Sample Exercise 6.1 Concepts of Wavelength and Frequency

Two electromagnetic waves are represented in the margin. (a) Which wave has the higher frequency? (b) If one wave represents visible light and the other represents infrared radiation, which wave is which?



Solution

- (a) Wave 1 has a longer wavelength (greater distance between peaks). The longer the wavelength, the lower the frequency ($v = c/\lambda$). Thus, Wave 1 has the lower frequency, and Wave 2 has the higher frequency.
- (b) The electromagnetic spectrum (Figure 6.4) indicates that infrared radiation has a longer wavelength than visible light. Thus, Wave 1 is infrared radiation.



Sample Exercise 6.1 Concepts of Wavelength and Frequency

Continued

Practice Exercise 1

A source of electromagnetic radiation produces infrared light. Which of the following could be the wavelength of the light?

(**a**) 3.0 nm (**b**) 4.7 cm (**c**) 66.8 m (**d**) 34.5 μm (**e**) 16.5 Å

Practice Exercise 2

Which type of visible light has a longer wavelelength, red or blue light?

Sample Exercise 6.2 Calculating Frequency from Wavelength

The yellow light given off by a sodium vapor lamp used for public lighting has a wavelength of 589 nm. What is the frequency of this radiation?

Solution

Analyze We are given the wavelength, λ , of the radiation and asked to calculate its frequency, v.

Plan The relationship between the wavelength and the frequency is given by Equation 6.1. We can solve for v and use the values of λ and c to obtain a numerical answer. (The speed of light, c, is 3.00×10^8 m/s to three significant figures.)

Solve Solving Equation 6.1 for frequency gives $v = c/\lambda$. When we insert the values for *c* and λ , we note that the units of length in these two quantities are different. We use a conversion factor to convert the wavelength from nanometers to meters, so the units cancel:

$$\nu = \frac{c}{\lambda} = \left(\frac{3.00 \times 10^8 \,\text{m/s}}{589 \,\text{nm}}\right) \left(\frac{1 \,\text{nm}}{10^{-9} \,\text{m}}\right)$$
$$= 5.09 \times 10^{14} \,\text{s}^{-1}$$

Check The high frequency is reasonable because of the short wavelength. The units are proper because frequency has units of "per second," or s^{-1} .

Sample Exercise 6.2 Calculating Frequency from Wavelength

Continued

Practice Exercise 1

Consider the following three statements: (i) For any electromagnetic radiation, the product of the wavelength and the frequency is a constant. (ii) If a source of light has a wavelength of 3.0 Å, its frequency is 1.0×10^{18} Hz. (iii) The speed of ultraviolet light is greater than the speed of microwave radiation. Which of these three statements is or are true? (a) Only one statement is true. (b) Statements (i) and (ii) are true. (c) Statements (i) and (iii) are true. (d) Statements (ii) and (iii) are true. (e) All three statements are true.

Practice Exercise 2

(a) A laser used in orthopedic spine surgery produces radiation with a wavelength of 2.10 μ m. Calculate the frequency of this radiation. (b) An FM radio station broadcasts electromagnetic radiation at a frequency of 103.4 MHz (megahertz; 1 MHz = 10⁶ s⁻¹). Calculate the wavelength of this radiation. The speed of light is 2.998 × 10⁸ m/s to four significant figures.

Sample Exercise 6.3 Energy of a Photon

Calculate the energy of one photon of yellow light that has a wavelength of 589 nm.

Solution

Analyze Our task is to calculate the energy, *E*, of a photon, given its wavelength, $\lambda = 589$ nm.

Plan We can use Equation 6.1 to convert the wavelength to frequency: $v = c/\lambda$. We can then use Equation 6.3 to calculate energy: E = hv

Solve The frequency, *v*, is calculated from the given wavelength, as shown in Sample Exercise 6.2:

$$\nu = (3.00 \times 10^8 \,\text{m/s})/(589 \times 10^{-9} \,\text{m}) = 5.09 \times 10^{14} \,\text{s}^{-1}$$

The value of the Planck constant, h, is given both in the text and in the table of physical constants on the inside back cover of the text; thus we can easily calculate E:

$$E = (6.626 \times 10^{-34} \text{ J-s})(5.09 \times 10^{14} \text{ s}^{-1}) = 3.37 \times 10^{-19} \text{ J}$$

Comment If one photon of radiant energy supplies 3.37×10^{-19} J, we calculate that one mole of these photons will supply:

$$(6.02 \times 10^{23} \text{ photons/mol})(3.37 \times 10^{-19} \text{ J/photon})$$

 $= 2.03 \times 10^5 \text{ J/mol}$

Sample Exercise 6.3 Energy of a Photon

Calculate the energy of one photon of yellow light that has a wavelength of 589 nm.

Practice Exercise 1

Which of the following expressions correctly gives the energy of a mole of photons with wavelength λ ?

(a)
$$E = \frac{h}{\lambda}$$
 (b) $E = N_A \frac{\lambda}{h}$ (c) $E = \frac{hc}{\lambda}$ (d) $E = N_A \frac{h}{\lambda}$ (e) $E = N_A \frac{hc}{\lambda}$

Practice Exercise 2

(a) A laser emits light that has a frequency of 4.69 $\times 10^{14}$ s⁻¹. What is the energy of one photon of this radiation? (b) If the laser emits a pulse containing 5.0 $\times 10^{17}$ photons of this radiation, what is the total energy of that pulse? (c) If the laser emits 1.3 $\times 10^{-2}$ J of energy during a pulse, how many photons are emitted?

In the Bohr model of the hydrogen atom, electrons are confined to orbits with fixed radii, and those radii can be calculated. The radii of the first four orbits are 0.53, 2.12, 4.76, and 8.46 Å, respectively, as depicted below.

- (a) If an electron makes a transition from the $n_i = 4$ level to a lower-energy level, $n_f = 3, 2, \text{ or } 1$, which transition would produce a photon with the shortest wavelength?
- (b) What are the energy and wavelength of such a photon, and in which region of the electromagnetic spectrum does it lie?
- (c) The image on the right shows the output of a detector that measures the intensity of light emitted from a sample of hydrogen atoms that have been excited so that each atom begins with an electron in the n = 4 state. What is the final state, $n_{\rm f}$, of the transition being detected?



Continued

Solution

Analyze We are asked to determine the energy and wavelength associated with various transitions involving an electron relaxing from the n = 4 state of the hydrogen atom to one of three lower-energy states.

Plan Given the integers representing the initial and final states of the electron, we can use Equation 6.6 to calculate the energy of the photon emitted and then use the relationships E = hv and $c = v\lambda$ to convert energy to wavelength. The photon with the highest energy will have the shortest wavelength because photon energy is inversely proportional to wavelength.

Solve

(a) The wavelength of a photon is related to its energy through the relationship $E = hv = hc/\lambda$. Hence, the photon with the smallest wavelength will have the largest energy. The energy levels of the electron orbits decrease as *n* decreases.

The electron loses the most energy on transitioning from the $n_i = 4$ state to the $n_f = 1$ state, and the photon emitted in that transition has the highest energy and the smallest wavelength.

(b) We first calculate the energy of the photon using Equation 6.6 with $n_i = 4$ and $n_f = 1$:

$$\Delta E = -2.18 \times 10^{-18} \,\mathrm{J} \Big(rac{1}{1^2} - rac{1}{4^2} \Big) = -2.04 \times 10^{-18} \,\mathrm{J}$$

 $E_{\rm photon} = -\Delta E = 2.04 \times 10^{-18} \,\mathrm{J}$

Continued

Next we rearrange Planck's relationship to calculate the frequency of the emitted photon.

$$\nu = E/h = (2.04 \times 10^{-18} \text{J})/(6.626 \times 10^{-34} \text{J-s}) = 3.02 \times 10^{15} \text{s}^{-1}$$

Finally, we use the frequency to determine the wavelength.

Light with this wavelength falls in the ultraviolet region of the electromagnetic spectrum.

$$\lambda = c/\nu = (2.998 \times 10^8 \,\text{m/s})/(3.02 \times 10^{15} \,\text{s}^{-1})$$
$$= 9.72 \times 10^{-8} \,\text{m} = 97.2 \,\text{nm}$$

(c) From the graph, we estimate the wavelength of the photon to be approximately 480 nm. Starting from the wavelength, it is easiest to estimate n_f using Equation 6.4:

$$rac{1}{\lambda} = R_{\mathrm{H}} \left(rac{1}{n_{\mathrm{f}}^2} - rac{1}{n_{\mathrm{i}}^2}
ight)$$

Rearranging:

So $n_f = 2$, and the photons seen by the detector are those emitted when an electron transitions from the $n_f = 4$ to the $n_f = 2$ state.

$$\frac{1}{n_{\rm f}^2} = \frac{1}{n_{\rm i}^2} + \frac{1}{R_{\rm H}\lambda} = \frac{1}{4^2} + \frac{1}{(1.097 \times 10^7 \,\mathrm{m}^{=1})(480 \times 10^{-9} \,\mathrm{m})}$$
$$\frac{1}{n_{\rm f}^2} = 0.25$$

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Continued

Check Referring back to Figure 6.12, we confirm that the n = 4 to n = 1 transition should have the largest energy of the three possible transitions.

Practice Exercise 1

In the top part of Figure 6.11, the four lines in the H atom spectrum are due to transitions from a level for which $n_i > 2$ to the $n_f = 2$ level. What is the value of n_i for the red line in the spectrum? (a) 3 (b) 4 (c) 5 (d) 6 (e) 7



Practice Exercise 2

For each of the following transitions, give the sign of ΔE and indicate whether a photon is emitted or absorbed. (a) n = 3 to n = 1 (b) n = 2 to n = 4

Sample Exercise 6.5 Matter Waves

What is the wavelength of an electron moving with a speed of 5.97 \times 10⁶ m/s? The mass of the electron is 9.11 \times 10⁻³¹ kg.

Solution

Analyze We are given the mass, *m*, and velocity, *v*, of the electron, and we must calculate its de Broglie wavelength, λ .

Plan The wavelength of a moving particle is given by Equation 6.8, so λ is calculated by inserting the known quantities *h*, *m*, and *v*. In doing so, however, we must pay attention to units.

Solve

Using the value of the Planck constant:

 $h = 6.626 \times 10^{-34} \text{ J-s}$

we have the following:

$$\lambda = \frac{h}{mv}$$

= $\frac{(6.626 \times 10^{-34} \text{ J-s})}{(9.11 \times 10^{-31} \text{ kg})(5.97 \times 10^6 \text{ m/s})} \left(\frac{1 \text{ kg-m}^2/\text{s}^2}{1 \text{ J}}\right)$
= $1.22 \times 10^{-10} \text{ m} = 0.122 \text{ nm} = 1.22 \text{ Å}$

Comment By comparing this value with the wavelengths of electromagnetic radiation shown in Figure 6.4, we see that the wavelength of this electron is about the same as that of X rays.

Sample Exercise 6.5 Matter Waves

Continued

Practice Exercise 1

Consider the following three moving objects: (i) a golf ball with a mass of 45.9 g moving at a speed of 50.0 m/s, (ii) An electron moving at a speed of 3.50×10^5 m/s, (iii) A neutron moving at a speed of 2.3×10^2 m/s. List the three objects in order from shortest to longest de Broglie wavelength. (a) i < iii < ii (b) ii < iii < i (c) iii < ii < i (d) i < ii < iii (e) iii < i < ii

Practice Exercise 2

Calculate the velocity of a neutron whose de Broglie wavelength is 505 pm. The mass of a neutron is given in the table inside the back cover of the text.

Sample Exercise 6.6 Subshells of the Hydrogen Atom

(a) Without referring to Table 6.2, predict the number of subshells in the fourth shell, that is, for n = 4. (b) Give the label for each of these subshells. (c) How many orbitals are in each of these subshells?

TAB	LE 6.2 Re	lationship among Values of n , l , and m_l through $n = 4$			
п	Possible Values of /	Subshell Designation	Possible Values of <i>m_l</i>	Number of Orbitals in Subshell	Total Number of Orbitals in Shel
1	0	1 <i>s</i>	0	1	1
2	0	2 <i>s</i>	0	1	
	1	2 <i>p</i>	1, 0, -1	3	4
3	0	3 <i>s</i>	0	1	
	1	3 <i>p</i>	1, 0, -1	3	
	2	3 <i>d</i>	2, 1, 0, -1, -2	5	9
4	0	4 <i>s</i>	0	1	
	1	4p	1, 0, -1	3	
	2	4d	2, 1, 0, -1, -2	5	
	3	4f	3, 2, 1, 0, -1, -2, -3	7	16

Solution

Analyze and Plan We are given the value of the principal quantum number, n. We need to determine the allowed values of l and m_l for this given value of n and then count the number of orbitals in each subshell.

Solve There are four subshells in the fourth shell, corresponding to the four possible values of l (0, 1, 2, and 3).

These subshells are labeled 4*s*, 4*p*, 4*d*, and 4*f*. The number given in the designation of a subshell is the principal quantum number, *n*; the letter designates the value of the angular momentum quantum number, *l*: for l = 0, *s*; for l = 1, *p*; for l = 2, *d*; for l = 3, *f*.

Sample Exercise 6.6 Subshells of the Hydrogen Atom

Continued

There is one 4*s* orbital (when l = 0, there is only one possible value of m_l : 0). There are three 4*p* orbitals (when l = 1, there are three possible values of m_l : 1, 0, -1). There are five 4*d* orbitals (when l = 2, there are five allowed values of m_l : 2, 1, 0, -1, -2). There are seven 4*f* orbitals (when l = 3, there are seven permitted values of m_l : 3, 2, 1, 0, -1, -2, -3).

Practice Exercise 1

An orbital has n = 4 and $m_l = -1$. What are the possible values of 1 for this orbital? (a) 0, 1, 2, 3 (b) -3, -2, -1, 0, 1, 2, 3 (c) 1, 2, 3 (d) -3, -2 (e) 1, 2, 3, 4

Practice Exercise 2

(a) What is the designation for the subshell with n = 5 and l = 1? (b) How many orbitals are in this subshell? (c) Indicate the values of m_l for each of these orbitals.

Sample Exercise 6.7 Orbital Diagrams and Electron Configurations

Draw the orbital diagram for the electron configuration of oxygen, atomic number 8. How many unpaired electrons does an oxygen atom possess?

Solution

Analyze and Plan Because oxygen has an atomic number of 8, each oxygen atom has eight electrons. Figure 6.25 shows the ordering of orbitals. The electrons (represented as half arrows) are placed in the orbitals (represented as boxes) beginning with the lowest-energy orbital, the 1s. Each orbital can hold a maximum of two electrons (the Pauli exclusion principle). Because the 2p orbitals are degenerate, we place one electron in each of these orbitals (spin-up) before pairing any electrons (Hund's rule).

Solve Two electrons each go into the 1s and 2s orbitals with their spins paired. This leaves four electrons for the three degenerate 2p orbitals. Following Hund's rule, we put one electron into each 2p orbital until all three orbitals have one electron each. The fourth electron is then paired up with one of the three electrons already in a 2p orbital, so that the orbital diagram is





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Sample Exercise 6.7 Orbital Diagrams and Electron Configurations

Continued

The corresponding electron configuration is written $1s^22s^22p^4$. The atom has two unpaired electrons.

Practice Exercise 1

How many of the elements in the second row of the periodic table (Li through Ne) will have at least one unpaired electron in their electron configurations? (a) 3 (b) 4 (c) 5 (d) 6 (e) 7

Practice Exercise 2

(a) Write the electron configuration for silicon, element 14, in its ground state. (b) How many unpaired electrons does a ground-state silicon atom possess?

Sample Exercise 6.8 Electron Configurations for a Group

What is the characteristic valence electron configuration of the group 7A elements, the halogens?

Solution

Analyze and Plan We first locate the halogens in the periodic table, write the electron configurations for the first two elements, and then determine the general similarity between the configurations.

Solve The first member of the halogen group is fluorine (F, element 9). Moving backward from F, we find that the noble-gas core is [He]. Moving from He to the element of next higher atomic number brings us to Li, element 3. Because Li is in the second period of the *s* block, we add electrons to the 2*s* subshell. Moving across this block gives $2s^2$. Continuing to move to the right, we enter the *p* block. Counting the squares to F gives $2p^5$. Thus, the condensed electron configuration for fluorine is

```
F: [He]2s^2 2p^5
```

The electron configuration for chlorine, the second halogen, is

Cl: [Ne] $3s^23p^5$

From these two examples, we see that the characteristic valence electron configuration of a halogen is ns^2np^5 , where *n* ranges from 2 in the case of fluorine to 6 in the case of astatine.

Sample Exercise 6.8 Electron Configurations for a Group

Continued

Practice Exercise 1

A certain atom has an ns^2np^6 electron configuration in its outermost occupied shell. Which of the following elements could it be? (a) Be (b) Si (c) I (d) Kr (e) Rb

Practice Exercise 2

Which group of elements is characterized by an ns^2np^2 electron configuration in the outermost occupied shell?

Sample Exercise 6.9 Electron Configurations from the Periodic Table

(a) Based on its position in the periodic table, write the condensed electron configuration for bismuth, element 83.(b) How many unpaired electrons does a bismuth atom have?

Solution

(a) Our first step is to write the noble-gas core. We do this by locating bismuth, element 83, in the periodic table. We then move backward to the nearest noble gas, which is Xe, element 54. Thus, the noble-gas core is [Xe].

Next, we trace the path in order of increasing atomic numbers from Xe to Bi. Moving from Xe to Cs, element 55, we find ourselves in period 6 of the *s* block. Knowing the block and the period identifies the subshell in which we begin placing outer electrons, 6s. As we move through the s block, we add two electrons: $6s^2$.

As we move beyond the *s* block, from element 56 to element 57, the curved arrow below the periodic table reminds us that we are entering the *f* block. The first row of the *f* block corresponds to the 4*f* subshell. As we move across this block, we add 14 electrons: $4f^{14}$.

With element 71, we move into the third row of the *d* block. Because the first row of the *d* block is 3*d*, the second row is 4*d* and the third row is 5*d*. Thus, as we move through the ten elements of the *d* block, from element 71 to element 80, we fill the 5*d* subshell with ten electrons: $5d^{10}$.

Moving from element 80 to element 81 puts us into the *p* block in the 6*p* subshell. (Remember that the principal quantum number in the *p* block is the same as that in the *s* block.) Moving across to Bi requires three electrons: $6p^3$. The path we have taken is Putting the parts together, we obtain the condensed electron configuration: $[Xe]6s^24f^{14}5d^{10}6p^3$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[Xe]4f^{14}5d^{10}6s^26p^3$.

Sample Exercise 6.9 Electron Configurations from the Periodic Table

Continued

Finally, we check our result to see if the number of electrons equals the atomic number of Bi, 83: Because Xe has 54 electrons (its atomic number), we have 54 + 2 + 14 + 10 + 3 = 83. (If we had 14 electrons too few, we would realize that we have missed the *f* block.)



(b) We see from the condensed electron configuration that the only partially occupied subshell is 6*p*. The orbital diagram representation for this subshell is



In accordance with Hund's rule, the three 6p electrons occupy the three 6p orbitals singly, with their spins parallel. Thus, there are three unpaired electrons in the bismuth atom.

Sample Exercise 6.9 Electron Configurations from the Periodic Table

Continued

Practice Exercise 1

A certain atom has a [noble gas] $5s^24d^{10}5p^4$ electron configuration. Which element is it? (a) Cd (b) Te (c) Sm (d) Hg (e) More information is needed

Practice Exercise 2

Use the periodic table to write the condensed electron configuration for (a) Co (element 27), (b) In (element 49).

Sample Integrative Exercise Putting Concepts Together

Boron, atomic number 5, occurs naturally as two isotopes, ¹⁰B and ¹¹B, with natural abundances of 19.9% and 80.1%, respectively. (**a**) In what ways do the two isotopes differ from each other? Does the electronic configuration of ¹⁰B differ from that of ¹¹B? (**b**) Draw the orbital diagram for an atom of ¹¹B. Which electrons are the valence electrons? (**c**) Indicate three ways in which the 1s electrons in boron differ from its 2s electrons. (**d**) Elemental boron reacts with fluorine to form BF₃, a gas. Write a balanced chemical equation for the reaction of solid boron with fluorine gas. (**e**) ΔH_f° for BF₃(*g*) is –1135.6 kJ/mol. Calculate the standard enthalpy change in the reaction of boron with fluorine. (**f**) Will the mass percentage of F be the same in ¹⁰BF₃ and ¹¹BF₃? If not, why is that the case?

Solution

- (a) The two isotopes of boron differ in the number of neutrons in the nucleus. ∞ (Sections 2.3 and 2.4) Each of the isotopes contains five protons, but ¹⁰B contains five neutrons, whereas ¹¹B contains six neutrons. The two isotopes of boron have identical electron configurations, $1s^22s^22p^1$, because each has five electrons.
- (b) The complete orbital diagram is



The valence electrons are the ones in the outermost occupied shell, the $2s^2$ and $2p^1$ electrons. The $1s^2$ electrons constitute the core electrons, which we represent as [He] when we write the condensed electron configuration, [He] $2s^22p^1$.

Sample Integrative Exercise Putting Concepts Together

Continued

(c) The 1*s* and 2*s* orbitals are both spherical, but they differ in three important respects: First, the 1*s* orbital is lower in energy than the 2*s* orbital. Second, the average distance of the 2*s* electrons from the nucleus is greater than that of the 1*s* electrons, so the 1*s* orbital is smaller than the 2*s*. Third, the 2*s* orbital has one node, whereas the 1*s* orbital has no nodes (Figure 6.19).



Sample Integrative Exercise Putting Concepts Together

Continued

(d) The balanced chemical equation is

 $2 \operatorname{B}(s) + 3 \operatorname{F}_2(g) \longrightarrow 2 \operatorname{BF}_3(g)$

(e) $\Delta H^{\circ} = 2(-1135.6) - [0+0] = -2271.2$ kJ. The reaction is strongly exothermic.

(f) As we saw in Equation 3.10 (Section 3.3), the mass percentage of an element in a substance depends on the formula weight of the substance. The formula weights of ${}^{10}\text{BF}_3$ and ${}^{11}\text{BF}_3$ are different because of the difference in the masses of the two isotopes (the isotope masses of ${}^{10}\text{B}$ and ${}^{11}\text{B}$ are 10.01294 and 11.00931 amu, respectively). The denominators in Equation 3.10 would therefore be different for the two isotopes, whereas the numerators would remain the same.