identifies it as nitrogen, N.
- c. Complete ground state electron configuration:  $1s^22s^22p^63s^23p^64s^23d^{10}4p^5$ ; this 1- charged ion has 35 electrons. Because the overall charge is 1-, this ion has 34 protons which identifies it as selenium. The ion is  $\text{Se}^-$ .
94. a. This atom has 10 electrons. Ne                      b. S
- c. The predicted ground state configuration is  $[\text{Kr}]5s^24d^9$ . From the periodic table, the element is Ag. *Note:*  $[\text{Kr}]5s^14d^{10}$  is the actual ground state electron configuration for Ag.
- d. Bi:  $[\text{Xe}]6s^24f^{14}5d^{10}6p^3$ ; the three unpaired electrons are in the 6p orbitals.
95. Hg:  $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}$
- a. From the electron configuration for Hg, we have  $3s^2$ ,  $3p^6$ , and  $3d^{10}$  electrons; 18 total electrons with  $n = 3$ .
- b.  $3d^{10}$ ,  $4d^{10}$ ,  $5d^{10}$ ; 30 electrons are in the d atomic orbitals.
- c.  $2p^6$ ,  $3p^6$ ,  $4p^6$ ,  $5p^6$ ; each set of  $np$  orbitals contain one  $p_z$  atomic orbital. Because we have 4 sets of  $np$  orbitals and two electrons can occupy the  $p_z$  orbital, there are  $4(2) = 8$  electrons in  $p_z$  atomic orbitals.
- d. All the electrons are paired in Hg, so one-half of the electrons are spin up ( $m_s = +1/2$ ) and the other half are spin down ( $m_s = -1/2$ ). 40 electrons have spin up.
96. Element 115, Uup, is in Group 5A under Bi (bismuth):
- Uup:  $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^25f^{14}6d^{10}7p^3$
- a.  $5s^2$ ,  $5p^6$ ,  $5d^{10}$ , and  $5f^{14}$ ; 32 electrons have  $n = 5$  as one of their quantum numbers
- b.  $\ell = 3$  are f orbitals.  $4f^{14}$  and  $5f^{14}$  are the f orbitals used. They are all filled, so 28 electrons have  $\ell = 3$ .
- c. p, d, and f orbitals all have one of the degenerate orbitals with  $m_\ell = 1$ . There are 6 orbitals with  $m_\ell = 1$  for the various p orbitals used; there are 4 orbitals with  $m_\ell = 1$  for the various d orbitals used; and there are 2 orbitals with  $m_\ell = 1$  for the various f orbitals used. We have a total of  $6 + 4 + 2 = 12$  orbitals with  $m_\ell = 1$ . Eleven of these orbitals are filled with

2 electrons, and the 7p orbitals are only half-filled. The number of electrons with  $m_\ell = 1$  is  $11 \times (2 e^-) + 1 \times (1 e^-) = 23$  electrons.

- d. The first 112 electrons are all paired; one-half of these electrons ( $56 e^-$ ) will have  $m_s = -1/2$ . The 3 electrons in the 7p orbitals singly occupy each of the three degenerate 7p orbitals; the three electrons are spin parallel, so the 7p electrons either have  $m_s = +1/2$  or  $m_s = -1/2$ . Therefore, either 56 electrons have  $m_s = -1/2$  or 59 electrons have  $m_s = -1/2$ .

97. B:  $1s^2 2s^2 2p^1$

	$n$	$\ell$	$m_\ell$	$m_s$
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  $-1/2$  for a total of six possibilities.

N:  $1s^2 2s^2 2p^3$

	$n$	$\ell$	$m_\ell$	$m_s$	
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	

98. Ti:  $[\text{Ar}]4s^2 3d^2$

	$n$	$\ell$	$m_\ell$	$m_s$
4s	4	0	0	+1/2
4s	4	0	0	-1/2
3d	3	2	-2	+1/2
3d	3	2	-1	+1/2

Only one of 10 possible combinations of  $m_\ell$  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.

99. Group 1A: 1 valence electron;  $ns^1$ ; Li:  $[\text{He}]2s^1$ ;  $2s^1$  is the valence electron configuration for Li.  
 Group 2A: 2 valence electrons;  $ns^2$ ; Ra:  $[\text{Rn}]7s^2$ ;  $7s^2$  is the valence electron configuration for Ra.  
 Group 3A: 3 valence electrons;  $ns^2np^1$ ; Ga:  $[\text{Ar}]4s^23d^{10}4p^1$ ;  $4s^24p^1$  is the valence electron configuration for Ga. Note that valence electrons for the representative elements of Groups 1A-8A are considered those electrons in the highest  $n$  value, which for Ga is  $n = 4$ . We do not include the 3d electrons as valence electrons because they are not in  $n = 4$  level.  
 Group 4A: 4 valence electrons;  $ns^2np^2$ ; Si:  $[\text{Ne}]3s^23p^2$ ;  $3s^23p^2$  is the valence electron configuration for Si.  
 Group 5A: 5 valence electrons;  $ns^2np^3$ ; Sb:  $[\text{Kr}]5s^24d^{10}5p^3$ ;  $5s^25p^3$  is the valence electron configuration for Sb.  
 Group 6A: 6 valence electrons;  $ns^2np^4$ ; Po:  $[\text{Xe}]6s^24f^{14}5d^{10}6p^4$ ;  $6s^26p^4$  is the valence electron configuration for Po.  
 Group 7A: 7 valence electrons;  $ns^2np^5$ ; 117:  $[\text{Rn}]7s^25f^{14}6d^{10}7p^5$ ;  $7s^27p^5$  is the valence electron configuration for 117.  
 Group 8A: 8 valence electrons;  $ns^2np^6$ ; Ne:  $[\text{He}]2s^22p^6$ ;  $2s^22p^6$  is the valence electron configuration for Ne.
100. a. 2 valence electrons;  $4s^2$                       b. 6 valence electrons;  $2s^22p^4$   
 c. 7 valence electrons;  $7s^27p^5$                   d. 3 valence electrons;  $5s^25p^1$   
 e. 8 valence electrons;  $3s^23p^6$                   f. 5 valence electrons;  $6s^26p^3$
101. O:  $1s^22s^22p_x^22p_y^2$  ( $\uparrow\downarrow \uparrow\downarrow \_$ ); 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 ( $\uparrow\downarrow \uparrow \uparrow$ ), energy would be released.
102. The number of unpaired electrons is in parentheses.
- a. excited state of boron            (1)                      b. ground state of neon            (0)  
 B ground state:  $1s^22s^22p^1$     (1)                      Ne ground state:  $1s^22s^22p^6$     (0)
- c. excited state of fluorine        (3)                      d. excited state of iron            (6)  
 F ground state:  $1s^22s^22p^5$     (1)                      Fe ground state:  $[\text{Ar}]4s^23d^6$     (4)
- $\begin{array}{c} \uparrow\downarrow \uparrow\downarrow \uparrow \\ 2p \end{array}$ 
 $\begin{array}{c} \uparrow\downarrow \uparrow \uparrow \uparrow \uparrow \\ 3d \end{array}$
103. None of the s block elements have 2 unpaired electrons. In the p block, the elements with either  $ns^2np^2$  or  $ns^2np^4$  valence electron configurations have 2 unpaired electrons. For elements 1-36, these are elements C, Si, and Ge (with  $ns^2np^2$ ) and elements O, S, and Se (with  $ns^2np^4$ ). For the d block, the elements with configurations  $nd^2$  or  $nd^8$  have two unpaired

electrons. For elements 1-36, these are Ti ( $3d^2$ ) and Ni ( $3d^8$ ). A total of 8 elements from the first 36 elements have two unpaired electrons in the ground state.

104. The s block elements with  $ns^1$  for a valence electron configuration have one unpaired electron. These are elements H, Li, Na, and K for the first 36 elements. The p block elements with  $ns^2np^1$  or  $ns^2np^5$  valence electron configurations have one unpaired electron. These are elements B, Al, and Ga ( $ns^2np^1$ ) and elements F, Cl, and Br ( $ns^2np^5$ ) for the first 36 elements. In the d block, Sc ( $[\text{Ar}]4s^23d^1$ ) and Cu ( $[\text{Ar}]4s^13d^{10}$ ) each have one unpaired electron. A total of 12 elements from the first 36 elements have one unpaired electron in the ground state.
105. 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:  $1s^2 2s^1 \uparrow$ ; paramagnetic with 1 unpaired electron.  
 $\quad\quad\quad 2s$

N:  $1s^2 2s^2 2p^3 \uparrow \uparrow \uparrow$ ; paramagnetic with 3 unpaired electrons.  
 $\quad\quad\quad 2p$

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

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

Ba:  $[\text{Xe}]6s^2 \uparrow \downarrow$ ; not paramagnetic because no unpaired electrons are present.  
 $\quad\quad\quad 6s$

Hg:  $[\text{Xe}]6s^2 4f^{14} 5d^{10} \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$ ; not paramagnetic because no unpaired electrons.  
 $\quad\quad\quad 5d$

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

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

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

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

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

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

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

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

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

**The Periodic Table and Periodic Properties**

107. Size (radius) decreases left to right across the periodic table, and size increases from top to bottom of the periodic table.

- a.  $S < Se < Te$       b.  $Br < Ni < K$       c.  $F < Si < Ba$

All follow the general radius trend.

108. a.  $Be < Na < Rb$       b.  $Ne < Se < Sr$       c.  $O < P < Fe$

All follow the general radius trend.

109. The ionization energy trend is the opposite of the radius 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.  $Te < Se < S$       b.  $K < Ni < Br$       c.  $Ba < Si < F$

All follow the general IE trend.

110. a.  $Rb < Na < Be$       b.  $Sr < Se < Ne$       c.  $Fe < P < O$

All follow the general IE trend.

111. a. He (From the general radius trend.)      b. Cl

c. Element 116 is the next oxygen family member to be discovered (under Po), element 119 is the next alkali metal to be discovered (under Fr), and element 120 is the next alkaline earth metal to be discovered (under Ra). From the general radius trend, element 116 will be the smallest.

d. Si

e.  $Na^+$ ; this ion has the fewest electrons as compared to the other sodium species present.  $Na^+$  has the smallest number of electron-electron repulsions, which makes it the smallest ion with the largest ionization energy.

112. a. Ba (From the general ionization energy trend.)      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.

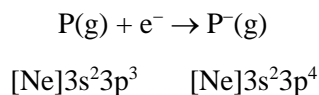
d.  $S^{2-}$ ; this ion has the most electrons compared to the other sulfur species present.  $S^{2-}$  has the largest number of electron-electron repulsions, which leads to  $S^{2-}$  having the largest size and smallest ionization energy.

e. Cs; this follows the general ionization energy trend.

113. a. Sg:  $[\text{Rn}]7s^25f^{14}6d^4$       b. W, which is directly above Sg in the periodic table.
114. a. Uus will have 117 electrons.  $[\text{Rn}]7s^25f^{14}6d^{10}7p^5$
- b. It will be in the halogen family and will be most similar to astatine (At).
115. 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.
116. Expected order from IE trend:  $\text{Be} < \text{B} < \text{C} < \text{N} < \text{O}$
- B and O are exceptions to the general IE trend. The IE of O is lower because of the extra electron-electron repulsions present when two electrons are paired in the same orbital. This makes it slightly easier to remove an electron from O compared to N. B is an exception because of the smaller penetrating ability of the 2p electron in B compared to the 2s electrons in Be. The smaller penetrating ability makes it slightly easier to remove an electron from B compared to Be. The correct IE ordering, taking into account the two exceptions, is  $\text{B} < \text{Be} < \text{C} < \text{O} < \text{N}$ .
117. 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:  $1s^22s^22p^63s^23p^1$ ; for  $I_4$ , we begin removing an electron with  $n = 2$ . For  $I_3$ , we remove an electron with  $n = 3$  (the last valence electron). In going from  $n = 3$  to  $n = 2$ , there is a big jump in ionization energy because the  $n = 2$  electrons are closer to the nucleus on average than the  $n = 3$  electrons. Since the  $n = 2$  electrons are closer, on average, to the nucleus, they are held more tightly and require a much larger amount of energy to remove compared to the  $n = 3$  electrons. In general, valence electrons are much easier to remove than inner-core electrons.
118. 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 orange plot is Al, the blue plot is Mg, and the pink 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 than valence electrons since they are closer to the nucleus, on average, than the valence electrons.
119. 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).

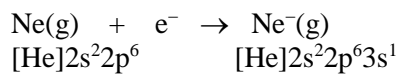


- b. Higher IE: N and Ar (follows the IE trend)
- c. Larger size: C and Br (follows the radius trend)
120. a. More favorable EA: K and Cl; Mg has a positive EA value, and F has a more positive EA value than expected from its position relative to Cl.
- b. Higher IE: Mg and F                      c. Larger radius: K and Cl
121. 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 negative as we go from left to right in the period. Phosphorus is out of line. The electron affinity equation for P is:



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

122. Electron affinity refers to the energy associated with the process of adding an electron to something. Be, N, and Ne all have positive (unfavorable) electron affinity values. In order to add an electron to Be, N, or Ne, energy must be added. Another way of saying this is that Be, N, and Ne become less stable (have a higher energy) when an electron is added to each. To rationalize why those three atoms have positive (unfavorable) electron affinity values, let's see what happens to the electron configuration as an electron is added.



In each case something energetically unfavorable occurs when an electron is added. For Be, the added electron must go into a higher-energy 2p atomic orbital because the 2s orbital is full. In N, the added electron must pair up with another electron in one of the 2p atomic orbitals; this adds electron-electron repulsions. In Ne, the added electron must be added to a much higher 3s atomic orbital because the  $n = 2$  orbitals are full.

123. 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 most negative.                      b.  $\text{I} < \text{Br} < \text{F} < \text{Cl}$ ; Cl is most negative. (F is an exception).
124. a.  $\text{N} < \text{O} < \text{F}$ , F is most negative.                      b.  $\text{Al} < \text{P} < \text{Si}$ ; Si is most negative.

125. Electron-electron repulsions are much greater in  $O^-$  than in  $S^-$  because the electron goes into a smaller 2p orbital versus the larger 3p orbital in sulfur. This results in a more favorable (more negative) electron affinity value for sulfur.
126. O; the electron-electron repulsions will be much more severe for  $O^- + e^- \rightarrow O^{2-}$  than for  $O + e^- \rightarrow O^-$ , resulting in O having the more negative electron affinity.
127. a.  $Se^{3+}(g) \rightarrow Se^{4+}(g) + e^-$       b.  $S^-(g) + e^- \rightarrow S^{2-}(g)$   
 c.  $Fe^{3+}(g) + e^- \rightarrow Fe^{2+}(g)$       d.  $Mg(g) \rightarrow Mg^+(g) + e^-$
128. a. The electron affinity for  $Mg^{2+}$  refers to:  $Mg^{2+}(g) + e^- \rightarrow Mg^+(g)$ ; this is just the reverse of the second ionization energy for Mg.  $EA(Mg^{2+}) = -IE_2(Mg) = -1445 \text{ kJ/mol}$  (Table 2-5). Note that when an equation is reversed, the sign of the energy change is reversed.  
 b. IE of  $Cl^-$ :  $Cl^-(g) \rightarrow Cl(g) + e^-$ ;  $IE(Cl^-) = -EA(Cl) = 348.7 \text{ kJ/mol}$  (Table 2-7)  
 c. EA for  $Cl^+$ :  $Cl^+(g) + e^- \rightarrow Cl(g)$ ;  $EA(Cl^+) = -IE_1(Cl) = -1255 \text{ kJ/mol}$  (Table 2-5)  
 d. IE for  $Mg^-$ :  $Mg^-(g) \rightarrow Mg(g) + e^-$ ;  $IE(Mg^-) = -EA(Mg) = -230 \text{ kJ/mol}$

### Alkali Metals

129. 
$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{455.5 \times 10^{-9} \text{ m}} = 6.582 \times 10^{14} \text{ s}^{-1}$$
  

$$E = h\nu = 6.6261 \times 10^{-34} \text{ J s} \times 6.582 \times 10^{14} \text{ s}^{-1} = 4.361 \times 10^{-19} \text{ J}$$
130. For 589.0 nm: 
$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8 \text{ m/s}}{589.0 \times 10^{-9} \text{ m}} = 5.090 \times 10^{14} \text{ s}^{-1}$$
  

$$E = h\nu = 6.6261 \times 10^{-34} \text{ J s} \times 5.090 \times 10^{14} \text{ s}^{-1} = 3.373 \times 10^{-19} \text{ J}$$
  
 For 589.6 nm:  $\nu = c/\lambda = 5.085 \times 10^{14} \text{ s}^{-1}$ ;  $E = h\nu = 3.369 \times 10^{-19} \text{ J}$   
 The energies in kJ/mol are:  

$$3.373 \times 10^{-19} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23}}{\text{mol}} = 203.1 \text{ kJ/mol}$$
  

$$3.369 \times 10^{-19} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23}}{\text{mol}} = 202.9 \text{ kJ/mol}$$
131. 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 2-8 confirm both of these general trends.



141. a. True for H only.                      b. True for all atoms.                      c. True for all atoms.
142.  $n = 5$ ;  $m_\ell = -4, -3, -2, -1, 0, 1, 2, 3, 4$ ; 18 electrons
143. From the radii trend, the smallest-size element (excluding hydrogen) would be the one in the most upper right corner of the periodic table. This would be O. The largest-size element would be the one in the most lower left of the periodic table. Thus K would be the largest. The ionization energy (IE) trend is the exact opposite of the radii trend. So K, with the largest size, would have the smallest first ionization energy. From the general IE trend, O should have the largest ionization energy. However, there is an exception to the general IE trend between N and O. Due to this exception, N would have the largest first ionization energy of the elements examined.
144. 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  $\ell$  can have is  $n - 1$ , not  $n$ .
145. 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.
146. All oxygen family elements have  $ns^2np^4$  valence electron configurations, so this nonmetal is from the oxygen family.
- $2 + 4 = 6$  valence electrons.
  - O, S, Se, and Te are the nonmetals from the oxygen family (Po is a metal).
  - Potassium, like the other alkali metals, forms 1+ charged ions when in compounds. Because oxygen family nonmetals form 2- charged ions in ionic compounds,  $K_2X$  would be the predicted formula, where X is the unknown nonmetal.
  - From the size trend, this element would have a smaller radius than barium.
  - From the ionization energy trend, this element would have a smaller ionization energy than fluorine.
147. None of the noble gases and no subatomic particles had been discovered when Mendeleev published his periodic table. There was no element out of place in terms of reactivity and there was no reason to predict that an entire family of elements was missing. Mendeleev ordered his table by mass; he had no way of knowing there were gaps in atomic numbers (they hadn't been discovered yet).
148.  $\lambda\nu = c, \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{660 \text{ nm} \times \frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}} = 4.5 \times 10^{14} \text{ s}^{-1}$
149.  $E = \frac{310 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 5.15 \times 10^{-22} \text{ kJ} = 5.15 \times 10^{-19} \text{ J/photon}$

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

### ChemWork Problems

150.  $\frac{476 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 7.90 \times 10^{-22} \text{ kJ} = 7.90 \times 10^{-19} \text{ J}$  to remove one electron

151. The longest wavelength light emitted will correspond to the transition with the smallest energy change (smallest  $\Delta E$ ). This is the transition from  $n = 5$  to  $n = 4$ .

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

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

The shortest wavelength emitted will correspond to the largest  $\Delta E$ ; this is  $n = 5 \rightarrow n = 1$ .

$$\Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{1^2} - \frac{1}{5^2} \right) = -2.091 \times 10^{-18} \text{ J}$$

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

152. There are 5 possible transitions for an electron in the  $n = 6$  level ( $6 \rightarrow 5$ ,  $6 \rightarrow 4$ ,  $6 \rightarrow 3$ ,  $6 \rightarrow 2$ , and  $6 \rightarrow 1$ ). If an electron initially drops to the  $n = 5$  level, four additional transitions can occur ( $5 \rightarrow 4$ ,  $5 \rightarrow 3$ ,  $5 \rightarrow 2$ , and  $5 \rightarrow 1$ ). Similarly, there are three more transitions from the  $n = 4$  level ( $4 \rightarrow 3$ ,  $4 \rightarrow 2$ ,  $4 \rightarrow 1$ ), two more transitions from the  $n = 3$  level ( $3 \rightarrow 2$ ,  $3 \rightarrow 1$ ), and one more transition from the  $n = 2$  level ( $2 \rightarrow 1$ ). There are a total of 15 possible transitions for an electron in the  $n = 6$  level for a possible total of 15 different wavelength emissions.
153.  $2f$  and  $2d_{xy}$  orbitals are forbidden energy levels (they do not exist), so zero electrons can occupy these. The  $3p$  and  $4p$  sets each contain three degenerate orbitals, so each set can hold 6 electrons, and the  $5d_{yz}$  represents a singular energy level which can hold 2 electrons.
154. As:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

$\ell = 1$  are p orbitals.  $2p^6$ ,  $3p^6$ , and  $4p^3$  are the p orbitals used. So 15 electrons have  $\ell = 1$ .

The s, p, and d orbitals all have one of the orbitals with  $m_\ell = 0$ . There are four orbitals with  $m_\ell = 0$  from the various s orbitals used, there are three orbitals with  $m_\ell = 0$  from the various p orbitals used, and there is one orbital with  $m_\ell = 0$  from the 3d orbitals used. We have a total of  $4 + 3 + 1 = 8$  orbitals with  $m_\ell = 0$ . Seven of these orbitals are filled with 2 electrons, and the  $4p$  orbitals are only half-filled. The number of electrons with  $m_\ell = 0$  is  $7 \times (2 e^-) + 1 \times (1 e^-) = 15$  electrons.

The p and d orbitals all have one of the degenerate orbitals with  $m_\ell = 1$ . There are 3 orbitals with  $m_\ell = 1$  from the various p orbitals used and there is one orbital with  $m_\ell = 1$  from the 3d orbitals used. We have a total of  $3 + 1 = 4$  orbitals with  $m_\ell = 1$ . Three of these orbitals are filled with 2 electrons, and the 4p orbitals are only half-filled. The number of electrons with  $m_\ell = 1$  is  $3 \times (2 e^-) + 1 \times (1 e^-) = 7$  electrons.

155. a. False; an electron in a 2s orbital would be on average, closer to the nucleus than an electron in a 3s orbital.  
 b. True; the Bohr model is fundamentally incorrect.  
 c. True;            d. False; these two terms come from different atomic structure models.  
 e. True; when  $n = 3$ ,  $\ell$  can equal 0 (s orbital), 1 (p orbitals), and 2 (d orbitals).
156. a. This element has  $36 + 2 + 10 + 4 = 52$  electrons. This is Te.  
 b. This element has 32 electrons; this is Ge.  
 c. This element has 9 electrons, so it is F.
157. More favorable (negative) electron affinity: K, Br, and Se (follows general electron affinity trend). Higher ionization energy: K, Br, and Se (follows general ionization energy trend). Larger size: Cs, Te, and Ge (follows general atomic radius trend).
158. a. True (follows general ionization energy trend)  
 b. False; cations are smaller than the parent atom.  
 c. False; all ionization energies are positive (energy must be added to remove electrons).  
 d. True  
 e. True; this is hard to predict because the general atomic radius trends go against each other when going from Li to Al. Figure 2-33 of the text was used to answer this question.
159. Applying the general trends in radii and ionization energy allows matching of the various values to the elements.

Mg :  $1s^2 2s^2 2p^6 3s^2$             : 0.734 MJ/mol    : 160 pm

S    :  $1s^2 2s^2 2p^6 3s^2 3p^4$         : 0.999 MJ/mol    : 104 pm

Ca   :  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$     : 0.590 MJ/mol    : 197 pm

**Challenge Problems**

$$160. \quad E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.6261 \times 10^{-34} \text{ J s} \times 2.9979 \times 10^8 \text{ m/s}}{253.4 \times 10^{-9} \text{ m}} = 7.839 \times 10^{-19} \text{ J}$$

$\Delta E = 7.839 \times 10^{-19} \text{ J}$ ; 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.

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

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

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

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

161. a. Because 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. Because this spectrum is for a one-electron ion,  $E_n = -2.178 \times 10^{-18} \text{ J } (Z^2/n^2)$ . To determine  $\Delta E$  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  $Z$ .

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

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

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

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

Solving for the wavelength of line A:

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

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

162. For hydrogen:  $\Delta E = -2.178 \times 10^{-18} \text{ J} \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = -4.574 \times 10^{-19} \text{ J}$

For a similar blue light emission,  $\text{He}^+$  will need about the same  $\Delta E$  value.

For  $\text{He}^+$ :  $E_n = -2.178 \times 10^{-18} \text{ J} (Z^2/n^2)$ , where  $Z = 2$ :

$$\Delta E = -4.574 \times 10^{-19} \text{ J} = -2.178 \times 10^{-18} \text{ J} \left( \frac{2^2}{n_f^2} - \frac{2^2}{4^2} \right)$$

$$0.2100 = \frac{4}{n_f^2} - \frac{4}{16}, \quad 0.4600 = \frac{4}{n_f^2}, \quad n_f = 2.949$$

The transition from  $n = 4$  to  $n = 3$  for  $\text{He}^+$  should emit a similar colored blue light as the  $n = 5$  to  $n = 2$  hydrogen transition; both these transitions correspond to very nearly the same energy change.

163. For one-electron species,  $E_n = -R_H Z^2/n^2$ . IE is for the  $n = 1 \rightarrow n = \infty$  transition. So:

$$\text{IE} = E_\infty - E_1 = -E_1 = R_H Z^2/n^2 = R_H Z^2$$

$$\frac{4.72 \times 10^4 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} \times \frac{1000 \text{ J}}{\text{kJ}} = 2.178 \times 10^{-18} \text{ J} (Z^2); \text{ solving: } Z = 6$$

Element 6 is carbon ( $X = \text{carbon}$ ), and the charge for a one-electron carbon ion is  $5+$  ( $m = 5$ ). The one-electron ion is  $\text{C}^{5+}$ .

164. A node occurs when  $\psi = 0$ .  $\psi_{300} = 0$  when  $27 - 18\sigma + 2\sigma^2 = 0$ .

$$\text{Solving using the quadratic formula: } \sigma = \frac{18 \pm \sqrt{(18)^2 - 4(2)(27)}}{4} = \frac{18 \pm \sqrt{108}}{4}$$

$\sigma = 7.10$  or  $\sigma = 1.90$ ; because  $\sigma = r/a_0$ , the nodes occur at  $r = (7.10)a_0 = 3.76 \times 10^{-10} \text{ m}$  and at  $r = (1.90)a_0 = 1.01 \times 10^{-10} \text{ m}$ , where  $r$  is the distance from the nucleus.

165. 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  $\theta = 90^\circ$ . As expected, the  $xy$  plane, which corresponds to  $\theta = 90^\circ$ , is a node for the  $2p_z$  atomic orbital.

166. 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





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

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

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

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.

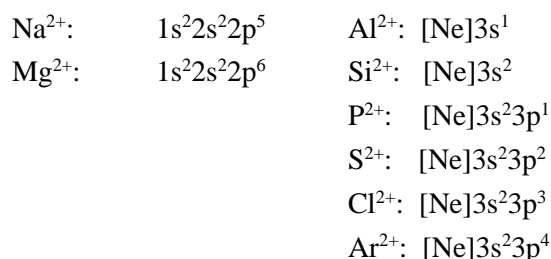
f.  $p = 6, q = 1, r = 0, s = \pm 1/2$  (2 electrons)

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

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

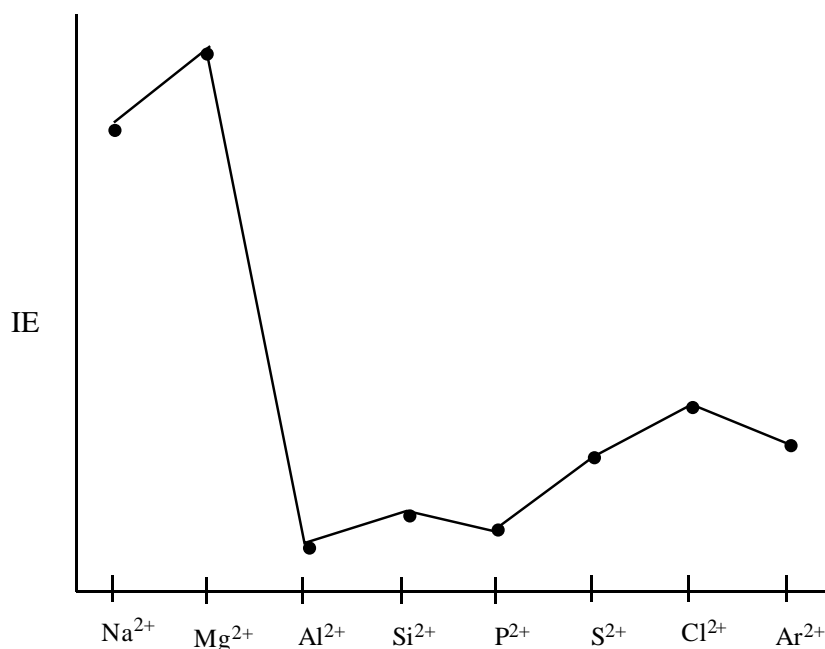
Eighteen electrons can have  $p = 6$ .

168.  $IE_3$  refers to:  $E^{2+}(g) \rightarrow E^{3+}(g) + e^-$ . The electron configurations for the 2+ charged ions of Na to Ar are:



$IE_3$  for sodium and magnesium should be extremely large compared with the others because  $n = 2$  electrons are much more difficult to remove than  $n = 3$  electrons. Between  $Na^{2+}$  and  $Mg^{2+}$ , one would expect to have the same trend as seen with  $IE_1(F)$  versus  $IE_1(Ne)$ ; these neutral atoms have identical electron configurations to  $Na^{2+}$  and  $Mg^{2+}$ . Therefore, the  $1s^2 2s^2 2p^5$  ion ( $Na^{2+}$ ) should have a lower ionization energy than the  $1s^2 2s^2 2p^6$  ion ( $Mg^{2+}$ ).

The remaining 2+ ions ( $Al^{2+}$  to  $Ar^{2+}$ ) should follow the same trend as the neutral atoms having the same electron configurations. The general IE trend predicts an increase from  $[Ne] 3s^1$  to  $[Ne] 3s^2 3p^4$ . The exceptions occur between  $[Ne] 3s^2$  and  $[Ne] 3s^2 3p^1$  and between  $[Ne] 3s^2 3p^3$  and  $[Ne] 3s^2 3p^4$ .  $[Ne] 3s^2 3p^1$  is out of order because of the small penetrating ability of the 3p electron as compared with the 3s electrons.  $[Ne] 3s^2 3p^4$  is out of order because of the extra electron-electron repulsions present when two electrons are paired in the same orbital. Therefore, the correct ordering for  $Al^{2+}$  to  $Ar^{2+}$  should be  $Al^{2+} < P^{2+} < Si^{2+} < S^{2+} < Ar^{2+} < Cl^{2+}$ , where  $P^{2+}$  and  $Ar^{2+}$  are out of line for the same reasons that Al and S are out of line in the general ionization energy trend for neutral atoms.



*Note:* The actual numbers in Table 2-5 support most of this plot. No  $IE_3$  is given for  $Na^{2+}$ , so you cannot check this. The only deviation from our discussion is  $IE_3$  for  $Ar^{2+}$  which is greater than  $IE_3$  for  $Cl^{2+}$  instead of less than.

169. The ratios for Mg, Si, P, Cl, and Ar are about the same. However, the ratios for Na, Al, and S are higher. For Na, the second IE is extremely high because the electron is taken from  $n = 2$  (the first electron is taken from  $n = 3$ ). For Al, the first electron requires a bit less energy than expected by the trend due to the fact it is a 3p electron versus a 3s electron. For S, the first electron requires a bit less energy than expected by the trend due to electrons being paired in one of the p orbitals.
170. Size also decreases going across a period. Sc and Ti along with Y and Zr are adjacent elements. There are 14 elements (the lanthanides) between La and Hf, making Hf considerably smaller.
171. a. Assuming the Bohr model applies to the 1s electron,  $E_{1s} = -R_H Z^2/n^2 = -R_H Z_{\text{eff}}^2$ , where  $n = 1$ . Ionization energy =  $E_\infty - E_{1s} = 0 - E_{1s} = R_H Z_{\text{eff}}^2$ .
- $$\frac{2.462 \times 10^6 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ mol}}{6.0221 \times 10^{23}} \times \frac{1000 \text{ J}}{\text{kJ}} = 2.178 \times 10^{-18} \text{ J } (Z_{\text{eff}})^2, \quad Z_{\text{eff}} = 43.33$$
- b. Silver is element 47, so  $Z = 47$  for silver. Our calculated  $Z_{\text{eff}}$  value is less than 47. Electrons in other orbitals can penetrate the 1s orbital. Thus a 1s electron can be slightly shielded from the nucleus by these penetrating electrons, giving a  $Z_{\text{eff}}$  close to but less than  $Z$ .

**Integrated Problems**

172. a.  $[\text{Kr}]5s^24d^{10}5p^6 = \text{Xe}$ ;  $[\text{Kr}]5s^24d^{10}5p^1 = \text{In}$ ;  $[\text{Kr}]5s^24d^{10}5p^3 = \text{Sb}$

From the general radii trend, the increasing size order is  $\text{Xe} < \text{Sb} < \text{In}$ .

b.  $[\text{Ne}]3s^23p^5 = \text{Cl}$ ;  $[\text{Ar}]4s^23d^{10}4p^3 = \text{As}$ ;  $[\text{Ar}]4s^23d^{10}4p^5 = \text{Br}$

From the general IE trend, the decreasing IE order is  $\text{Cl} > \text{Br} > \text{As}$ .

173. a. 
$$\nu = \frac{E}{h} = \frac{7.52 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J s}} = 1.13 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{1.13 \times 10^{15} \text{ s}^{-1}} = 2.65 \times 10^{-7} \text{ m} = 265 \text{ nm}$$

b.  $E_{\text{photon}}$  and  $\lambda$  are inversely related ( $E = hc/\lambda$ ). Any wavelength of electromagnetic radiation less than or equal to 265 nm ( $\lambda \leq 265$ ) will have sufficient energy to eject an electron. So, yes, 259-nm electromagnetic radiation will eject an electron.

c. This is the electron configuration for copper, Cu, an exception to the expected filling order.