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> 2.1 The Nature of Light



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2.1 The Nature of Light



Learning Objectives

By the end of this section, you will be able to:

- Explain the basic behavior of waves.
- Describe the wave nature of light.
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy.
- Describe the particle nature of light.

Visible light and other forms of electromagnetic radiation play important roles in chemistry since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, energy is transferred through matter (the rope, water, or air) while the matter remains essentially

in place.

Electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c). The units of meters per second, m/s, can also be written ms^{-1} .

All waves, including forms of electromagnetic radiation, are characterized by a **wavelength** (denoted by λ , the lowercase Greek letter lambda), a **frequency** (denoted by ν , the lowercase Greek letter nu), and an **amplitude**. The wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range; wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz (Hz)**. Common multiples of this unit are megahertz, (1 MHz = 1×10^6 Hz) and gigahertz (1 GHz = 1×10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement, which is one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness and for sound is the loudness.

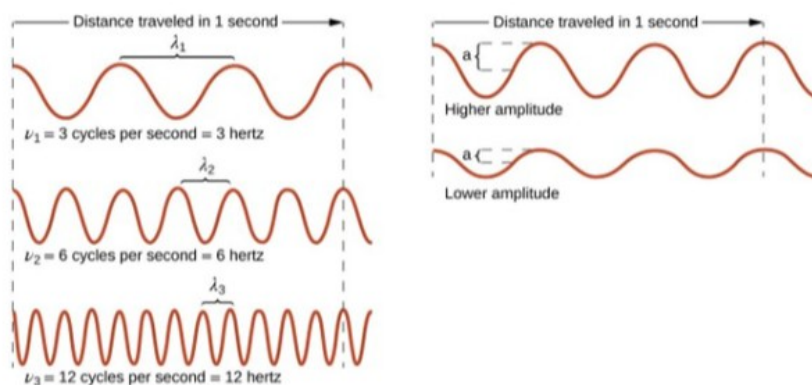


Figure 2.1 One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum, speed is equal to the fundamental constant, c :

$$c = 2.998 \times 10^8 \frac{\text{m}}{\text{s}} = \lambda\nu$$

All electromagnetic radiation, therefore, is assumed to travel at the speed of light, regardless of its energy, amplitude, frequency, or wavelength.

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The **electromagnetic spectrum**, the range of all types of electromagnetic radiation, is represented in **Figure 2.2**. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Since the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

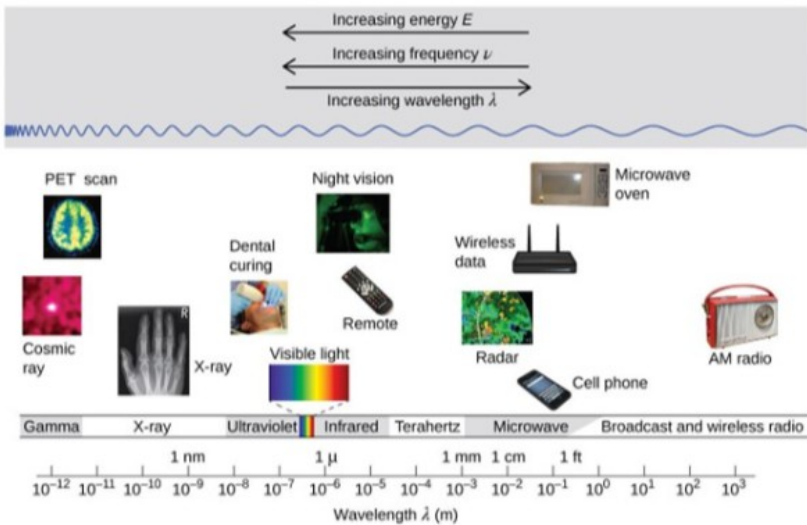


Figure 2.2 Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. (credit “Cosmic ray”: modification of work by NASA; credit “PET scan”: modification of work by the National Institute of Health; credit “X-ray”: modification of work by Dr. Jochen Lengerke; credit “Dental curing”: modification of work by the Department of the Navy; credit “Night vision”: modification of work by the Department of the Army; credit “Remote”: modification of work by Emilian Robert Vicol; credit “Cell phone”: modification of work by Brett Jordan; credit “Microwave oven”: modification of work by Billy Mabray; credit “Ultrasound”: modification of work by Jane Whitney; credit “AM radio”: modification of work by Dave Clausen)

Example: Determining the Frequency and Wavelength of Radiation

A sodium street light gives off yellow light that has a wavelength of 589 nm ($1 \text{ nm} = 1 \times 10^{-9} \text{ m}$). What is the frequency of this light?

Solution

We can rearrange the equation $c = \lambda \nu$ to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998 \times 10^8 \frac{\text{m}}{\text{s}}}{589 \text{ nm}} \right) \left(\frac{1 \times 10^9 \text{ nm}}{1 \text{ m}} \right) = 5.09 \times 10^{14} \frac{1}{\text{s}}$$



Check Your Learning: Determining Frequency

and Wavelength of Radiation

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Complete the following calculation and select the correct answer.

The frequency of an AM radio station is 680. kHz ($1 \text{ kHz} = 1,000 \text{ Hz}$). What is the wavelength of the station?

☐ 441 m

☐ 441,000 m

☐ I don't know!

☐ $2.04 \times 10^{14} \text{ m}$

✓ Check

The Wave-Particle Duality

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. He postulated that light was streams of extremely tiny particles traveling at high speeds according to his laws of motion. Others in the seventeenth century had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves (not particles) traveling at high speed. Early in the nineteenth century, it was shown that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion and electromagnetic radiation consisting of waves governed by Maxwell's equations.

Neither of these two frameworks, the particle nor wave explanation, fully described the nature of light. Maxwell's equations were accepted as correct and light was considered to be made of waves alone, but there were still many paradoxes that this framework could not explain. In the early twentieth century, the particle nature of light could no longer be ignored. Max Planck's work in blackbody radiation and Albert Einstein's work with the photoelectric effect paved the way for a contemporary framework that intimately connected particles and waves at a fundamental level called wave-particle duality.

Blackbody Radiation

A blackbody is an object that absorbs light of any frequency in the electromagnetic spectrum, ideally reflecting no light whatsoever (making it appear "black" under normal conditions). Upon heating, a blackbody will emit radiation across the electromagnetic spectrum. The heating element in an oven, which glows orange

when heated, is an example of a blackbody emitting such radiation. The wavelength and intensity of the light emitted depends on the temperature of the blackbody, and experimental observations could be well-described by mathematical expressions derived from the wave and particle view of light at longer wavelengths. However, at shorter wavelengths, the equations did not hold true, and the reason for this could not be explained. Finally, around 1900, Max Planck derived an equation to describe blackbody radiation that fit the experimental observations exactly (within experimental error). Planck treated the atoms of the blackbody as particles (not just waves) and assumed they were vibrating at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. However, instead of allowing the vibrating atoms to have any energy value obtained from a continuous set of energies (perfectly reasonable, according to classical physics), he restricted the vibrational energies to discrete values for each frequency. The equation that relates the energy of light (E) to the frequency (ν) is shown below:

$$E = nh\nu, n = 1, 2, 3, \dots$$

The quantity h is a constant now known as Planck's constant, in his honor. In multiplying the frequency by this constant (h) and by any integer value (n), the energies that could be calculated must be a multiple of this constant. This revelation forced Planck to assume that the vibrating atoms of a blackbody, and consequently all matter, required quantized energies (energies of specific magnitude, not just any energy), which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (Js), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

The Photoelectric Effect

It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. This led Albert Einstein, in 1905, to show that the light striking the metal surface should not be viewed as a wave but instead as a stream of particles (later called **photons**) whose energy depended on their frequency. He also noted that the energy sufficient to eject an electron from the metal surface was quantized, meaning that it had to be a discrete and specific

amount, not just any energy would suffice. Building on the work of Planck, who first recognized the quantized nature of light, he deduced that the energy of each photon of a given frequency was a finite and constant amount. The equation he used related the energy (E) of a photon of light to the frequency (ν) multiplied by a Planck's constant (h).

$$E = h\nu$$

Energy (E) can also be related to wavelength by using the relationship of $c = \nu\lambda$ and substituting $\frac{c}{\lambda}$ for ν .

$$E = \frac{hc}{\lambda}$$

This equation is very similar to Planck's, without being multiplied by an integer value. This is because this equation calculates the energy of a single photon of light at a given frequency or wavelength ($n=1$) instead of the sum of the energies of many photons ($n>1$).

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality**. It is only in considering light as both a particle and a wave that it can be fully understood.

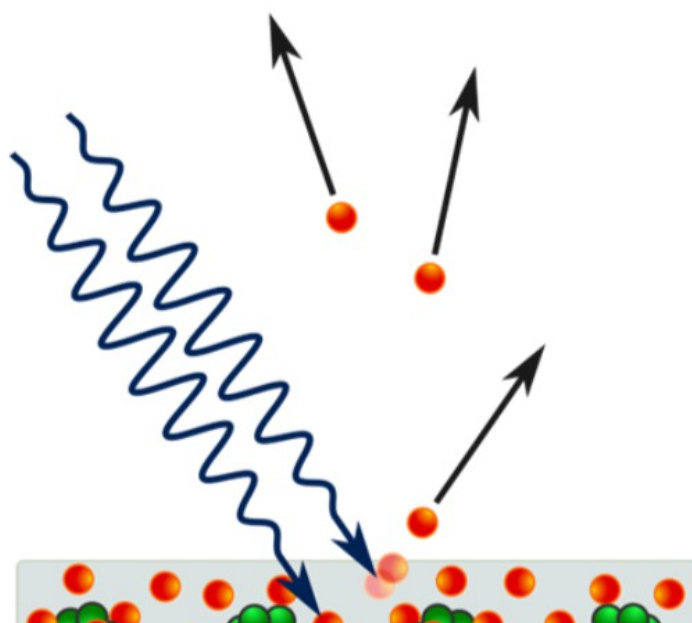




Figure 2.3 In the photoelectric effect, electrons are ejected from the surface of a metal when light of a certain frequency is shone on it.

Example: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ , and convert units of nanometers to meters so that the units of λ and c are the same.

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \frac{\text{m}}{\text{s}})}{(640 \text{ nm})(\frac{1 \text{ m}}{1 \times 10^9 \text{ nm}})}$$

$$E = 3.10 \times 10^{-19} \text{ J}$$



Check Your Learning: Calculating the Energy of

Radiation

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Complete the following calculation and select the correct answer.

What is the energy of a photon being emitted by UV radiation with a wavelength of 130 nm?

☐ I don't know!

☐ $5.09 \times 10^{-27} \text{ J}$

☐ $1.53 \times 10^{-27} \text{ J}$

☐ $1.53 \times 10^{-18} \text{ J}$

☒ Check

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2.2 The Bohr Model



Learning Objectives

By the end of this section, you will be able to:

- Describe the Bohr model of the hydrogen atom.
- Calculate the energies of light emitted or absorbed by hydrogen atoms.
- Calculate the energies of electron transitions.

The Bohr Model

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model since it pictured the atom as a miniature “solar system” with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. This description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to the laws of physics, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron’s orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by incorporating into the classical physical description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation, but it would emit or absorb a photon (a single particle of light) if it moved to a different orbit. The energy absorbed or emitted by the electron would reflect differences in the orbital energies according to this equation:

$$\Delta E = |E_f - E_i| = h\nu = \frac{hc}{\lambda}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used since frequencies and wavelengths are always positive. Instead of allowing for continuous values of energy, Bohr assumed the energies of these electron orbitals were also quantized:

$$E_n = -\frac{k}{n^2}, \quad n = 1, 2, 3, \dots$$

In this expression, k is a constant that relates the discrete energies to the electron orbitals (E_n) and is equal to 2.179×10^{-18} J. His equation and constant fit experimental data so well that **Bohr's model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, in Bohr's model, the electron in a hydrogen atom would move in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is at the lowest energy possible, the atom is said to be in its **ground electronic state** (or simply ground state). If the atom receives energy from an outside source, Bohr postulated that it was possible for the electron to move to an orbit with a higher n value. This atom is now said to be in an **excited electronic state** (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of

conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state.

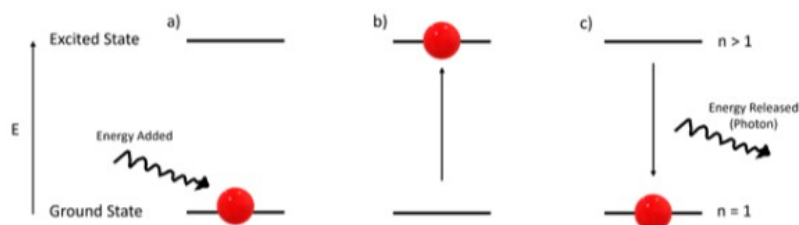


Figure 2.4 Energy is added to an electron in its ground state. b) The energy that was added to the electron allows it to move to its excited state. c) When the electron moves from the excited state to the ground state, energy is released as a photon.

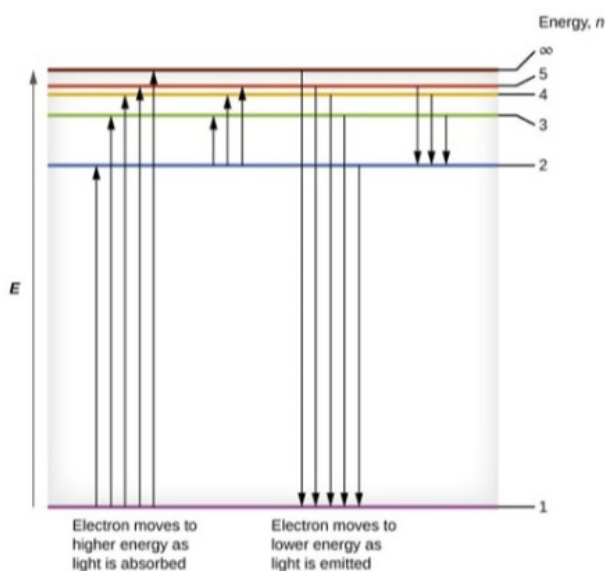


Figure 2.5 The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Bohr also recognized that as an electron's energy increases (as n increases), the electron is found at greater distances from the nucleus. As the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases and it is held less tightly in the atom. Note that as n gets larger and the orbits get larger, their energies get closer to zero. When n approaches ∞ , E approaches zero and the electron is completely removed from the nucleus.

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the behavior of an electron in the hydrogen atom, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. ***Bohr's model was severely flawed since it was still based on the classical mechanics notion of precise orbits.*** He based his model on the idea that electrons orbited the nucleus at a defined distance from the nucleus, which was directly proportional to the energy of the electron. The orbits he proposed corresponded to the quantum number n , with $n=1$ being the closest possible orbit. Much like the planets of our solar system traveling in their orbits around the sun, he postulated that electrons would stay in their orbit around the nucleus unless acted upon. These orbits were seen as discrete because of the quantized energy to which they corresponded, meaning that an electron could only orbit on a set path and nowhere in between. Bohr proposed that an electron could jump from a lower energy orbit to higher energy orbit when energy was added to the atom, or a higher energy orbit to a lower energy orbit when energy was released from the atom, but this transition would transport the electron to one of the next allowed energy levels only. This was a concept that was later found to be untenable in the microscopic domain when a proper model of quantum mechanics was developed to supersede classical mechanics.

Example: Calculating the Energy of an Electron in a Bohr Atom

Early researchers were very excited when they were able to predict the energy of an electron in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with $n = 3$, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by this equation:

$$E_n = -\frac{k}{n^2}$$

$k = 2.179 \times 10^{-18} \text{ J}$; and the electron is characterized by an n value of 3. Thus,

$$E_n = -\frac{2.179 \times 10^{-18} \text{ J}}{3^2}$$

$$E = -2.421 \times 10^{-19} \text{ J}$$



Check Your Learning: Calculating the Energy of an Electron in a Bohr Atom

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Complete the following calculation and select the correct answer.

A source of energy promotes an electron in a hydrogen atom into an orbit with $n = 5$. What is the calculated energy of the electron?

☐ $-4.36 \times 10^{-19} \text{ J}$

☐ $-8.72 \times 10^{-20} \text{ J}$

☐ $-5.83 \times 10^{-16} \text{ J}$

☐ I don't know!

Example: Calculating the Energy and Wavelength of Electron Transitions

What is the energy (in joules) and the wavelength (in meters) of the light emitted by hydrogen by an electron transitioning from the orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\Delta E = |E_f - E_i|$$

Additionally, the energy of each electron can be found using the equation:

$$E_n = -\frac{k}{n^2}$$

Where k is $2.179 \times 10^{-18} \text{ J}$

$$E_f = E_6 = -\frac{2.179 \times 10^{-18} \text{ J}}{6^2} = -6.053 \times 10^{-20} \text{ J}$$

and

$$E_i = E_4 = -\frac{2.179 \times 10^{-18} \text{ J}}{4^2} = -1.362 \times 10^{-19} \text{ J}$$

$$\Delta E = |E_f - E_i| = |-6.053 \times 10^{-20} \text{ J} - (-1.362 \times 10^{-19} \text{ J})|$$

$$\Delta E = 7.567 \times 10^{-20} \text{ J}$$

This energy difference results from a photon entering the system (being absorbed) to excite the electron from the $n = 4$ orbit up to the $n = 6$ orbit. The wavelength of a photon with this energy is found by the expression $E = \frac{hc}{\lambda}$. Rearrangement gives the following:

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (2.998 \times 10^8 \frac{\text{m}}{\text{s}})}{7.567 \times 10^{-20} \text{ J}}$$

$$\lambda = 2.625 \times 10^{-6} \text{ m}$$

From the illustration of the electromagnetic spectrum in Electromagnetic Energy, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.



Check Your Learning: Calculating the Energy and

Wavelength of Electron Transitions

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Complete the following calculations and select the correct answer.

An electron in a hydrogen atom transitions from an orbit with $n = 4$ to $n = 8$. What is the calculated energy absorbed by the electron?

☐ I don't know!

☐ $1.02 \times 10^{-19} \text{ J}$

☐ $5.43 \times 10^{-18} \text{ J}$

☐ $3.89 \times 10^{-20} \text{ J}$

☒ Check



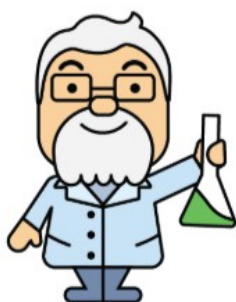
Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron-electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.

- The discrete energies of light emitted by elements in an excited state result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms.

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2.3 Development of Quantum Theory



Learning Objectives

By the end of this section, you will be able to:

- Understand the general idea of the quantum mechanical description of electrons in an atom and orbitals.
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom.

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number $n = 1, 2, 3$, and so on but never in between? Why did the model work so well describing hydrogen but could not correctly predict the energies for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

Erwin Schrödinger took the wave-particle duality and the work of his contemporaries in the field of physics to derive what is today known as the Schrödinger equation. When Schrödinger applied his equation to atoms, he was able to reproduce Bohr's expression for the energy not only for hydrogen but for all atoms. Additionally, the Schrödinger equation can be used to give a three-dimensional map of where an electron is most probably located in the atom. The resulting map is called an atomic orbital (note that this is different from an "orbit"). This allows us to determine the

distribution of the electron's density with respect to the nucleus in an atom. This work is the foundation of the field of **quantum mechanics**.

Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding of these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where $n = 1, 2, 3, \dots$. Generally speaking, the energy of an electron in an atom is greater for greater values of n . This number, n , is referred to as the principal quantum number. The **principal quantum number** defines the location of the energy level. It is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The **shells** of an atom can be thought of as concentric spheres radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding spherical area. (Note, within the spherical area is not the same as being on the boundary of the sphere). The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level. The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. Therefore, the further away the electron is from the nucleus, the greater the energy it has.

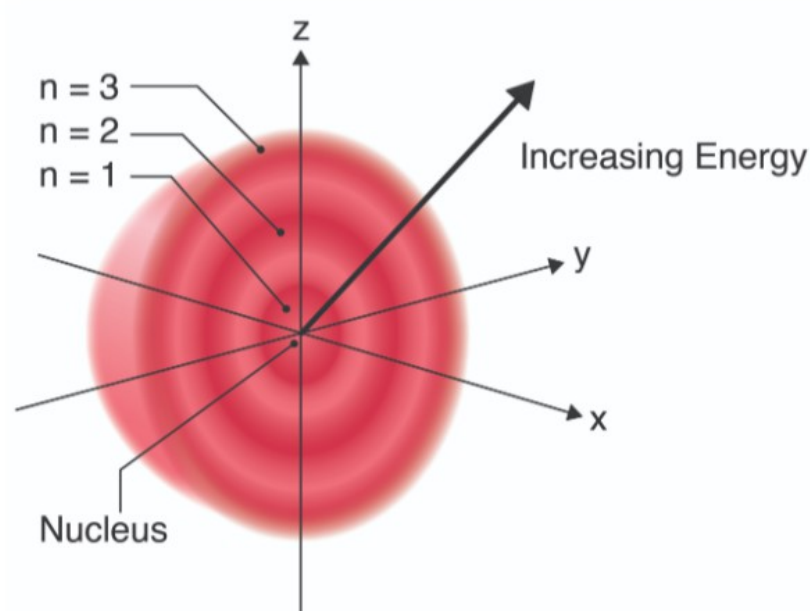


Figure 2.6 Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events that occur when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\Delta E = | E_f - E_i |$$

Recall the following from section 2.1:

$$E_n = -\frac{k}{n^2}$$

$$k = 2.179 \times 10^{-18} \text{ J}$$

Substituting these in for the original equation, we obtain the following:

$$\Delta E = E_f - E_i = \left(-\frac{k}{n_f^2}\right) - \left(-\frac{k}{n_i^2}\right) = -k \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -2.179 \times 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

The values n_f and n_i are the final and initial energy states of the electron, respectively. The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital** is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation.

Another quantum number is l , the **secondary (angular momentum) quantum number**. It is an integer that may take the values, $l = 0, 1, 2, \dots, n - 1$. The highest possible value of l is one less than the principal quantum number. This means that an orbital with $n = 1$ can have only one value of l , $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. Whereas the principal quantum number, n , defines the general size and energy of the orbital, the secondary quantum number l specifies the shape of the orbital. Orbitals with the same value of l define a **subshell**.

Orbitals with $l = 0$ are called **s orbitals**, and they make up the s subshells. The value $l = 1$ corresponds to the **p orbitals**. For a given n , **p orbitals** constitute a **p subshell** (e.g., $3p$ if $n = 3$). The orbitals with $l = 2$ are called the **d orbitals**, followed by the **f**-, **g**-, and **h**-orbitals for $l = 3, 4$, and 5 .

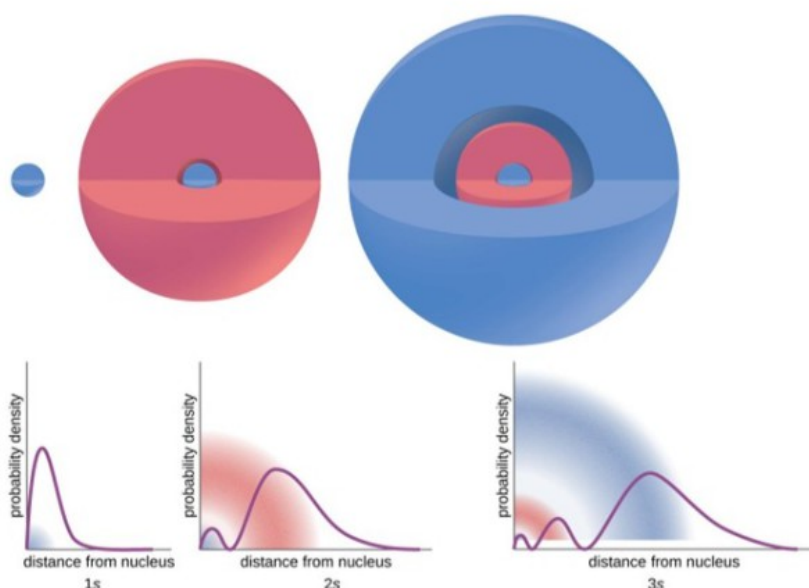


Figure 2.7 The graphs show the probability (y axis) of finding an electron for the 1s, 2s, and 3s orbitals as a function of distance from the nucleus.

The s subshell electron density distribution is spherical, and the p subshell has a dumbbell shape. The d and f orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

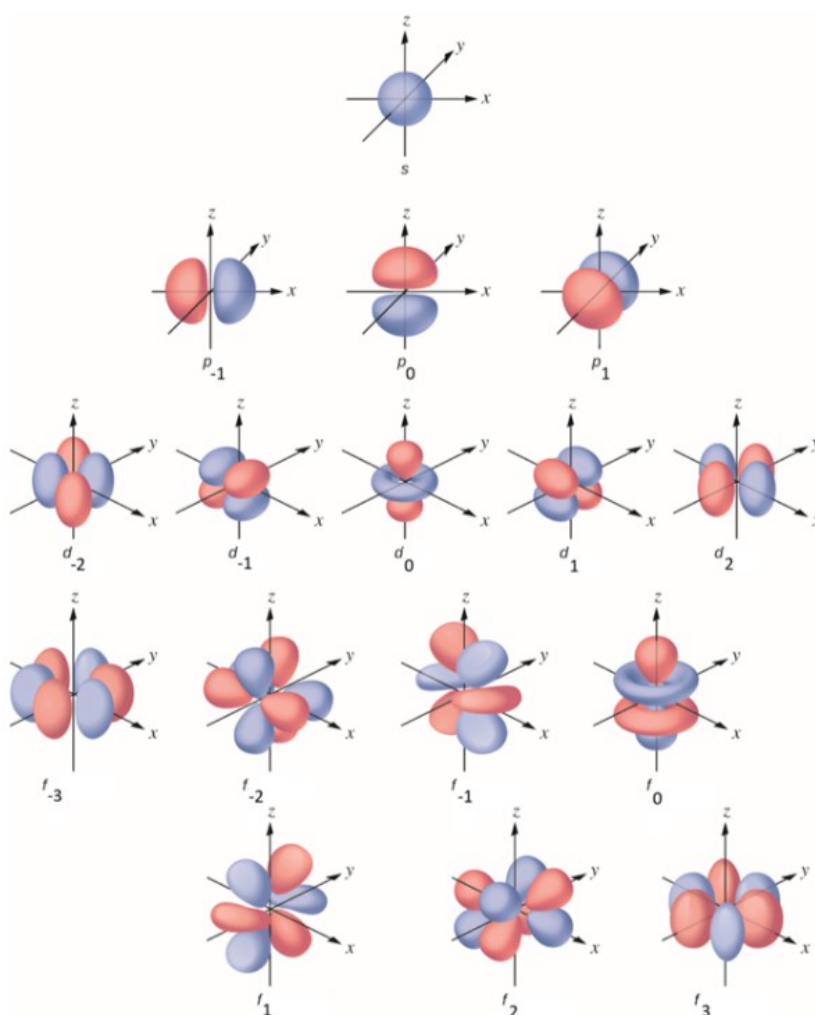


Figure 2.8 Shapes of s , p , d , and f orbitals.

The **magnetic quantum number**, m_l , specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l can equal all integers from $-l$ to $+l$. The total number of possible orbitals with the same value of l (that is, in the same subshell) is $2l + 1$. Thus, there is one s -orbital in an s subshell ($l = 0$), there are three p -orbitals in a p subshell ($l = 1$), five d -orbitals in a d subshell ($l = 2$), seven f -orbitals in an f subshell ($l = 3$), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. In addition, the magnetic quantum number specifies orientation of the orbital in space.

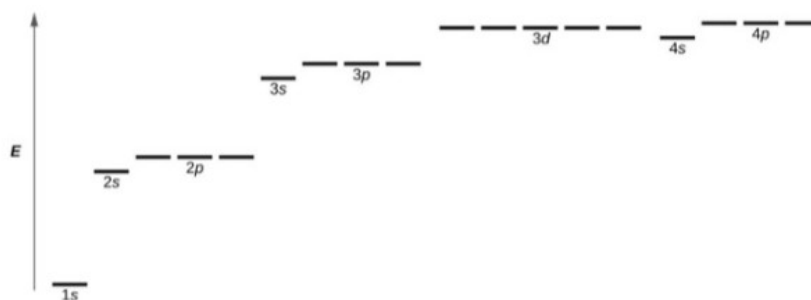


Figure 2.9 The chart shows the energies of electron orbitals commonly found in most atoms.

Figure 2.9 above illustrates the energy levels for various orbitals. The number before the orbital name (such as 2s, 3p, and so forth) stands for the principal quantum number, n . The letter in the orbital name defines the subshell with a specific angular momentum quantum number $l = 0$ for s orbitals, 1 for p orbitals, and 2 for d orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l . Orbitals within the same subshell have the same energy and are said to be “degenerate”. For example, in the 2p subshell there are 3 degenerate orbitals. Another way to say this is that the degeneracy, or number of orbitals of the same energy, of the p subshell is 3.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led scientists to propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or m_s .

The other three quantum numbers, n , l , and m_l , are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian x, y, and z). Electron spin describes an intrinsic electron “rotation” or “spinning”. Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only “spin” in one of two quantized states. One is termed the α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number $m_s = +\frac{1}{2}$. The other is called the β state, with the z component of the spin being negative and $m_s = -\frac{1}{2}$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$ are different if an external magnetic field is applied.

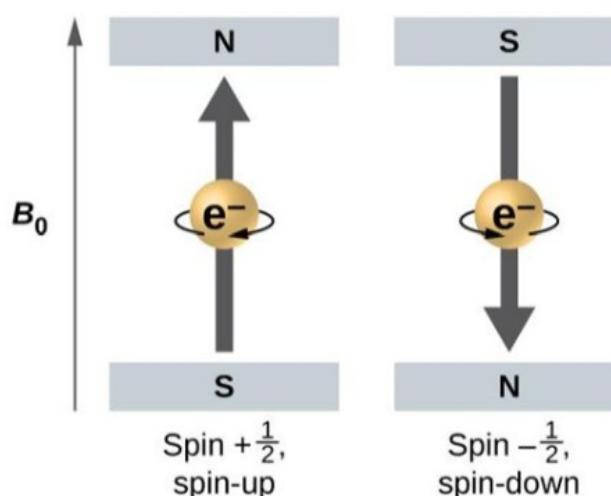


Figure 2.10 Electrons with spin values $\pm \frac{1}{2}$ in an external magnetic field.

Figure 2.10 above illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the z axis) for the $+\frac{1}{2}$ spin quantum number and down (in the negative z direction) for the spin quantum number of $-\frac{1}{2}$.

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n , l , m_l , and m_s . The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The Pauli exclusion principle can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that two electrons can share the same orbital (the same set of the quantum numbers n , l , and m_l) only if their spin

quantum numbers m_s have different values. Since the spin quantum number can only have two values ($\pm \frac{1}{2}$), no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons.

The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in the table below.

Quantum Numbers, Their Properties, and Significance			
Name	Symbol	Allowed Values	Physical Meaning
principal quantum number	n	1, 2, 3, 4,	shell, the general region for the value of energy for an electron on the orbital
angular momentum	l	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	orientation of the orbital
spin quantum number	m_s	$+\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum "spinning" of the electron

Table 2.1



Check Your Learning: Quantum Numbers

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Answer the questions by selecting the correct images.

What are the symbol, allowed values, and physical meaning of the principal quantum number?

n	l
m_l	1, 2, 3, 4...
$+\frac{1}{2}, -\frac{1}{2}$	m_s
$-l \leq m_l \leq l$	$0 \leq l \leq n - 1$
	orientation of the orbital

Example: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, s , p , d , and f subshells are found in the $n = 4$ shell of an atom. For $l = 0$ (the s subshell), m_l can only be 0. Thus, there is only one $4s$ orbital. For $l = 1$ (p -type orbitals), m can have values of -1 , 0 , $+1$, so we find three $4p$ orbitals. For $l = 2$ (d -type orbitals), m_l can have values of -2 , -1 , 0 , $+1$, $+2$, so we have five $4d$ orbitals. When $l = 3$ (f -type orbitals), m_l can have values of -3 , -2 , -1 , 0 , $+1$, $+2$,

+3, and we can have seven 4f orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.



Check Your Learning: Working with Shells and Subshells

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Identify the subshell in which electrons with the listed quantum numbers are found. Turn the card over and compare your answer to the correct answer.

Front: $n = 3, l = 1$

Turn

Card 1 of 3



Example: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) $n = 2$, (b) $n = 5$, and (c) n as a variable. Note that you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.

(b) When $n = 5$, there are five subshells of orbitals that we need to sum:

1 orbital labeled 5s

3 orbitals labeled 5p

5 orbitals labeled 5d

7 orbitals labeled 5f

+ 9 orbitals labeled 5g

25 orbitals total

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell n will equal n^2 . There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$.

Example: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	n	l	m_l degeneracy
4f			
	4	1	
	7		7
5d			

Solution

The table can be completed using the following rules:

- The orbital designation is nl , where $l = 0, 1, 2, 3, 4, 5, \dots$ is mapped to the letter sequence s, p, d, f, g, h, \dots
- The m_l degeneracy is the number of orbitals within an l subshell and so is $2l + 1$ (there is one s orbital, three p orbitals, five d orbitals, seven f orbitals, and so forth).

Orbital	n	l	m_l degeneracy
4f	4	3	7
4p	4	1	3
7f	7	3	7
5d	5	2	5



Check Your Learning: Maximum Number of Electrons & Quantum Numbers

Instructions:

Determine the maximum number of electrons for the indicated shells. Turn the card over and compare your answer to the correct answer.

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

$n = 5$

 Turn

Card 1 of 4



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> 2.4 Electron Configurations of Atoms and Ions



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2.4 Electron Configurations of Atoms and Ions



Learning Objectives

By the end of this section, you will be able to:

- Derive the predicted ground-state electron configurations of atoms.
- Relate electron configurations to element classifications in the periodic table.

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n , increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. **Figure 2.11** below depicts how these two trends in increasing energy relate. The 1s orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2s and

then $2p$, $3s$, and $3p$ orbitals, showing that the increasing n value has more influence on energy than the increasing l value for small atoms. However, this pattern does not hold for larger atoms. The $3d$ orbital is higher in energy than the $4s$ orbital. Such overlaps continue to occur frequently as we move up the chart.

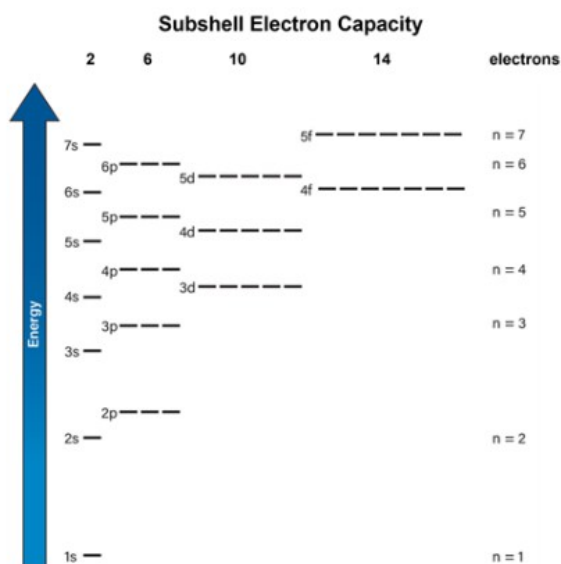


Figure 2.11 Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the $5p$ orbitals fill immediately after the $4d$, and immediately before the $6s$. The filling order is based on observed experimental results and has been confirmed by theoretical calculations. As the principal quantum number, n , increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). However, this is not the only effect we have to take into account. Within each shell, as the value of l increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron-nucleus attractions slightly (recall that all electrons have -1 charges, but nuclei have $+Z$ charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and, thus, higher in energy. For small orbitals ($1s$ through $3p$), the increase in energy due to n is more significant than the increase due to l ; however, for larger orbitals, the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information:

1. The number of the principal quantum shell, n ,
2. The letter that designates the orbital type (the subshell, l), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two-p-four") indicates four electrons in a p subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three-d-eight") indicates eight electrons in the d subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

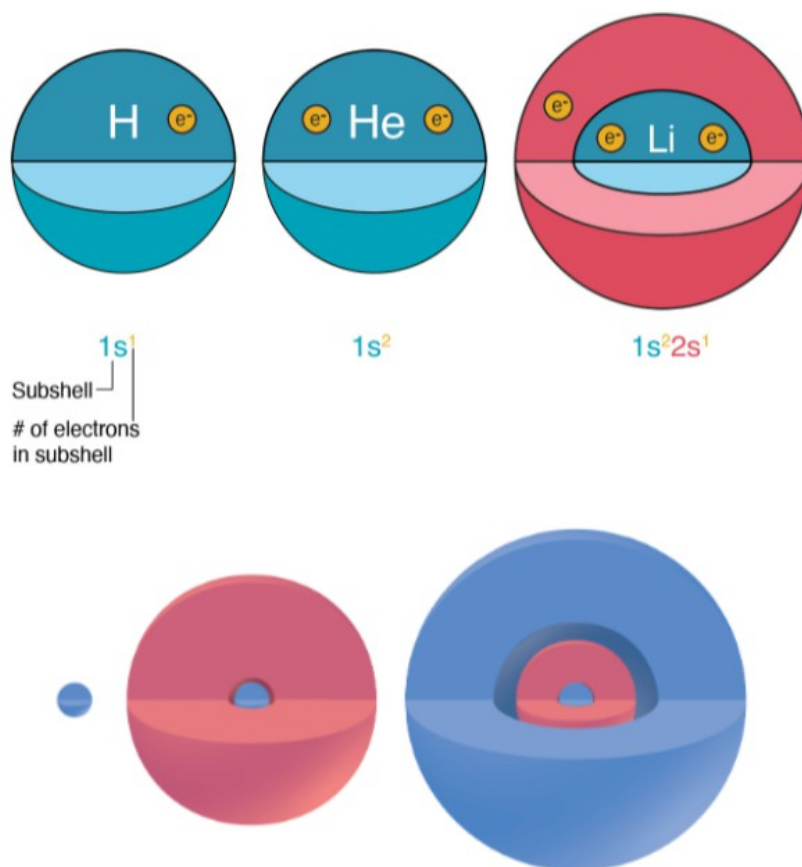


Figure 2.12 The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can "build" the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* ("to build

up”). Each added electron occupies the subshell of lowest energy available, subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. **Figure 2.13** below illustrates the traditional way to remember the filling order for atomic orbitals.

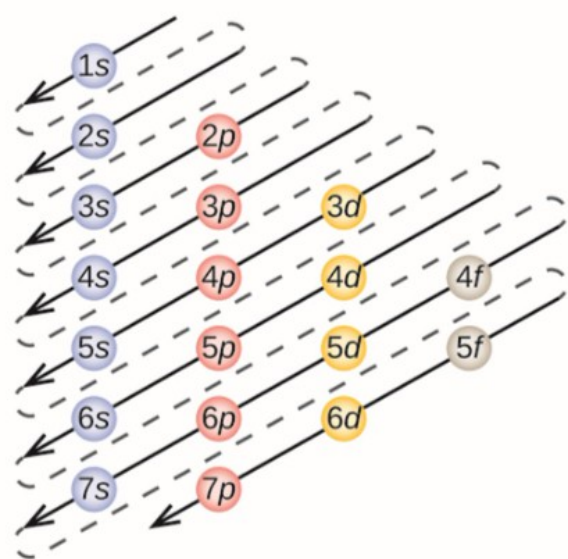
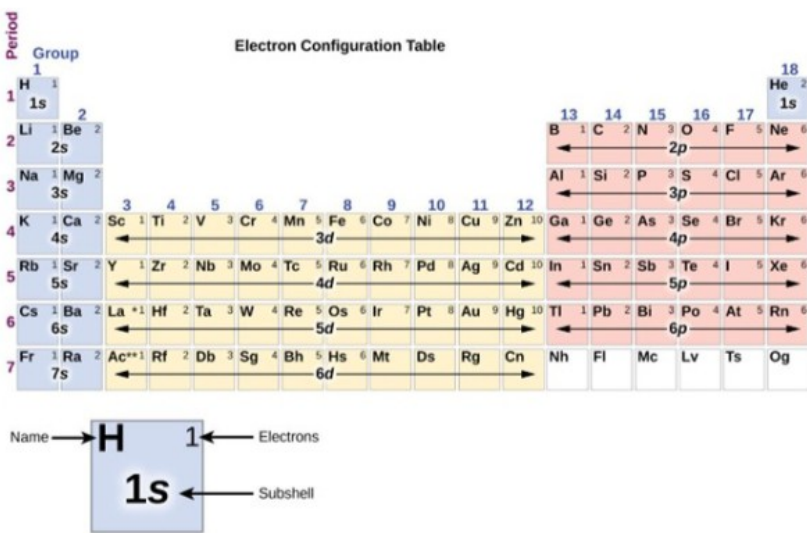


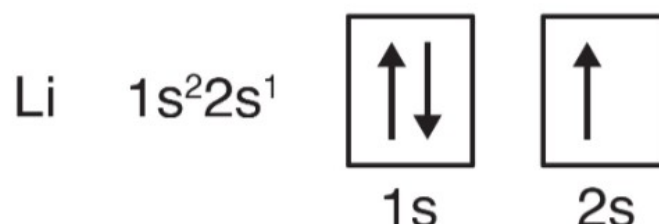
Figure 2.13 This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

Since the arrangement of the periodic table is based on the electron configurations, **Figure 2.14** below provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4*s* (K, Ca), followed by the 3*d* orbitals.



The $n = 1$ shell is completely filled in a helium atom.

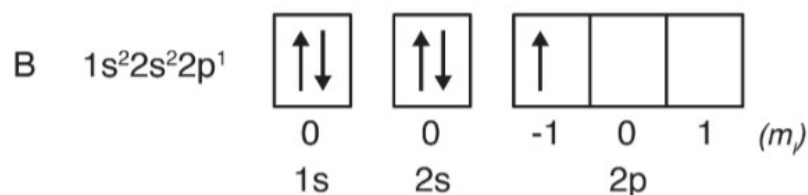
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital. Thus, the electron configuration and orbital diagram of lithium are as follows:



An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.

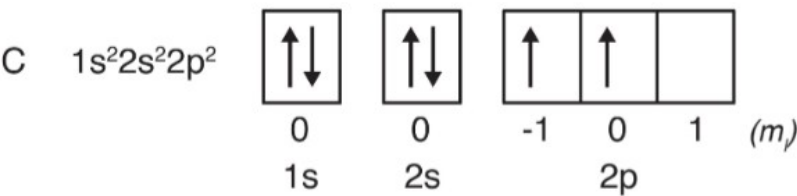


An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Since any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2p orbital. There are three degenerate 2p orbitals ($m_l = -1, 0, +1$) and the electron can occupy any one of these p orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling. By convention, we number the degenerate orbitals from left to right, -1 to 1, corresponding to the m_l values.



Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2p subshell. We now have a choice of filling one of the 2p orbitals and pairing the electrons or leaving the electrons unpaired in two

different, but degenerate, p orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon $2p$ orbitals have identical n , l , and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are as follows:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^22s^22p^63s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons**. Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^22s^22p^6$) and our abbreviated or condensed configuration is $[\text{Ne}]3s^1$.



Figure 2.15 A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[\text{He}]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence s subshell outside a filled set of inner shells.



The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a $[\text{Ne}]3s^2$ configuration, is analogous to its family member beryllium, $[\text{He}]2s^2$. Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration $[\text{Ne}]3s^23p^1$ is analogous to its family member boron, $[\text{He}]2s^22p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the $3d$ subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium and that the next electron is not added to the $3d$ level but is, instead, added to the $4s$ level. As discussed previously, the $3d$ orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the $4s$, which has three radial nodes. Thus, potassium has an electron configuration of $[\text{Ar}]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the $4s$ subshell and calcium has an electron configuration of $[\text{Ar}]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

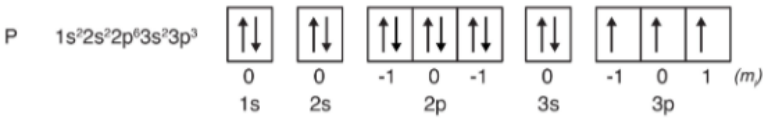
Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the $3d$ subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [d orbitals], there are $2l + 1 = 5$ values of m_l , meaning that there are five d orbitals that have a combined capacity of 10 electrons). The $4p$ subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 d electrons are successively added to the $(n - 1)$ shell next to the n shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 f electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

Example: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is $1s, 2s, 2p, 3s, 3p, 4s, \dots$. The 15 electrons of the phosphorus atom will fill up to the $3p$ orbital, which will contain three electrons:



The last electron added is a 3*p* electron. Therefore, *n* = 3 and, for a *p*-type orbital, *l* = 1. The value that corresponds to the third degenerate orbital is *m_l* = +1. For unpaired electrons, convention assigns the value of $\frac{1}{2}$ for the spin quantum number; thus, *m_s* = + $\frac{1}{2}$.



Check Your Learning: Quantum Numbers

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Use a piece of scratch paper to determine the answer to the following questions and then choose the the correct answer.

What is the full electron configuration for a Ni atom?

- ☐ 1s² 2s² 2p⁶ 3s² 3p⁶ 4s²
- ☐ 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁸ 4s²
- ☐ 1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d⁵
- ☐ 1s² 2s² 2p⁶ 3s² 3p⁶ 4s² 3d⁸
- ☐ 1s² 2s² 2p⁶ 3s² 3p⁶

✓ Check



Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When the electron configurations of elements grouped together in the periodic table are observed, we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Since they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in the “Electron Configuration Table” figure above, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration $[\text{Ar}]4s^23d^{10}4p^1$, which contains three valence electrons ($4s^2$ and $4p^1$). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals.** These are metallic elements in which the last electron added enters a *d* orbital.

The valence electrons (those added after the last noble gas configuration) in these elements include the ns and $(n - 1)d$ electrons.

3. **Inner transition elements** are metallic elements in which the last electron added occupies an f orbital. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the ns subshells. There are two inner transition series:
1. The lanthanide series: lanthanum (La) through lutetium (Lu)
 2. The actinide series: actinium (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no f electrons.

Electron Configurations of Ions

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the s orbital are easier to remove than the d or f electrons, and so the highest ns electrons are lost, and then the $(n - 1)d$ or $(n - 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example: Predicting Electron Configurations of Ions

What is the electron configuration of:

- (a) Na^+
- (b) P^{3-}
- (c) Al^{2+}
- (d) Fe^{2+}
- (e) Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost.

Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

(a) Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so $1s^2 2s^2 2p^6 3s^1 - 3s^1 =$

Na^+ : $1s^2 2s^2 2p^6$.

(b) P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus anion gains three electrons, so $1s^2 2s^2 2p^6 3s^2 3p^3 + 3p^3 =$

P^{3-} : $1s^2 2s^2 2p^6 3s^2 3p^6$.

(c) Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum cation loses two electrons, so $1s^2 2s^2 2p^6 3s^2 3p^1 - 3p^1$ and $3s^1 =$

Al^{2+} : $1s^2 2s^2 2p^6 3s^1$.

(d) Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4s orbital, so $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 - 4s^2 =$

Fe^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.

(e). Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$.

Samarium cation loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the 4f orbital, so $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 - 6s^2$ and $4f^1 =$

Sm^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.



Check Your Learning: Predicting Electronic

Configurations of Ions

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Instructions:

Using a piece of scratch paper, determine the answer to the following question and then choose the the correct answer.

What is the electron configuration of a Hg^{2+} ion?

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

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

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



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2.5 Periodic Variations in Element Properties



Learning Objectives

By the end of this section, you will be able to:

- Explain and apply the observed trends in atomic size, ionization energy, and electron affinity of the elements.

Periodic Variations in Element Properties

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-gray solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine

some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structures of the elements change. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius**, which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in the table below and for the entire periodic table in **Figure 2.16** below.

Table 2.2: Covalent Radii of the Halogen Group Elements

Atom	Covalent Radius (pm)	Nuclear Charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

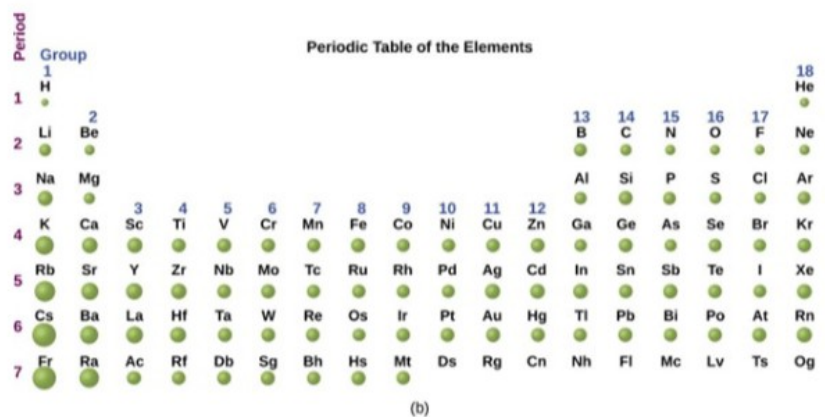
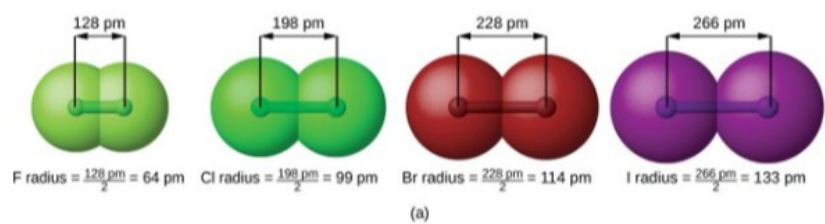


Figure 2.16 (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

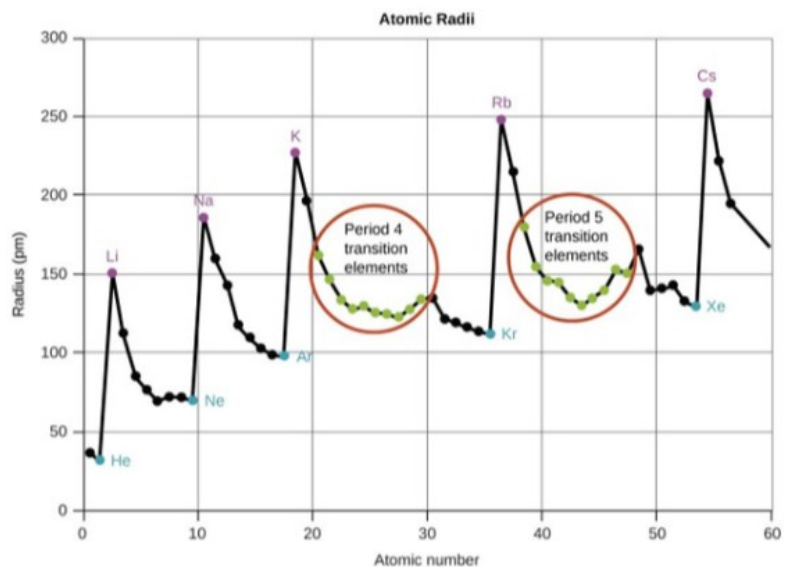


Figure 2.17 Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

As shown in **Figure 2.17** above, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge, Z_{eff}** . This is the pull exerted on a specific electron by the nucleus, taking into account any

electron-electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{eff} = Z - \text{shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron-electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the ns or np electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the ns electrons before they begin to lose the $(n - 1)d$ electrons, even though the ns electrons are added first, according to the Aufbau principle.

Example - Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, and Kr.

Solution

Radius increases as we move down a group, so $\text{Ge} < \text{Fl}$ (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so $\text{Kr} < \text{Br} < \text{Ge}$. Putting the trends together, we obtain $\text{Kr} < \text{Br} < \text{Ge} < \text{Fl}$.

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived. For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} and are drawn even closer to the nucleus.



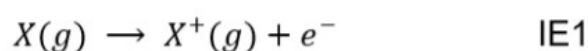
Figure 2.18 The radius of a cation is smaller than the parent atom (Al) due to the lost electrons; the radius of an anion is larger than the parent (S) due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n .

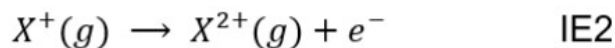
An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom, as seen in **Figure 2.18**. For example, a sulfur atom ($[\text{Ne}]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[\text{Ne}]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE1). The first ionization energy for an element, X , is the energy required to form a cation with +1 charge:



The energy required to remove the second most loosely bound electron is called the second ionization energy (IE2).



The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure 2.19 below graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in **Figure 2.20**. Within a period, the IE1 generally increases with increasing *Z*. Down a group, the IE1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. For example, within any one shell, the *s* electrons are lower in energy than the *p* electrons, therefore, an *s* electron is harder to remove from an atom than a *p* electron in the same shell and we see a small deviation from the predicted trend occurring each time a new subshell begins.

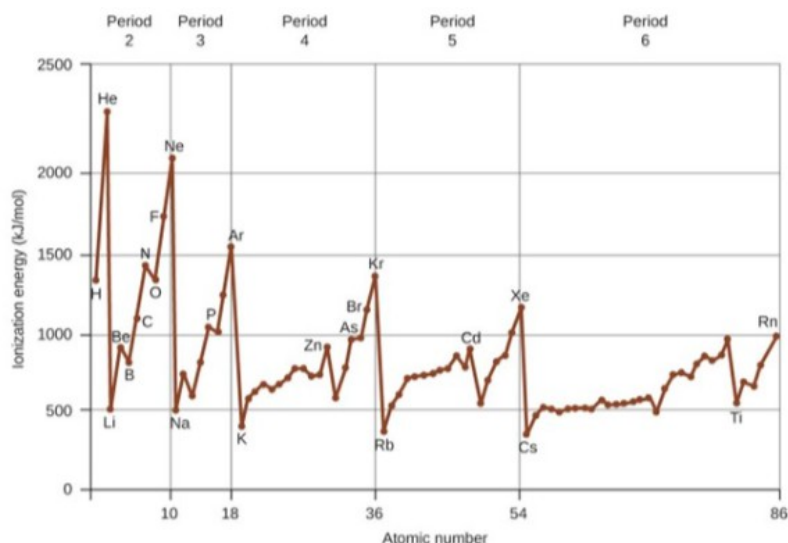


Figure 2.19 The first ionization energy of the elements in the first five periods are plotted against their atomic number.

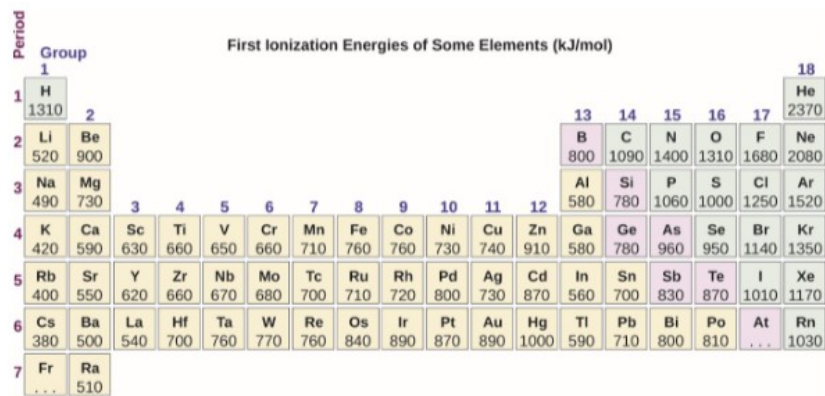
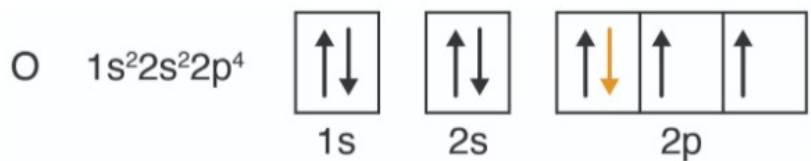


Figure 2.20 This version of the periodic table shows the first ionization energy (IE1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron-electron repulsion caused by pairing the electrons in the 2p orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 2.20).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 2.3 below, there is a large increase in the ionization energies for each element (see the transition between the blue and orange highlighted sections). This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Successive Ionization Energies for Selected Elements (kJ/mol)							
Element	IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	IE ₆	IE ₇
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Table 2.3

Example: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE₁ for Al, IE₁ for Tl, IE₂ for Na, and IE₃ for Al.

Solution

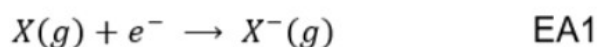
Removing the 6p¹ electron from Tl is easier than removing the 3p¹ electron from Al because the higher *n* orbital is farther from the nucleus, so IE₁(Tl) < IE₁(Al). Ionizing the third electron from Al

Al²⁺(g) → Al³⁺(g) + e[−] requires more energy because the cation Al²⁺ exerts a stronger pull on the electron than the neutral Al atom, so IE₁(Al) < IE₃(Al). The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain the following:

IE₁(Tl) < IE₁(Al) < IE₃(Al) < IE₂(Na).

Variation in Electron Affinities

The **electron affinity** (EA) is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).



This process can absorb or give off/release energy depending on the element. The EA of some of the elements is given in **Figure 2.21** below. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron (improving the stability of the atom). However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a -2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher n level, which is more difficult to do. Group 2 (2A) has a filled ns subshell, and so the next electron added goes into the higher energy np , so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled np subshell and the next electron must be paired with an existing np electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the most negative EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the *second* element in the group most often has the most negative EA. This can be attributed to the small size of the $n = 2$ shell and the resulting large electron-electron repulsions. For example, chlorine, with an EA value of -348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is -322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^{-}), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a

considerably larger region of space and the electron-electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily, resulting in a more negative EA.

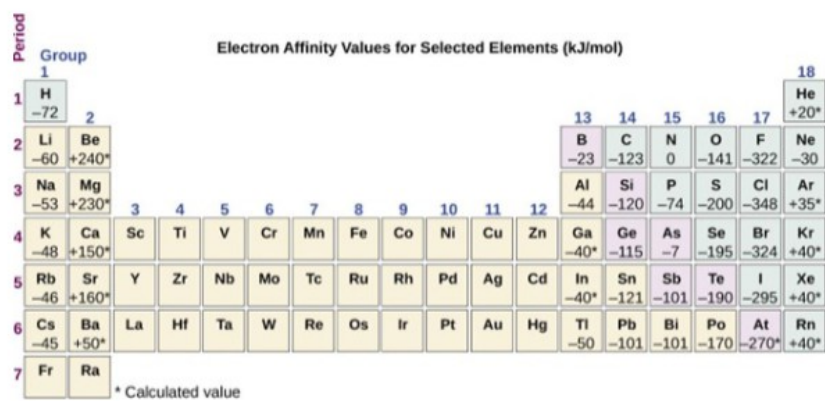


Figure 2.21 This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

Example: Sorting by Electron Affinity

Predict which atoms have the higher electron affinity based on the general trend:

- a.) Cs vs. Bi
- b.) Cs vs. Li

Solution

The general trend is that electron affinity increases from left to right across a period and increases from the bottom to the top of a group. Thus, (a) Bi would have a higher electron affinity compared to Cs, and, (b) Li would have a high electron affinity compared to Cs.



Check Your Learning: Flashcard Review

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Answer the following question for each pair of atoms. Check your answer when you are finished.

Sorting Effective Nuclear Charge

Which atom has a smaller Z_{eff} ?

1. Ba or Bi

Turn

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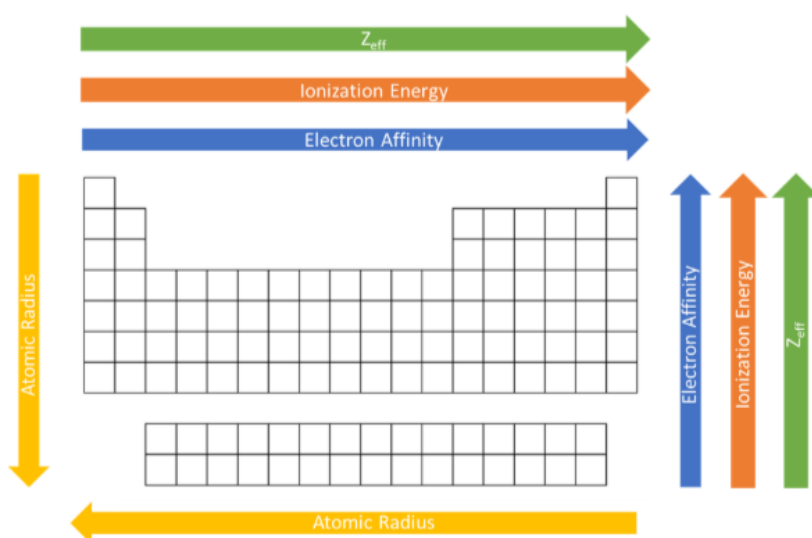


Figure 2.22 General periodic trends for atomic radius, Z_{eff} , ionization energy, and electron affinity.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) and summarized above are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend

observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.



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2.6 The Periodic Table



Learning Objectives

By the end of this section, you will be able to:

- State the periodic law and explain the organization of elements in the periodic table.
- Predict the general properties of elements based on their location within the periodic table.
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table.

The Periodic Table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example, Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to *increasing atomic mass*. However, Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized.

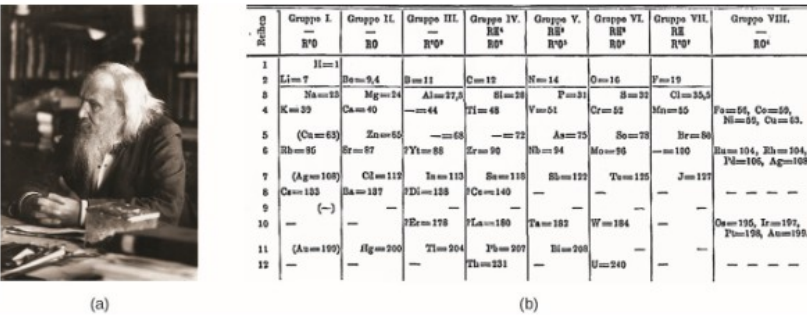


Figure 2.23 (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 2.24). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, the lanthanides and actinides, are usually written below the main body of the table.

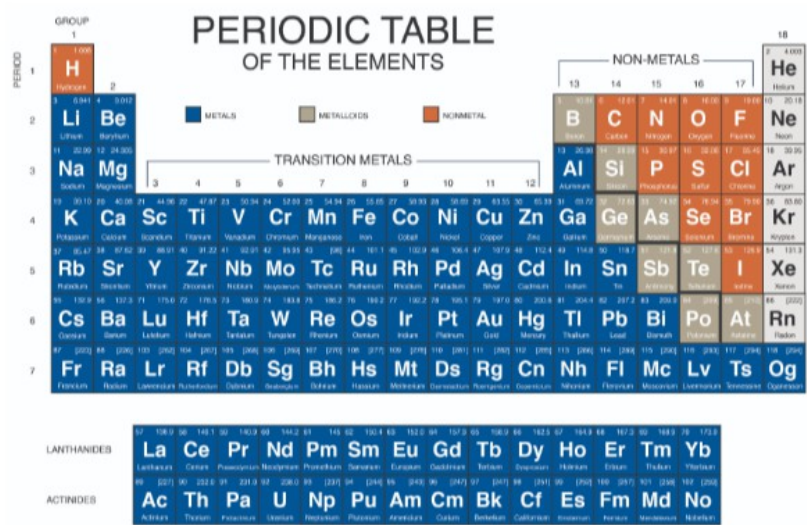


Figure 2.24 Elements in the periodic table are organized according to their properties.

Even after the periodic nature of elements and the table itself were widely accepted, gaps remained. Mendeleev had predicted, and others including Henry Moseley had later confirmed, that there should be elements below Manganese in Group 7. German chemists Ida Tacke and Walter Noddack set out to find the elements, a quest being pursued by scientists around the world. Their method was unique in that they did not only consider the properties of manganese but also the elements horizontally adjacent to the missing elements 43 and 75 on the table. Thus, by investigating ores containing minerals of ruthenium (Ru), tungsten (W), osmium (Os), and so on, they were able to identify naturally occurring elements that helped complete the table. Rhenium, one of their discoveries, was one of the last natural elements to be discovered and is the last stable element to be discovered. (Francium, the last natural (but unstable) element to be discovered, was identified by Marguerite Perey in 1939.)

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded blue); **nonmetals** (elements that appear dull, poor conductors of heat and electricity—shaded orange); and **metalloids** (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded gold).



Check Your Learning: Metals, Nonmetals, and Metalloids

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Classify the following descriptions as a property of either a metal, nonmetal, or metalloid. Turn the card over to check your answer.

Dull

Turn

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The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12; 1 and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen. These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and the **noble gases** (group 18, also known as **inert gases**). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique,

Periodic Table of the Elements

Group 1 2 13 14 15 16 17 18

Alkali metals Alkaline earth metals Main group elements Transition metals Pnictogens Chalcogens Halogens Noble gases

Lanthanides Actinides

Example: Naming Groups of Elements

(a) chlorine
(b) calcium
(c) sodium
(d) sulfur

The family names are as follows:

- (a) halogen
(b) alkaline earth metal
(c) alkali metal
(d) chalcogen



Check Your Learning: Naming Groups of Elements

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Determine the group name for the following elements and type it in the box. Be sure to spell your answer correctly. Check your answer when you are finished. The terms you will use are: alkali metal, alkaline earth metal, transition metal, pnictogen, chalcogen, halogen, noble gas.

As

Turn

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As you will learn in your further study of chemistry, elements in groups often behave in a somewhat similar manner. This is partly due to the number of electrons in their outer shell and their similar readiness to bond. These shared properties can have far-ranging implications in nature, science, and medicine.

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry module). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.



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2.7 Ionic and Molecular Compounds



Learning Objectives

By the end of this section, you will be able to:

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions.

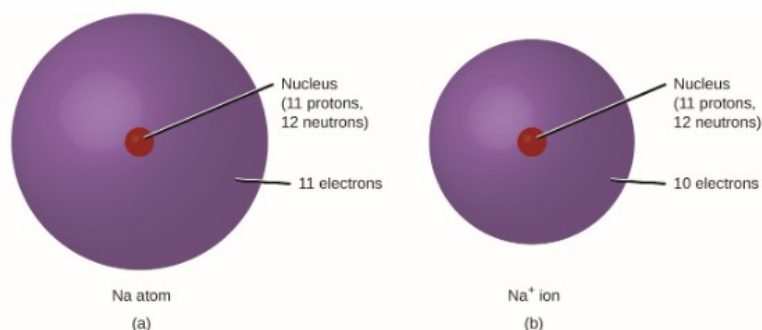


Figure 2.26 (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na⁺) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscript plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+} . The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1- charge; atoms of group 16 gain two electrons and form ions with a 2- charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1- charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^- .

Note the usefulness of the periodic table in predicting likely ion formation and charge. Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1- ions; group 16 elements (two groups left) form 2- ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

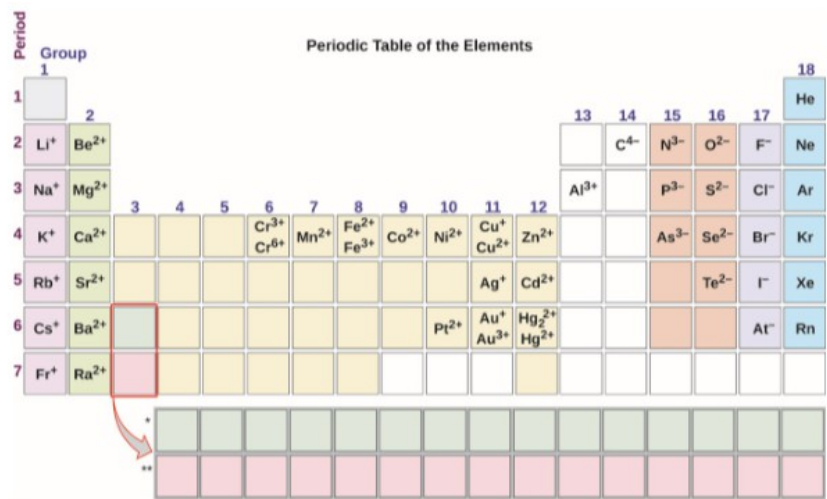


Figure 2.27 Some elements exhibit a regular pattern of ionic charge when they form ions.

Example: Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al³⁺.



Check Your Learning: Composition of Ions

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Determine the symbol for the ions described below. Turn the card over to check your answer.

34 protons and 36 electrons

Turn

Card 1 of 3



Example: Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+} .

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3-. The symbol for the ion is N^{3-} .



Check Your Learning: Formation of Ions

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Predict whether the following atoms form a cation or an anion and predict the charge. Turn the card over to check your answer.

Aluminum

Turn

Card 1 of 4



The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in the table below. **Oxyanions** are polyatomic ions that contain one or more oxygen atoms. The names, formulas, and charges of some of the most common polyatomic ions can be found in the table below.

Table 2.4: Common Polyatomic Ions

Name	Formula
ammonium	NH_4^+
hydroxide	OH^-
acetate	CH_3COO^-
cyanide	CN^-
carbonate	CO_3^{2-}
nitrate	NO_3^-
nitrite	NO_2^-
sulfate	SO_4^{2-}
sulfite	SO_3^{2-}
phosphate	PO_4^{3-}
perchlorate	ClO_4^-
chlorate	ClO_3^-
chlorite	ClO_2^-
hypochlorite	ClO^-
chromate	CrO_4^{2-}
dichromate	$\text{Cr}_2\text{O}_7^{2-}$
permanganate	MnO_4^-

You will be required to memorize the names, formulas, and charges of the above polyatomic groups. While you will see different polyatomic groups used in other portions of this course, these are the only groups that must be memorized for the purposes of naming and writing the formulas of different chemical species.



Check Your Learning: Polyatomic Groups

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Write down the polyatomic group that matches the name listed. Turn the card over and compare your answer to the correct answer.

acetate

Turn

Card 1 of 17



Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for “hyper”) and *hypo-* (meaning “under”) are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is ClO_4^- , chlorate is ClO_3^- , chlorite is ClO_2^- and hypochlorite is ClO^- . Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-} . This will be covered in more detail later in the module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are “shared” and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+ , and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^- , the resulting compound, NaCl , is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form CaCl_2 , which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, AlCl_3 , is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at $801\text{ }^\circ\text{C}$ and boils at $1413\text{ }^\circ\text{C}$. (As a comparison, the molecular compound water melts at $0\text{ }^\circ\text{C}$ and boils at $100\text{ }^\circ\text{C}$.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid.

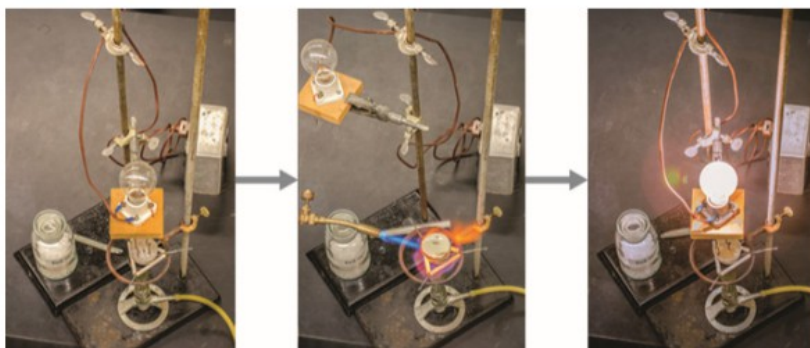


Figure 2.28 Sodium chloride melts at $801\text{ }^\circ\text{C}$ and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example: Predicting the Formula of an Ionic Compound

The purple gemstone sapphire is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+} , and oxygen anions, O^{2-} . What is the formula of this compound?

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of $3+$, would give us six positive charges, and three oxide ions, each with a charge of $2-$, would give us six negative charges. The formula would be Al_2O_3 .

Many ionic compounds contain polyatomic ions as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $\text{Ca}_3(\text{PO}_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate (PO_4^{3-}) groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of $3-$. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms. Notice that the charges are not written for the ions in an electrically neutral compound.

Example: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and H_2PO_4^- . What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two H_2PO_4^- ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as CaSO_4), these formulas are just the empirical formulas introduced earlier. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $\text{C}_2\text{O}_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $\text{Na}_2\text{C}_2\text{O}_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, NaCO_2 . However, this is not the accepted formula for sodium oxalate as it does not accurately represent the compound's polyatomic anion, $\text{C}_2\text{O}_4^{2-}$.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These **molecular compounds** (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail later in this course. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table

to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example: Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

- (a) KI, the compound used as a source of iodine in table salt
- (b) H_2O_2 , the bleach and disinfectant hydrogen peroxide
- (c) CHCl_3 , the anesthetic chloroform
- (d) Li_2CO_3 , a source of lithium in antidepressants

Solution

- (a) Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
- (b) Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.
- (c) Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; CHCl_3 is predicted to be molecular.
- (d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.



Check Your Learning: Ionic Compounds

If you are using a smaller screen and the right side of the puzzle appears offscreen, close the course navigation menu at left.

Turn the card over and compare your answer to the correct answer.

An ionic compound forms between the atoms listed on the card. Determine the ions that form and the formula of each compound.

sodium and sulfur

 Turn

Card 1 of 10



◀ Previous

Next ▶



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6

Module 2 Problem Set

Started: Jun 13 at 2:49pm

Quiz Instructions

[Resource Bank](#)

[Scientific Calculator](#)

[Periodic Table](#)



Question 1

0 pts

Which observations and/or theories support the wave nature of light?

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Light works as both a wave and a particle.

As a wave, it has a length and an amplitude and is driven by hertz.

There is also the relationship that

$$c = 2.998 \times 10^8 \text{ m/s} = \lambda \nu$$

p



30 words

</>





Question 2

0 pts

Which observations and/or theories support the particle nature of light?

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Maxwell developed a theory about particles and used an equation. Then Max Planck. Then unfortunately the wave equation mentioned in the last question does not hold true for shorter wavelengths. Thus a new theory had to be made.

$E = h\nu$

where h is Plancks' constant, 6.626×10^{-34}

This equation helps explain why energy

p 63 words



Question 3

0 pts

What is the wavelength of microwave radiation with a frequency of 350 MHz?

Equation:

Equation with values substituted:

Answer (with correct units and to 3 significant figures):

$$\begin{aligned}\lambda &= c \, \nu \\ &= c = 2.998 \times 10^8 \, m/s * 350 \, \text{MHz} \\ &= 1.05 \times 10^{11}\end{aligned}$$

p   | 16 words |   



Question 4

0 pts

What is the energy of a photon being emitted by a radio wave that has a wavelength of 160 m?

Equation:

Equation with values substituted:

Answer (with correct units and to 3 significant figures):

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$$E = hc / \lambda$$

p   | 7 words |   



Question 5

0 pts

What are the main features from Bohr's model of the hydrogen atom that apply to all models used to describe the distribution of electrons in an atom?

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Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron-electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used

p 169 words



Question 6

0 pts

A source of energy promotes an electron in a hydrogen atom from ground state into an orbit with $n = 8$. What is the calculated energy (in Joules) of the electron in this excited state?

Equation:

Equation with values substituted:

Answer (with correct units and to 3 significant figures):

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$$E_n = \frac{-k}{n^2}$$

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1

0 words

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Question 7

0 pts

An electron in a hydrogen atom transitions from an orbit with $n = 4$ to the orbit with $n = 7$.

1. What is the calculated energy absorbed by the electron?
2. What is the wavelength of light emitted by the hydrogen atom when the electron falls from $n = 7$ back down to $n = 4$.

A. Equation:
Equation with values substituted:
Answer (with correct units and all digits):

B. Equation:
Equation with values substituted:
Answer (with correct units and to 3 significant figures):

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$$E_n = \frac{-k}{n^2}$$

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Question 8

0 pts

What is the symbol, allowed values, and physical meaning of the principal quantum number?

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Question 9

0 pts

What is the symbol, allowed values, and physical meaning of the secondary (or angular momentum) quantum number?

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Name	Symbol	Allowed Values	Physical Meaning
principal quantum number	n	1, 2, 3, 4,	shell, the general region for the value of energy for an electron on the orbital
angular momentum	l	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	orientation of the orbital

p



1

0 words

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Question 10

0 pts

What is the symbol, allowed values, and physical meaning of the magnetic quantum number?

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Quantum Numbers, Their Properties, and Significance			
Name	Symbol	Allowed Values	Physical Meaning
principal quantum number	n	1, 2, 3, 4,	shell, the general region for the value of energy for an electron on the orbital
angular momentum	l	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	orientation of the orbital

p

0 words

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Question 11

0 pts

What is the symbol, allowed values, and physical meaning of the spin quantum number?

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Quantum Numbers, Their Properties, and Significance			
Name	Symbol	Allowed Values	Physical Meaning
principal quantum number	n	1, 2, 3, 4,	shell, the general region for the value of energy for an electron on the orbital
angular momentum	l	$0 \leq l \leq n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \leq m_l \leq l$	orientation of the orbital

p

0 words

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<https://getfireshot.com>



Question 12

0 pts

What is the maximum number of electrons that can occupy a shell with $n = 9$?

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Question 13

0 pts

Fill in the following table:

Orbital	n	l	m_l degeneracy
5f	1._____	2._____	3._____
6p	4._____	5._____	6._____
4d	7._____	8._____	9._____
2s	10._____	11._____	12._____

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Question 140 pts

Indicate which atoms have the following electron configurations:

- 1. [Ar]4s² 3d⁵
- 2. [Ne]3s² 3p³
- 3. [Kr]5s²
- 4. [Kr]5s² 4d¹⁰ 5p⁵

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Question 15

0 pts

Write the full electron configurations for the following ions:

- 1. Sr^{2+}
- 2. Sn^{4+}
- 3. Te^{2-}

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Question 16

0 pts

Draw the orbital diagrams for the following atoms:

- 1. Ca
- 2. Cl
- 3. As

For help with inserting arrows [click here](#) ↓ .

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Question 17

0 pts

Determine the four quantum numbers for the last electron added for the following atoms:

- 1. N
- 2. K
- 3. Br
- 4. In
- 5. Ti

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Question 180 pts

What are the 3 categories of elements that are classified based on what orbitals are filled? Identify which orbital their last electron is added to.

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Question 19

0 pts

State the general trends for the following elemental properties and explain the reasoning behind each trend:

1. Atomic Radius
2. Z_{eff}
3. Ionization Energy
4. Electron Affinity

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Question 20

0 pts

Answer the following according to the general trends outlined in the course:

1. Which atom has a higher Z_{eff} ?
- S or Po
2. Which atom has a smaller atomic radius?
- Sn or Sr
3. Which atom has a larger IE1 value?
- K or Ge

4. Which atom has a lower electron affinity?
- Fr or K

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12pt Paragraph

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Question 21

0 pts

Identify the group name for the following elements:

- 1. U
- 2. Pt
- 3. Ar
- 4. Sr
- 5. Ce
- 6. As
- 7. Li
- 8. Br
- 9. Te

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Question 220 pts

Compare and contrast metals, nonmetals, and metalloids.

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Question 23

0 pts

Classify the following as either an ionic compound or a molecular compound:

Compound	Type
$\text{Al}_2(\text{CO}_3)_3$	<div>[Select]</div>
N_2O_4	<div>[Select]</div>
PCl_5	<div>[Select]</div>
KCH_3COO	<div>[Select]</div>
CaI_2	<div>[Select]</div>
SO_2	<div>[Select]</div>



Question 24

0 pts

An ionic compound forms between the atoms below.

- What are the ions that form?
 - What is the formula of each compound?
- calcium and phosphorus
 - cesium and fluorine
 - aluminum and bromine

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Question 250 pts

An ionic compound forms between the atoms below.

- What is the formula of each compound?
1. sodium and phosphate
 2. potassium and nitrate
 3. magnesium and permanganate

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12pt ▾Paragraph ▾|⋮

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0 words

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Question 26

5 pts

As a reminder, the questions in this review quiz are a requirement of the course and the best way to prepare for the module exam. Did you complete all questions in their entirety and show your work?

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p

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Quiz saved at 7:57pm

Submit Quiz

Questions

- ✓ Question 1
- ✓ Question 2
- ✓ Question 3
- ✓ Question 4
- ✓ Question 5
- ✓ Question 6

- ✓ Question 7
- ✓ Question 8

Time Elapsed:

Hide Time

10 Days, 5 Hours, 8 Minutes, 15 Seconds