Chapter 6: Electronic Structure and Periodic Properties of Elements

6.1 Electromagnetic Energy

Question 32-1.

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

Solution
The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

Question 32-2.

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^8\ s^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

Solution

$$c = \lambda \nu$$

$$= \lambda \times 1.031 \times 10^8\ s^{-1}$$

$$\lambda = \frac{2.998 \times 10^8\ m\ s^{-1}}{1.031 \times 10^8\ s^{-1}} = 2.908\ m$$

Question 32-3.

FM–95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^7\ s^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?

Solution

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8\ m\ s^{-1}}{9.51 \times 10^7\ s^{-1}} = 3.15\ m$$

Question 32-4.

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

Solution

$$c = \lambda \nu$$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8\ \cancel{m}\ s^{-1}}{435.8 \times 10^{-9}\ \cancel{m}} = 6.879 \times 10^{14}\ s^{-1}$$

$$E = h\nu = 6.626 \times 10^{-34}\ J\ \cancel{s} \times 6.879 \times 10^{14}\ \cancel{s^{-1}}$$

$$= 4.558 \times 10^{-19}\ J$$

Question 32-5.

Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV (1 eV = 1.602 × 10^{-19} J)?

Solution

$c = \lambda v$

$$\lambda = \frac{c}{v} = \frac{2.998 \times 10^{8} \cancel{m}\ s^{-1}}{614.5 \times 10^{-9} \cancel{m}} = 4.879 \times 10^{14}\ s^{-1}$$

$$E = hv = 6.626 \times 10^{-34}\ J\ \cancel{s} \times 4.879 \times 10^{14}\ \cancel{s}^{-1} = 3.233 \times 10^{-19}\ J$$

$$E = \frac{3.233 \times 10^{-19}\ \cancel{J}}{1.602 \times 10^{-19}\ \cancel{J}\ eV^{-1}} = 2.018\ eV$$

Question 32-6.

Heated lithium atoms emit photons of light with an energy of 2.961 × 10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

Solution

$$E = 2.961 \times 10^{-19}\ J = hv = 6.626 \times 10^{-34}\ J\ s \times v$$

$$v = 2.961 \times 10^{-19} \frac{\cancel{J}}{6.626 \times 10^{-34}\ \cancel{J}} = 4.4688 \times 10^{14}\ s^{-1}$$

$$c = \lambda v;\ \lambda = \frac{c}{v} = 2.998 \times 10^{8} \frac{\cancel{s^{-1}}}{4.4699 \times 10^{14}\ \cancel{s^{-1}}} = 6.709 \times 10^{-7}\ m$$

This is a red light wavelength.

$$E = 2.961 \times 10^{-19}\ J \times 6.022 \times 10^{23}\ mol^{-1} = 178.3\ kJ\ mol^{-1}$$

Question 32-7.

A photon of light produced by a surgical laser has an energy of 3.027 × 10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

Solution

$E = hv$

$$v = \frac{3.027 \times 10^{-19}\ \cancel{J}}{6.626 \times 10^{-34}\ \cancel{J}\ s^{-1}} = 4.568 \times 10^{14}\ s^{-1}$$

$$\lambda = \frac{c}{v} = \frac{2.998 \times 10^{8}\ m\ \cancel{s^{-1}}}{4.568 \times 10^{14}\ \cancel{s^{-1}}} = 6.563 \times 10^{-7}\ m = 6563\ Å = 656.3\ nm$$

Energy mol^{-1} = 3.027 × 10^{-19} J × 6.022 × 10^{23} mol^{-1} = 1.823 × 10^{5} J mol^{-1}; red.

Question 32-8.

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9 × 10^{-7} m and (b) 4.2 × 10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

Solution

(a) $\nu = \dfrac{c}{\lambda} = \dfrac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \text{s}^{-1}}{7.9 \times 10^{-7}\ \cancel{\text{m}}} = 3.8 \times 10^{14}\ \text{s}^{-1}$; this has a color of blue to violet. (b) $\nu = \dfrac{c}{\lambda} = \dfrac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \text{s}^{-1}}{4.2 \times 10^{-7}\ \cancel{\text{m}}} = 7.1 \times 10^{14}\ \text{s}^{-1}$; This has a color or red. Unseparated, the blue-violet color predominates and we see blue-violet.

Question 32-9.

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

Solution

From $c = \lambda v$

(a) $\lambda = \dfrac{c}{v} = \dfrac{2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{3.45 \times 10^{14}\ \cancel{\text{s}^{-1}}} = 8.69 \times 10^{-7}\ \text{m}$

$E = hv = 6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times 3.45 \times 10^{14} \cancel{\text{s}^{-1}} = 2.29 \times 10^{-19}\ \text{J}$

(b) $\lambda = \dfrac{c}{v} = \dfrac{2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}^{-1}}}{6.53 \times 10^{14}\ \cancel{\text{s}^{-1}}} = 4.59 \times 10^{-7}\ \text{m}$

$E = hv = 6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times 6.53 \times 10^{14} \cancel{\text{s}^{-1}} = 4.33 \times 10^{-19}\ \text{J}$

The color of (a) is red; (b) is blue.

Question 32-10.

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

Solution

The heat required is $q = cm\Delta T = 4.184\ \text{J}\ \cancel{\text{g}^{-1}}\ \cancel{°\text{C}^{-1}} \times 175\ \cancel{\text{g}} \times (40.0 - 25.0)\ \cancel{°\text{C}} = 1.1 \times 10^{4}\ \text{J}$

The wavelength corresponds to energy of

$$E = hv = h\frac{c}{\lambda} = 6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times \frac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \cancel{\text{s}^{-1}}}{1.5 \times 10^{-6}\ \cancel{\text{m}}} = 1.3 \times 10^{-19}\ \text{J photon}^{-1}$$

$$\text{Number of photons} = \frac{1.1 \times 10^{4}\ \cancel{\text{J}}}{1.3 \times 10^{-19}\ \cancel{\text{J}}\ \text{photons}^{-1}} = 8.5 \times 10^{22}\ \text{photons}$$

Question 32-11.

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

Solution

$c = \lambda v$,

$$v = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \text{s}^{-1}}{2.090 \times 10^{-11}\ \cancel{\text{m}}} = 1.434 \times 10^{19}\ \text{s}^{-1}$$

$E = hv = 6.626 \times 10^{-34}\ \text{J}\ \cancel{\text{s}} \times 1.434 \times 10^{19} \cancel{\text{s}^{-1}} = 9.502 \times 10^{-15}\ \text{J}$

Question 32-12.

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

Solution

Determine the frequency of the photons and then their energy. Divide the total energy by the energy per photon to determine the number of photons needed.

850 nm = 8.5×10^{-7} m

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ \cancel{\text{m}}\ \text{s}^{-1}}{8.50 \times 10^{-7}\ \cancel{\text{m}}} = 3.527 \times 10^{14}\ \text{s}^{-1}$$

$E = h\nu = 6.626 \times 10^{34}\ \text{J}\ \cancel{\text{s}^{-1}} \times 3.527 \times 10^{14}\ \text{s}^{-1} = 2.337 \times 10^{-19}\ \text{J}$

$$\text{Total energy/energy per photon} = \frac{3.15 \times 10^{-14}\ \cancel{\text{J}}}{2.337 \times 10^{-19}\ \cancel{\text{J}}\ \text{photon}^{-1}} = 1.35 \times 10^{5}\ \text{photons}]$$

Question 32-13.

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

Solution

See Figure 6.13. Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

Question 32-14.

Answer the following questions about a Blu-ray laser:

(a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?

(b) A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?

(c) The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = 0.60(λ/NA), where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm
laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?

(d) The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^{7} bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by A = πr^2, where the radius r is one-half of the diameter.)

Solution
(a) The laser is in the visible spectrum range (violet) with a frequency of 7.40×10^{14} s^{-1}. (b) The energy per one photon is 4.90×10^{-19} J. $\dfrac{0.005\ \text{W}}{4.90 \times 10^{-19}\ \text{J}} = 1.02 \times 10^{16}$ photons s^{-1}. $1.02 \times 10^{16} \times 3600 = 3.67 \times 10^{19}$ photons/h. (c) 2.6×10^{-7} m. (d) 1.7×10^{11} bits; a page requires 1.8×10^{4} bits.

Question 32-15.

What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects a photon with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

Solution
$E_{\text{photon}} = h\nu = (6.626 \times 10^{-34}\ \text{J s}) \times (6.66 \times 10^{14}\ \text{s}^{-1}) = 4.41 \times 10^{-19}$ J
$E_{\text{photon}} = E_{\text{kinetic}} + E_{\text{threshold}}$,.which means that $4.41 \times 10^{-19}\ \text{J} = 7.74 \times 10^{-20}\ \text{J} + E_{\text{threshold}}$, thus $E_{\text{threshold}} = 3.64 \times 10^{-19}$ J, which corresponds to a threshold frequency of 5.49×10^{14} s^{-1}. Orange light is roughly 620 nm or 4.84×10^{14} s^{-1}, which is less than the threshold, so no electrons will be ejected.

6.2 The Bohr Model

Question 33-1.

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

Solution
The electron with $n = 3$ is farther from the nucleus and, since the Coulomb potential varies inversely with the distance between the electron and the nucleus, the electrostatic attraction between it and the nucleus is less than for an electron with $n = 1$.

Question 33-2.

What does it mean to say that the energy of the electrons in an atom is quantized?

Solution
Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

Question 33-3.

Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

Solution

$$\Delta E = E_{\text{i}} - E_{\text{f}} = R_{\infty}\left(\frac{1}{n_{\text{i}}^2} - \frac{1}{n_{\text{f}}^2}\right) = R_{\infty}\left(\frac{1}{1^2} - 0\right) = R_{\infty} = 2.179 \times 10^{-18}\ \text{J}$$

Question 33-4.

The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; 1 eV = 1.602 × 10^{-19} J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

Solution

$$\Delta E = E_2 - E_5 = 2.179 \times 10^{-18}\left(\frac{1}{n_2^2} - \frac{1}{n_5^2}\right)\text{ J}$$

$$= 2.179 \times 10^{-18}\left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 4.576 \times 10^{-19}\text{ J}$$

$$= \frac{4.576 \times 10^{-19}\ \cancel{\text{J}}}{1.602 \times 10^{-19}\ \cancel{\text{J}}\ \text{eV}^{-1}} = 2.856\text{ eV}$$

Question 33-5.

Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.

Solution

$E = -2.179 \times 10^{-18}\text{ J }(Z^2)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 3$ for Li.

$$E = -2.179 \times 10^{-18}\text{ J}(9)\left(\frac{1}{1}\right) = 1.961 \times 10^{-17}\text{ J}$$

Question 33-6.

Using the Bohr model, determine the lowest possible energy for the electron in the He^{+} ion.

Solution

$E = -2.179 \times 10^{-18}\text{ J}\left(Z^2\right)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 2$ for He. $E = -2.179 \times 10^{-18}\text{ J}(4)\left(\frac{1}{1}\right) = -8.716 \times 10^{-18}\text{ J}$

Question 33-7.

Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

Solution

$E = -2.179 \times 10^{-18}\text{ J}\left(Z^2\right)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 1$ for H.

$$E = -2.179 \times 10^{-18}\text{ J}(1)\left(\frac{1}{36}\right) = -6.053 \times 10^{-20}\text{ J}$$

Question 33-8.

Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

Solution

$E = -2.179 \times 10^{-18}\ \text{J}\left(Z^2\right)\left(\frac{1}{n^2}\right)$. Since Z is the number of protons in the nucleus, $Z = 1$ for H.

$$E = -2.179 \times 10^{-18}\ \text{J}(1)\left(\frac{1}{64}\right) = -3.405 \times 10^{-20}\ \text{J}$$

Question 33-9.

How far from the nucleus in angstroms (1 angstrom = 1×10^{-10} m) is the electron in a hydrogen atom if it has an energy of -8.72×10^{-20} J?

Solution

$E = -2.179 \times 10^{-18}\ \text{J}\left(Z^2\right)\left(\frac{1}{n^2}\right)$; $-8.72 \times 10^{-20}\ \text{J} = -2.179 \times 10^{-18}\ \text{J}(1)\left(\frac{1}{n^2}\right)$. So,

$n = \sqrt{\frac{-2.179 \times 10^{-18}\,\text{J}(1)}{8.72 \times 10^{-20}\ \text{J}}} = 5$, and

$$r = \frac{n^2}{Z}a_0 = \frac{5^2}{1} \times 5.292 \times 10^{-11}\ \text{m} = 1.32 \times 10^{-9}\ \cancel{\text{m}} \times \frac{10^{10}\ \text{Å}}{1\ \cancel{\text{m}}} = 13.2\ \text{Å}.$$

Question 33-10.

What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?

Solution

$r = \frac{n^2 a_0}{Z}$. For hydrogen, Z = 1; $a_0 = 0.529$ Å ; $n = 8$.

$$r = \frac{8^2(0.529\ \text{Å})}{1} = 64(0.529) = 33.9\ \text{Å}$$

Question 33-11.

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^{+} ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.

Solution

$$E = 2.179 \times 10^{-18}\ \text{J}(Z^2)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$= 2.179 \times 10^{-18}\ \text{J}(2^2)\left(\frac{1}{2^2} - \frac{1}{5^2}\right) \qquad 1.830 \times 10^{-18}\ \text{J}$$

$$= 1.830 \times 10^{-18}\ \text{J}$$

Question 33-12.

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.

Solution

$$E = 2.179 \times 10^{-18}\ \text{J}(Z^2)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$
$$= 2.179 \times 10^{-18}\ \text{J}(3^2)\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$
$$= 1.471 \times 10^{-17}\ \text{J}$$

Question 33-13.

Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1$, 2, 3, and 4 orbits.

(a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbits?

(b) Calculate the lowest and highest energies of light produced by the transitions described in part (a).

(c) Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

Solution

(a) 6; (b) the lowest energy transition will be $4 \longrightarrow 3$ $4 \longrightarrow 3$, which emits 1.059×10^{-19} J: the highest energy transition will be $4 \longrightarrow 1$, which emits 2.043×10^{-18} J; (c) low: $1.598 \times 10^{14}\ \text{s}^{-1}$, 1876 nm; high: $3.083 \times 10^{15}\ \text{s}^{-1}$, 97.23 nm

Question 33-14.

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

Solution

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, n. The orbiting electron in Bohr’s model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such “quantum jumps” will produce discrete spectra, in agreement with observations.

Question 33-15.

The spectra of hydrogen and of calcium are shown in Figure 6.13. What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

Solution

The lines are caused by the transition of electrons between different energy states. The lines have different colors because the energies of transition vary for different states, resulting in a variety of wavelengths and colors. The spectrum for calcium is more complicated because calcium has many more electrons than hydrogen and, therefore, many more possible electronic states and transitions.

6.3 Development of Quantum Theory

Question 34-1.

How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

Solution

Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, $n = 1,2,3,\ldots$, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function ψ called a wave function that can be used to determine the electron's spatial probability distribution. These wave functions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, n (the same one used by Bohr), which specifies shells such that orbitals having the same n all have the same energy and approximately the same spatial extent; the angular momentum quantum number l, which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same l (and n) all have the same energy; and the orientation quantum number m, which is a measure of the z component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [*s* orbitals] can have zero angular momentum).

Question 34-2.

What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

Solution

$n = 1\ldots\infty$; $l = 0\ldots n - 1$; $m_l = -l, -1 + 1,\ldots,l- 1, l$; $m_s = \pm\frac{1}{2}$

Question 34-3.

Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

Solution

n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. l determines the shape of the orbital. m_l determines the orientation of the orbitals of the same l value with respect to one another. m_s determines the spin of an electron.

Question 34-4.

Answer the following questions:

(a) Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.
(b) How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

Solution

(a) A shell consists of one or more subshells; each subshell contains a different type of orbital. A subshell consists of one or more orbitals of the same type with the same energy, unless an external magnetic field is applied. An orbital describes a region of space that can be occupied by a maximum of two electrons. (b) Quantum numbers of shells give the overall energy of the electrons in the respective shell. Those subshells define the shape and volume of spaces that the electrons can occupy. The quantum numbers for individual orbitals of an atom distinguish the orbitals' orientation in space.

Question 34-5.

Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 2$, $l = 1$
(b) $n = 4$, $l = 2$
(c) $n = 6$, $l = 0$

Solution

(a) 2*p*, (b) 4*d*, (c) 6*s*

Question 34-6.

Which of the subshells described in Exercise 35 contain degenerate orbitals? How many degenerate orbitals are in each?

Solution

(a) Three, (b) five, (c) one orbital, but degeneracy does not apply to single orbitals.

Question 34-7.

Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 3, l = 2$
(b) $n = 1, l = 0$
(c) $n = 4, l = 3$

Solution

(a) 3*d;* (b) 1*s;* (c) 4*f*

Question 34-8.

Which of the subshells described in Exercise 37 contain degenerate orbitals? How many degenerate orbitals are in each?

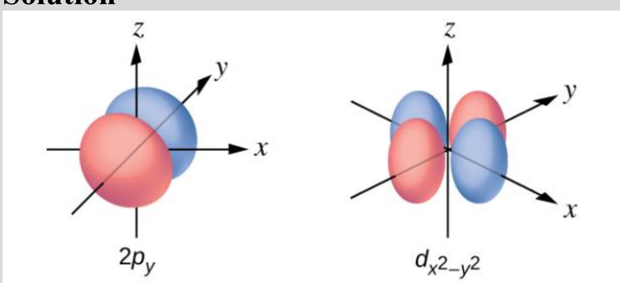
Solution

(a) 3*d* and 4*f*; (b) five in 3*d*, seven in 4*f*

Question 34-9.

Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.

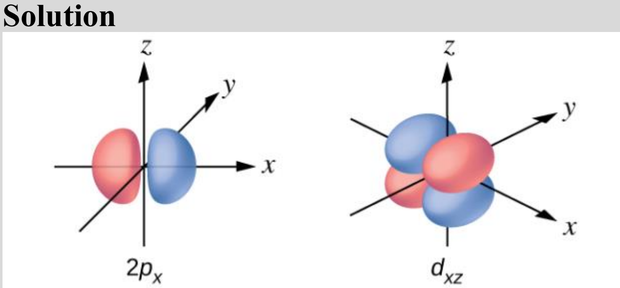
Solution



Question 34-10.

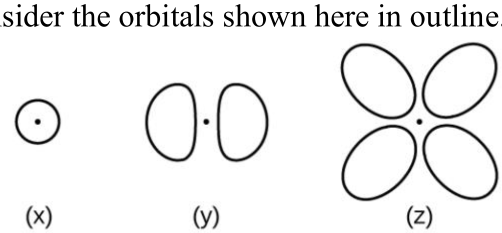
Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

Solution



Question 34-11.

Consider the orbitals shown here in outline.



(a) What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?
(b) How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?
(c) Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.
(d) What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?
(e) What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

Solution

(a) x. 2, y. 2, z. 2; (b) x. 1, y. 3, z. 0; (c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$, z. 3 2 0 $\frac{1}{2}$; (d) x. 1, y. 2, z. 3; (e) x. $l = 0$, $m_l = 0$, y. $l = 1$, $m_l = -1$ 0 or +1, z. $l = 2$, $m_l = -2$ –1 0 +1 +2

Question 34-12.

State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

Solution

The Heisenberg uncertainty principle states that it is impossible to precisely determine both the momentum and the position of a particle at the same time. The uncertainty principle means that the more exactly you learn either the momentum or the position of a quantum particle, the less exactly you can know the other quantity. A similar relationship with energy and time is covered by the uncertainty principle: The better that we know the energy of a particle, the less knowledge we have of the time of its emission from an atom.

Question 34-13.

How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

Solution

In the second subshell ($n = 2$), there are two possible angular momentum (l) values (0 and 1). When $l = 0$, the magnetic quantum number (m_l) can only be 0. When $l = 1$, the magnetic quantum number (m_l) can be equal to –1, 0, or 1. Therefore, in the second shell, there are four orbitals (the number of orbitals in a shell is equal to n^2). If there were three possible values for the spin quantum number, each orbital could hold three different electrons and still obey the Pauli exclusion principle. In other words, each orbital could hold three electrons and none of those three electrons would have the exact same four quantum numbers. If each orbital could hold three electrons, the second shell, which has four orbitals, could hold a total of 12 electrons.

Question 34-14.

Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

(a) $c = \lambda v$

(b) $E = \dfrac{mv^2}{2}$

(c) $r = \frac{n^2 a_0}{Z}$

(d) $E = hv$

(e) $\lambda = \frac{h}{mv}$

Solution

(a) Wavelike behavior. This is the formula for a wave of electromagnetic radiation (it can be applied to other waves if *c* is modified to be the speed of the wave, not necessarily of light). (b) Particle-like behavior. This is the formula for energy of a particle of rest mass *m* using a definite velocity value of *v*. (c) This is a formula for particle-like behavior, as it assumes that an electron is moving around the nucleus at a distance *r*; thus, it has a definite trajectory. (d) Wavelike behavior. This is a formula for energy of an electromagnetic wave. (e) Both wave and particle, since it shows that there is a wavelength that belongs to a particle with a rest mass *m*.

Question 34-15.

Write a set of quantum numbers for each of the electrons with an *n* of 4 in a Se atom.

Solution

n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

6.4 Electronic Structure of Atoms (Electron Configurations)

Question 35-1.

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

Solution

For example, Fe^{3+}: $1s^22s^22p^63s^23p^63d^5$; Cu^{2+}: $1s^22s^22p^63s^23p^63d^9$; Ti^{4+}: $1s^22s^22p^63s^23p^6$; Cr^{3+}: $1s^22s^22p^63s^23p^63d^3$

Question 35-2.

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

Solution

For example, Na^{+}: $1s^22s^22p^6$; Ca^{2+}: $1s^22s^22p^63s^23p^6$; Sn^{2+}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^2$; F^{-}: $1s^22s^22p^6$; O^{2-}: $1s^22s^22p^6$; Cl^{-}: $1s^22s^22p^63s^23p^6$.

Question 35-3.

Using complete subshell notation (not abbreviations, $1s^22s^22p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) C
(b) P
(c) V
(d) Sb
(e) Sm

Solution

(a) $1s^22s^22p^2$; (b) $1s^22s^22p^63s^23p^3$; (c) $1s^22s^22p^63s^23p^64s^23d^3$; (d) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^3$; (e) $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^24f^6$

Question 35-4.

Using complete subshell notation ($1s^22s^22p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) N
(b) Si
(c) Fe
(d) Te
(e) Tb

Solution

(a) $1s^22\ s^22p^3$; (b) $1s^22\ s^22p^63s^23p^2$; (c) $1s^22\ s^22p^63s^23p^64s^23d^6$; (d) $1s^22\ s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^4$; (e) $1s^22\ s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^9$

Question 35-5.

Is $1s^22s^22p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

Solution

A microscopic property; it describes the electronic configuration, which is a property of an atom.

Question 35-6.

What additional information do we need to answer the question "Which ion has the electron configuration $1s^22s^22p^63s^23p^6$"?

Solution

The charge on the ion.

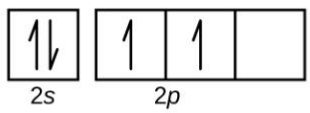
Question 35-7.

Draw the orbital diagram for the valence shell of each of the following atoms:

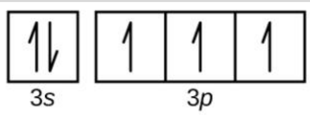
(a) C
(b) P
(c) V
(d) Sb
(e) Ru

Solution

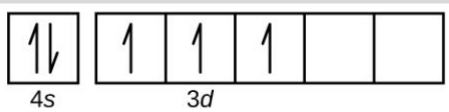
(a)



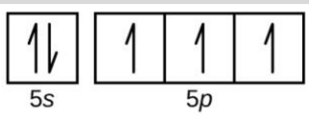
(b)



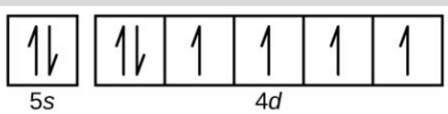
(c)



(d)



(e)



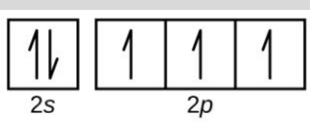
Question 35-8.

Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

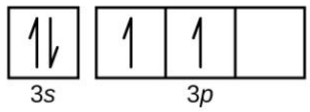
(a) N
(b) Si
(c) Fe
(d) Te
(e) Mo

Solution

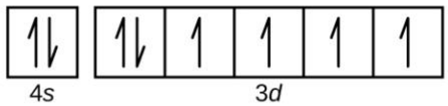
(a)



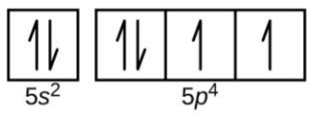
(b)



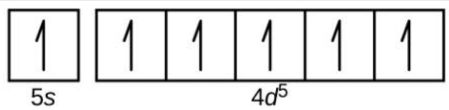
(c)



(d)



(e)



Question 35-9.

Using complete subshell notation ($1s^22s^22p^6$, and so forth), predict the electron configurations of the following ions.

(a) N^{3-}
(b) Ca^{2+}
(c) S^{-}
(d) Cs^{2+}
(e) Cr^{2+}
(f) Gd^{3+}

Solution

(a) $1s^22s^22p^6$; (b) $1s^22s^22p^63s^23p^6$; (c) $1s^22s^22p^63s^23p^5$; (d) $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^24d^{10}5p^5$; (e) $1s^22s^22p^63s^23p^63d^4$; (f) $1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^24d^{10}5s^25p^64f^5$

Question 35-10.

Which atom has the electron configuration $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^2$?

Solution

Zr

Question 35-11.

Which atom has the electron configuration $1s^22s^22p^63s^23p^63d^74s^2$?

Solution

Co

Question 35-12.

Which ion with a +1 charge has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$? Which ion with a –2 charge has this configuration?

Solution

Rb^{+}, Se^{2-}

Question 35-13.

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

Solution

B

Question 35-14.

Which of the following has two unpaired electrons?

(a) Mg
(b) Si
(c) S
(d) Both Mg and S
(e) Both Si and S.

Solution

Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

Question 35-15.

Which atom would be expected to have a half-filled 6*p* subshell?

Solution

Bi

Question 35-16.

Which atom would be expected to have a half-filled 4*s* subshell?

Solution

K

Question 35-17.

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

Solution

Co^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$; Co^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

Question 35-18.

Thallium was used as a poison in the Agatha Christie mystery story "The Pale Horse." Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

Solution

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

Question 35-19.

Write the electron configurations for the following atoms or ions:

(a) B^{3+}
(b) O^-
(c) Cl^{3+}

(d) Ca^{2+}
(e) Ti

Solution
(a) $1s^2$; (b) $1s^22s^22p^5$; (c) $1s^22s^22p^63s^23p^2$; (d) $1s^22s^22p^63s^23p^6$; (e) $1s^22s^22p^63s^23p^64s^23d^2$

Question 35-20.

Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

Solution
Co has 27 protons, 27 electrons, and 33 neutrons: $1s^22s^22p^63s^23p^64s^23d^7$.
I has 53 protons, 53 electrons, and 78 neutrons: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$.

Question 35-21.

Write a set of quantum numbers for each of the electrons with an n of 3 in a Sc atom.

Solution
$n = 3, l = 0, m_l = 0, m_s = \frac{1}{2}$; $n = 3, l = 0, m_l = 0, m_s = -\frac{1}{2}$; $n = 3, l = 1, m_l = -1, m_s = \frac{1}{2}$; $n = 3, l = 1, m_l = -1, m_s = -\frac{1}{2}$; $n = 3, l = 1, m_l = 0, m_s = \frac{1}{2}$; $n = 3, l = 1, m_l = 0, m_s = -\frac{1}{2}$; $n = 3, l = 1, m_l = 1, m_s = \frac{1}{2}$; $n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}$; $n = 3, l = 2, m_l = -2, -1, 0, 1, \text{or } 2, m_s = \pm\frac{1}{2}$

6.5 Periodic Variations in Element Properties

Question 36-1.

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

Solution
Cl

Question 36-2.

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

Solution
Rb

Question 36-3.

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

Solution

O

Question 36-4.

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

Solution

Cs

Question 36-5.

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

Solution

Rb < Li < N < F

Question36-6.

Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si

Solution

Mg < Si < S < O

Question 36-7.

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

Solution

15 (5A)

Question 36-8.

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

Solution

2 (2A)

Question 36-9.

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

Solution

Mg < Ca < Rb < Cs

Question 36-10.

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

Solution

Cl < Si < Ca <Sr

Question 36-11.

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

Solution

$Si^{4+} < Al^{3+} < Ca^{2+} < K^+$

Question 36-12.

List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.

Solution

$Mg^{2+} < Li^+ < Br^- < Te^{2-}$

Question 36-13.

Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?

Solution

Se, As^-

Question 36-14.

Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

Solution

Cl^{3+}, Si

Question 36-15.

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^-, K^+, Mg^{2+}.

Solution

$Mg^{2+} < K^+ < Br^- < As^{3-}$

Question 36-16.

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? (Hint: Note the process depicted does *not* correspond to electron affinity.)

$$E^+(g) + e^- \longrightarrow E(g)$$

Solution

Cl, this is the reverse of first ionization energy, $-IE_1$. It is not EA_1.

Question 36-17.

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$$E(g) \longrightarrow E^+(g) + e^-$$

Solution

O, IE_1

Question 36-18.

The ionic radii of the ions S^{2-}, Cl^{-}, and K^{+} are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

Solution

The S^{2-} ion has the smallest nuclear charge and attracts the electrons least strongly.

Question 36-19.

Which main group atom would be expected to have the lowest second ionization energy?

Solution

Ra

Question 36-20.

Explain why Al is a member of group 13 rather than group 3?

Solution

Al is a member of group 13 to allow space for the 10 groups that contain *d* orbitals that are being filled after group 2.