CHEMTEN S1



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TEN-S1

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Detailed Licensing

Licensing

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SECTION OVERVIEW

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Heat

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1.1.1: The Nature and Types of Energy

; the potential energies of electrons in the force field created by atomic nuclei lie at the heart of the chemical behavior of and molecules. "" usually refers to the energy that is stored in the of molecules. These bonds form when electrons are able to respond to the force fields created by two or more atomic nuclei, so they can be regarded as manifestations of electrostatic potential energy. In an chemical reaction, the electrons and nuclei within the reactants undergo rearrangement into products possessing lower energies, and the difference is released to the environment in the form of heat. chemical reaction heats surrounding , the kinetic energy gets dispersed into the molecular units in the environment. This "microscopic" form of kinetic energy, unlike that of a speeding bullet, is completely random in the kinds of motions it exhibits and in its direction. We refer to this as "thermalized" kinetic energy, or more commonly simply as . We observe the effects of this as a rise in the temperature of the . The temperature of a body is direct measure of the quantity of thermal energy is contains. , energy comes in different types. Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the : (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car’s engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders’ pistons. The is also one version of the first law of thermodynamics, as you will learn later. in glucose to keep us warm and to move our muscles. In fact, life itself depends on the conversion of to other forms. So when you go uphill, your kinetic energy is transformed into potential energy, which gets changed back into kinetic energy as you coast down the other side. And where did the kinetic energy you expended in peddling uphill come from? By conversion of some of the chemical potential energy in your breakfast cereal.). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (or first law of thermodynamics). has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat () or release heat (). The SI unit of energy, heat, and work is the .

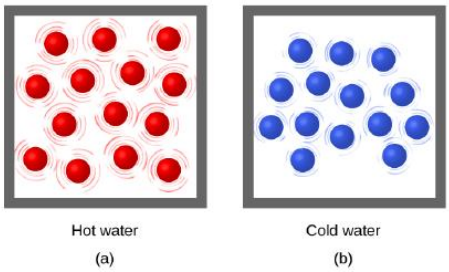
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1.1.2: Quantifying Heat and Work

Learning Objectives

- To calculate changes in internal energy
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

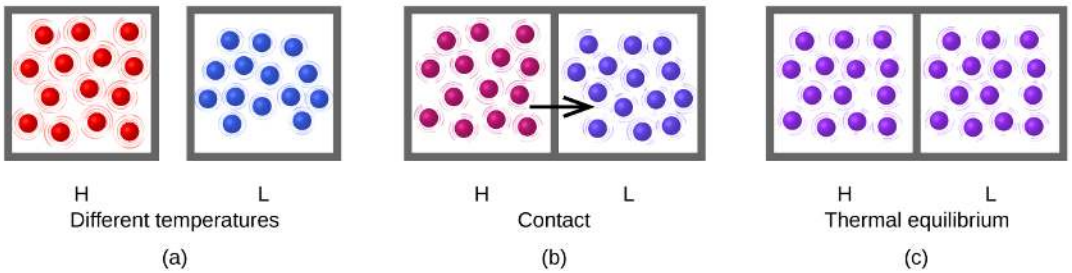
Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of “hot” or “cold.” When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is “hot.” When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is “cold” (Figure **1.1.2.1**). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.



Drawing a is a box containing red spheres that are surrounded by lines indicating that the particles are moving rapidly. Drawing b depicts another box which also contains spheres, but these are blue. They are all surrounded by smaller lines that depict a slower motion compared to drawing a.

Figure **1.1.2.1**: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure **1.1.2.2**).



Drawing a shows two separated boxes with red and blue spheres respectively. The radial lines along each sphere are more concentrated for the box containing hotter molecules. Drawing b shows the two boxes in contact as well as the direction of heat transfer from the hotter to colder region. The colors of the two molecules are turning into two different shades of maroon. The final drawing depicts two boxes where molecules in each box are exactly identical in terms of color and motion.

Figure 1.1.2.2: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach “thermal equilibrium” when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch’s flame (Figure 1.1.2.3*a*). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Two pictures are shown and labeled a and b. Picture a shows a metal railroad tie being cut with the flame of an acetylene torch. Picture b shows a chemical cold pack containing ammonium nitrate.

Figure 1.1.2.3: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by “Skatebiker”/Wikimedia commons).

Historically, energy was measured in units of *calories* (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

$$1\,cal \equiv 4.184\,J \tag{1.1.2.1}$$

Application: Heat can do more than increase temperature

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 1.1.2.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

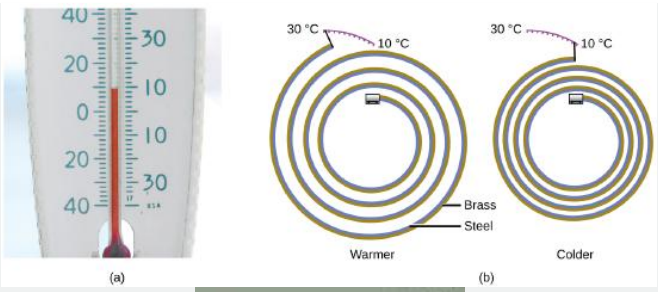




Figure 1.1.2.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)

Picture a shows the lower portion of an alcohol thermometer. The two images labeled b both depict a metal strip coiled into a spiral and composed of brass and steel. The left coil, which is loosely coiled, is labeled along its upper edge with the 30 degrees C and 10 degrees C. The end of the coil is near the 30 degrees C label. The right hand coil is much more tightly wound and the end is near the 10 degree C label.

Direction of Heat Flow: Endothermic vs. Exothermic Processes

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel. The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \tag{1.1.2.2}$$

We can also write this chemical equation as

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + \mathrm{heat} \tag{1.1.2.3}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.



When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\text{heat} + \mathrm{H_2O_{(s)}} \rightarrow \mathrm{H_2O_{(l)}} \tag{1.1.2.4}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

> *By convention, $q < 0$ for an exothermic reaction and $q > 0$ for an endothermic reaction.*

Exercise 1.1.2.1

Decide whether the following are endothermic or exothermic processes

a. water evaporates off a shower door
b. an acid tablet being added to a pool and the surrounding water heats up
c. $\mathrm{NH_4Cl}$ is dissolved in water and the solution cools
d. the burning of a log in a campfire

Hint

During an endothermic process heat is absorbed from surroundings, causing them to cool, so in every case where there is cooling there is most likely an endothermic process taking place. For exothermic reactions energy is being released to the surroundings and so the surroundings feel like they have been heated by the process.

Answer a

endothermic

Answer b

exothermic

Answer c

endothermic

Answer d

exothermic

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a *heat* term in the chemical reaction like in Equations 1.1.2.3 and 1.1.2.4 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

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Learning Objectives

- To know the relationship between energy, work, and heat.

One definition of energy is the capacity to do work. There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work and focus on the work done during changes in the pressure or the volume of a gas.

Mechanical Work

The easiest form of work to visualize is mechanical work (Figure 1.1.2.5), which is the energy required to move an object a distance d when *opposed* by a force F, such as gravity:

$$w = F\,d \tag{1.1.2.5}$$

with w is work, F is opposing force, and d is distance.



GIF

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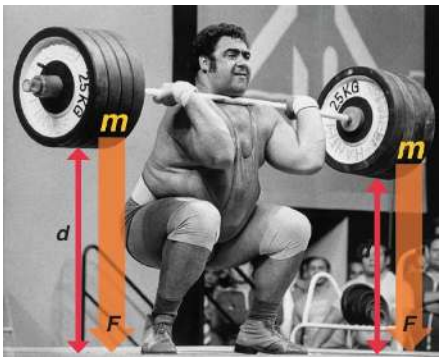


Figure 1.1.2.5: One form of energy is mechanical work, the energy required to move an object of mass m through distance d when opposed by a force F, i.e., as gravity.

A powerlifter in the middle of lifting a barbell bar with multiple weights attached on each side. The weights are labeled m and an arrow labeled F is shown pointing downwards. The height of the weights from the ground is labeled d.

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), Equation 1.1.2.5 can be rewritten to:

$$w = m\,a\,d \tag{1.1.2.6}$$

with w is work, m is mass, a is acceleration, and d is distance.

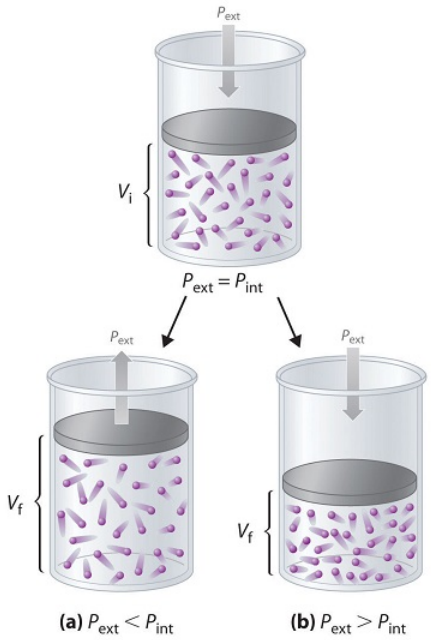
Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth. Hence for works against gravity (on Earth), a can be set to $g = 9.8\ m/s^2$). Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the opposing force of gravity. The amount of work done (w) and thus the energy required depends on three things:

1. the height of the second floor (the distance d);
2. your mass, which must be raised that distance against the downward acceleration due to gravity; and

3. your path.

Pressure-Volume (PV) Work

To describe this pressure–volume work (PV work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions. Imagine, for example, an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure 1.1.2.6). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.



The three diagrams which represents the different cases show gaseos molecules shown as spheres in motion in an enclosed cylinder with piston acting from above. The top diagram shows the equilibrium case while the two diagram below it shows cases where external pressure is not equal to internal pressure.

Figure 1.1.2.6: PV Work demonstrated with a frictionless piston. (a) if the external pressure is less than P_{int}, the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. (b) Alternatively, if the external pressure is greater than P_{int}, the gas will be compressed, and the surroundings will perform work on the system.

If the piston has cross-sectional area A, the external pressure exerted by the piston is, by definition, the force per unit area:

$$P_{ext} = \frac{F}{A} \tag{1.1.2.7}$$

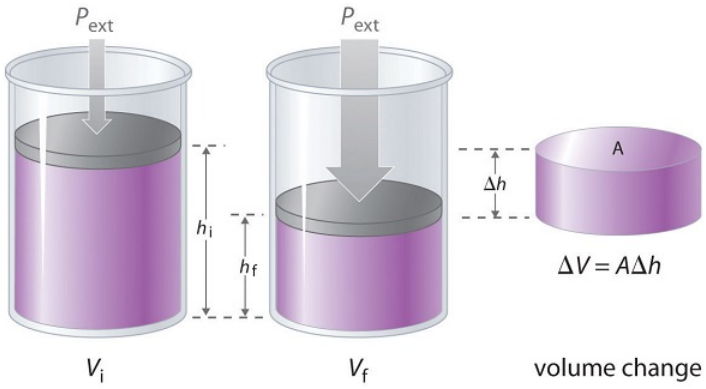
The volume of any three-dimensional object with parallel sides (such as a cylinder) is the cross-sectional area times the height ($V = Ah$). Rearranging Equation 1.1.2.7 to give

$$F = P_{ext}A \tag{1.1.2.8}$$

and defining the distance the piston moves (d) as Δh, we can calculate the magnitude of the work performed by the piston by substituting into Equation 1.1.2.5:

$$w = Fd = P_{ext}A\Delta h \tag{1.1.2.9}$$

The change in the volume of the cylinder (ΔV) as the piston moves a distance d is $\Delta V = A\Delta h$, as shown in Figure 1.1.2.7.



A cylinder containing an initial volume of fluid has a height labeled h subscript i and volume V subscript i. The following diagram shows a compressed volume labeled V subscript f and height of fluid h subscript f. The diagram on the right shows the cylindrical portion of fluid which represents the change in volume as a result of the piston pushing down. It has height of delta h and area A.

Figure 1.1.2.7: Work Performed with a change in volume. The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by Equation 1.1.2.10.

The PV work performed is thus

$$w = P_{ext}\Delta V \tag{1.1.2.10}$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \left(\frac{F}{A}\right)_{ext}(\Delta V) = \frac{\text{newton}}{\text{m}^2} \times \text{m}^3 = \text{newton} \cdot \text{m} = \text{joule} \tag{1.1.2.11}$$

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R = \frac{0.08206\ \text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = \frac{8.314\ \text{J}}{\text{mol} \cdot \text{K}} \tag{1.1.2.12}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J.

Exercise: Expansion (PV) work

a. How much work is done by a gas that expands from 2 liters to 5 liters against an external pressure of 750 mmHg?
b. How much work is done by 0.54 moles of a gas that has an initial volume of 8 liters and expands under the following conditions: 30 ^oC and 1.3 atm?
c. How much work is done by a gas (P=1.7 atm, V=1.56 L) that expands against an external pressure of 1.8 atm?

Solution a

$$w = -P\Delta V \tag{1.1.2.13}$$

$$\Delta V = V_{final} - V_{Initial} = 5\,L - 2\,L = 3L \tag{1.1.2.14}$$

Convert 750 mmHg to atm:

$$750mmHg * 1/760(atm/mmHg) = 0.9868atm. \tag{1.1.2.15}$$

$$W = -p\Delta V = -(.9868\,atm)(3\,L) = -2.96\,L\,atm. \tag{1.1.2.16}$$

Solution b

First we must find the final volume using the ideal gas law:

$$pV = nRT \tag{1.1.2.17}$$

or

$$V = \frac{nRT}{P} = \frac{[(0.54\,moles)(0.082057(L\,atm)/(mol\,K))(303\,K)]}{1.3\,atm} = 10.33\,L \tag{1.1.2.18}$$

$$\Delta V = V_{final} - V_{initial} = 10.3\,L - 8\,L = 2.3\,L \tag{1.1.2.19}$$

$$w = -p\Delta V = -(1.3\,atm)(2.3\,L) = -3\,L\,atm. \tag{1.1.2.20}$$

Solution c

$$w = -p * \Delta V\backslash) = -(1.8\,atm)\,\Delta V. \tag{1.1.2.21}$$

Given p_1, V_1, and p_2, find V_2: $p_1V_1 = p_2V_2$ (at constant T and n)

$V_2 = (V_1 * P_1)/P_2$ = (1.56 L * 1.7 atm) / 1.8 atm = 1.47 L

Now,

$$\Delta V = V_2 - V_1 = 1.47\,L - 1.56\,L = -0.09 \tag{1.1.2.22}$$

$$w = -(1.8atm) * (-0.09L) = 0.162Latm. \tag{1.1.2.23}$$

Whether work is defined as having a positive sign or a negative sign is a matter of convention. Heat flow is defined from a system to its surroundings as negative; using that same sign convention, we define work done by a system on its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings. This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done on the surroundings than in the work done by the system and therefore use the opposite convention. Because ΔV > 0 for an expansion, Equation 1.1.2.10 must be written with a negative sign to describe PV work done by the system as negative:

$$w = -P_{ext}\Delta V \tag{1.1.2.24}$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done by a system on its surroundings. Conversely, when a gas is compressed by an external pressure, ΔV < 0 and the work is positive because work is being done on a system by its surroundings.

A Matter of Convention

- Heat flow is defined from the system to its surroundings as **negative**
- Work is defined as by the system on its surroundings as **negative**

Suppose, for example, that the system under study is a mass of steam heated by the combustion of several hundred pounds of coal and enclosed within a cylinder housing a piston attached to the crankshaft of a large steam engine. The gas is not ideal, and the cylinder is not frictionless. Nonetheless, as steam enters the engine chamber and the expanding gas pushes against the piston, the piston moves, so useful work is performed. In fact, PV work launched the Industrial Revolution of the 19th century and powers the internal combustion engine on which most of us still rely for transportation.

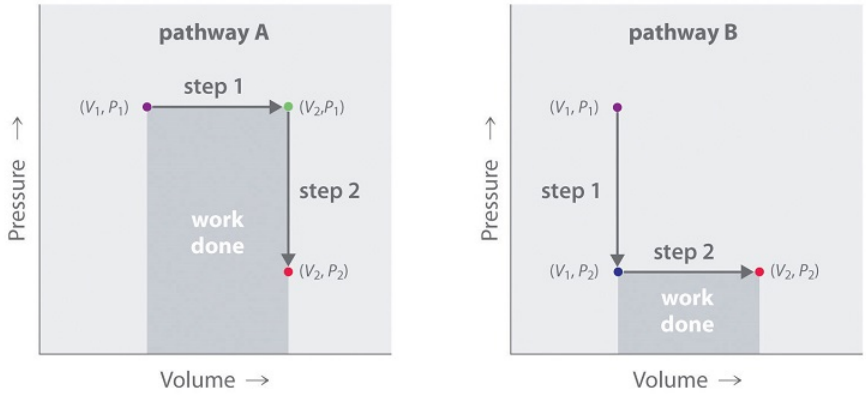


Figure **1.1.2.8**: Work Is Not a State Function. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken.

Two graphs are shown with pressure on the vertical axis and volume on the horizontal axis. Pathway A with arrow pointing right then step 2 has arrow which points from the first arrow straight down. Pathway B has step 1 with arrow pointing straight down then step 2 with an arrow pointing from step 1 straight to the right. The area in pathway A is encompassed by the two arrows. The area in pathway B is found under the step 2 arrow.

In contrast to internal energy, work is not a state function. We can see this by examining Figure **1.1.2.8**, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is **not** a state function.

> *Internal energy is a state function, whereas work is not.*

Example 1.1.2.1: Internal Combustion Engine

A small high-performance internal combustion engine has six cylinders with a total nominal displacement (volume) of 2.40 L and a 10:1 compression ratio (meaning that the volume of each cylinder decreases by a factor of 10 when the piston compresses the air–gas mixture inside the cylinder prior to ignition). How much work in joules is done when a gas in one cylinder of the engine expands at constant temperature against an opposing pressure of 40.0 atm during the engine cycle? Assume that the gas is ideal, the piston is frictionless, and no energy is lost as heat.

Given: final volume, compression ratio, and external pressure

Asked for: work done

Strategy:

Calculate the final volume of gas in a single cylinder. Then compute the initial volume of gas in a single cylinder from the compression ratio. Use Equation 1.1.2.24 to calculate the work done in liter-atmospheres. Convert from liter-atmospheres to joules.

Solution:

A To calculate the work done, we need to know the initial and final volumes. The final volume is the volume of one of the six cylinders with the piston all the way down: V_f = 2.40 L/6 = 0.400 L. With a 10:1 compression ratio, the volume of the same cylinder with the piston all the way up is V_i = 0.400 L/10 = 0.0400 L. Work is done by the system on its surroundings, so work is negative.

$$\begin{aligned} w &= -P_{ext}\Delta V \\ &= -(40.0\,atm)(0.400\,L - 0.0400\,L) \\ &= -14.4\,L \cdot atm \end{aligned}$$

Converting from liter-atmospheres to joules,

$$w = -(14.4\ \text{L} \cdot \text{atm})[101.3\ \text{J}/(\text{L} \cdot \text{atm})]$$
$$= -1.46 \times 10^3\ \text{J}$$

In the following exercise, you will see that the concept of work is not confined to engines and pistons. It is found in other applications as well.

Exercise 1.1.2.1: Work to Breath

Breathing requires work, even if you are unaware of it. The lung volume of a 70 kg man at rest changed from 2200 mL to 2700 mL when he inhaled, while his lungs maintained a pressure of approximately 1.0 atm. How much work in liter-atmospheres and joules was required to take a single breath? During exercise, his lung volume changed from 2200 mL to 5200 mL on each in-breath. How much additional work in joules did he require to take a breath while exercising?

Answer

−0.500 L·atm, or −50.7 J; −304 J; if he takes a breath every three seconds, this corresponds to 1.4 Calories per minute (1.4 kcal).

Work and Chemical Reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just *PV work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2H_2O_{(l)} + 2NO_{2(g)} \tag{1.1.2.25}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 1.1.2.9). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV* work done by multiplying the external pressure *P* by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V \tag{1.1.2.26}$$

The negative sign associated with PV work done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

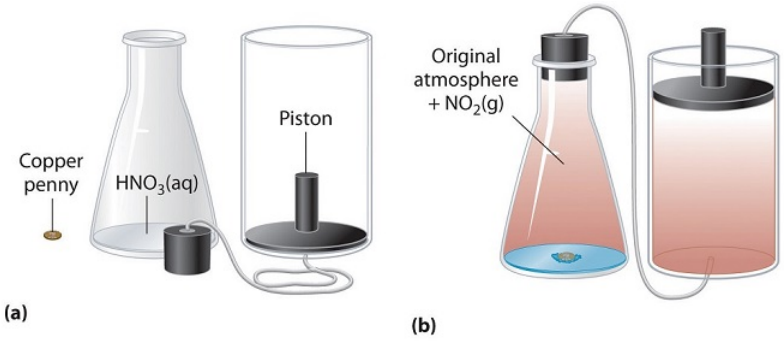


Figure 1.1.2.9: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

Diagram a shows an Erlenmeyer flask with nitric acid in it and a copper penny beside the flask. A cylidrical container with a piston is shown connected by a tube to a flask stopper. The second diagram shows the copper penny inside the flask and the stopper placed on the neck of the flask. The flask and the cylindrical container is filled with a brownish vapor. The piston is at an elevated position compared to the first diagram since it's pushed upwards by the vapor.

The symbol U represents the internal energy of a system, which is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

$$H = U + PV \tag{1.1.2.27}$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) = \Delta U + \Delta PV = \Delta U + P\Delta V \tag{1.1.2.28}$$

Substituting $q + w$ for ΔU (Equation 1.1.2.28) and $-w$ for $P\Delta V$ (Equation 1.1.2.26), we obtain

$$\Delta H = \Delta U + P\Delta V = q_p + w - w = q_p \tag{1.1.2.29}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 1.1.2.29 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p \tag{1.1.2.30}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p under constant pressure.*

Summary

All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work.

Outside Links

- Gasparro, Frances P. "Remembering the sign conventions for q and w in deltaU = q - w." J. Chem. Educ. 1976: 53, 389.
- Koubek, E. "PV work demonstration (TD)." J. Chem. Educ. 1980: 57, 374. '

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1.1.3: The First Law of Thermodynamics

Learning Objectives

- To calculate changes in internal energy

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure **1.1.3.1**). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

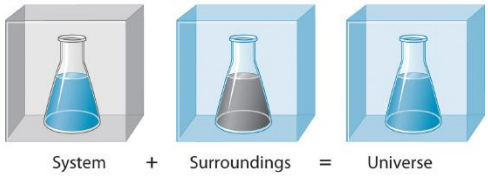


Figure **1.1.3.1**: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Three kinds of systems are important in chemistry. An **open system** can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A **closed system** can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An **isolated system** exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure **1.1.3.2**). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.



Figure **1.1.3.2**: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (Figure **1.1.3.3**). The balanced chemical equation for the reaction is as follows:

$$\mathrm{2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2\,Fe\,(s) + Al_2O_3\,(s)} \tag{1.1.3.1}$$



Figure **1.1.3.3**: The thermite reaction produces so much heat that the iron it produces comes out molten, a property that makes this reaction useful in welding. Image by Kingfisher [CC BY-SA 3.0 (Creative Commons [creativecommons.org])], from Wikimedia Commons.

We can also write this chemical equation as

$$\mathrm{2\,Al\,(s) + Fe_2O_3\,(s) \rightarrow 2\,Fe\,(s) + Al_2O_3\,(s) + heat} \tag{1.1.3.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\mathrm{heat + H_2O\,(s) \rightarrow H_2O\,(l)} \tag{1.1.3.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a ***heat*** term in the chemical reaction like in Equations 1.1.3.2 and 1.1.3.3 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

The First Law

The relationship between the energy change of a system and that of its surroundings is given by the **first law of thermodynamics**, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{1.1.3.4}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{1.1.3.5}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/ O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta U_{sys} = q + w \tag{1.1.3.6}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed.

Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a state function.

Thus, because of the first law, we can determine ΔU for any process if we can measure both q and w. Heat, q, may be calculated by measuring a change in temperature of the surroundings. Work, w, may come in different forms, but it too can be measured. One important form of work for chemistry is *pressure-volume work* done by an expanding gas. At a constant external pressure (for example, atmospheric pressure)

$$w = -P\Delta V \tag{1.1.3.7}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. That is, an expanding gas does work on its surroundings, while a gas that is compressed has work done on it by the surroundings.

Example 1.1.3.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 1.1.3.6.

B. From Equation 1.1.3.7 calculate w from the values given. Substitute this value into Equation 1.1.3.6 to calculate ΔU.

Solution

A From Equation 1.1.3.6, we know that ΔU = q + w. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 1.1.3.6,

$$w = -P_{ext}\Delta V = -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) = 284\ \text{J}$$

Thus

$$\begin{aligned}\Delta U &= q + w \\ &= -140\,J + 284\,J \\ &= 144\,J\end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 1.1.3.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer

−216 J

By convention (to chemists), both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**. The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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1.1.4: Constant Volume Calorimetry- Measuring ΔU for Chemical Reactions

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter(A device used to measure energy changes in chemical processes. shown schematically in Figure **1.1.4.1**). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the "bomb"). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

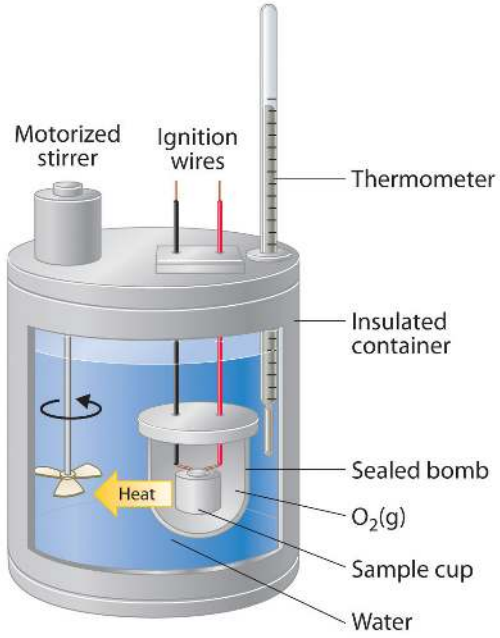


Figure **1.1.4.1**: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔE) rather than the enthalpy change (ΔH); ΔE is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta E < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 1.1.4.1, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{1.1.4.1}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used in Equation ??? to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example **1.1.4.4**.

Example 1.1.4.4: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation $ref5.5.9$ to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 1.1.4.1 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$qcomb = \left(0.579\ \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ \tag{1.1.4.2}$$

From Equation 1.1.4.1,

$$-Cbomb = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC \tag{1.1.4.3}$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^oC)\,(3.64\ ^oC) = -26.7\ kJ \tag{1.1.4.4}$$

Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol = 2.78 \times 10^3\ kJ/mol \tag{1.1.4.5}$$

This result is in good agreement (< 1% error) with the value of ΔH_{comb} = −2803 kJ/mol that calculated using enthalpies of formation.

Exercise 1.1.4.4: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Answer

-1.30×10^3 kJ/mol

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SECTION OVERVIEW

1.2: ENTHALPY

ENTHALPY

1.2.1: Enthalpy- The Heat Evolved in a Chemical Reaction at Constant Pressure

1.2.2: Constant Pressure Calorimetry- Measuring ΔH for Chemical Reactions

1.2.3: Relationships Involving Enthalpy of Reactions

1.2.4: Enthalpies of Reaction from Standard Heats of Formation

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1.2.1: Enthalpy- The Heat Evolved in a Chemical Reaction at Constant Pressure

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just *PV work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$\mathrm{Cu\,(s) + 4\,HNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + 2\,H_2O\,(l) + 2\,NO_2\,(g)}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 1.2.1.1). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of PV work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure),

$$w = -P\Delta V \tag{1.2.1.1}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

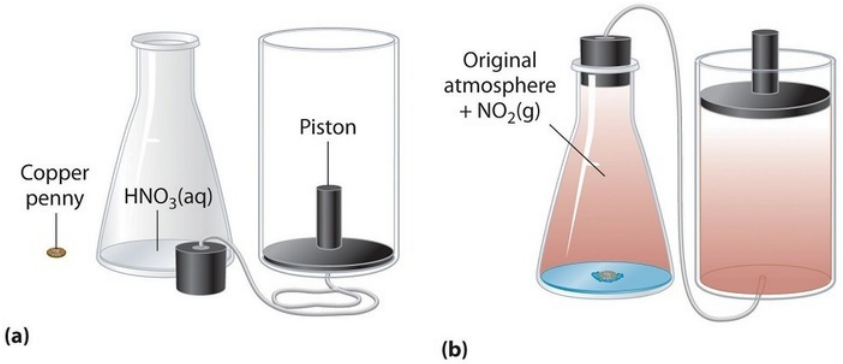


Figure 1.2.1.1: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings. (CC BY-NC-SA; anonymous)

The internal energy U of a system is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called **enthalpy** (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

\[H =U + PV \label{5.4.3} \]

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function. So we can define a change in enthalpy (ΔH) accordingly

$$\Delta H = H_{final} - H_{initial}$$

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) \tag{1.2.1.2}$$
$$= \Delta U + \Delta PV \tag{1.2.1.3}$$
$$= \Delta U + P\Delta V \tag{1.2.1.4}$$

Substituting $q + w$ for ΔU (First Law of Thermodynamics) and $-w$ for $P\Delta V$ (Equation 1.2.1.1) into Equation 1.2.1.4, we obtain

$$\Delta H = \Delta U + P\Delta V \tag{1.2.1.5}$$
$$= q_p + \cancel{w} - \cancel{w} \tag{1.2.1.6}$$
$$= q_p \tag{1.2.1.7}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 1.2.1.7 we see that at constant pressure the change in enthalpy, ΔH of the system, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} \tag{1.2.1.8}$$
$$= q_p \tag{1.2.1.9}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p.*

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus:

- $\Delta H_{rxn} < 0$ for an *exothermic reaction*, and
- $\Delta H_{rxn} > 0$ for an *endothermic reaction*.

In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

sign conventions for heat flow and enthalpy changes

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure **1.2.1.2*a***). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure **1.2.1.2*b***). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

> *Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.y.*

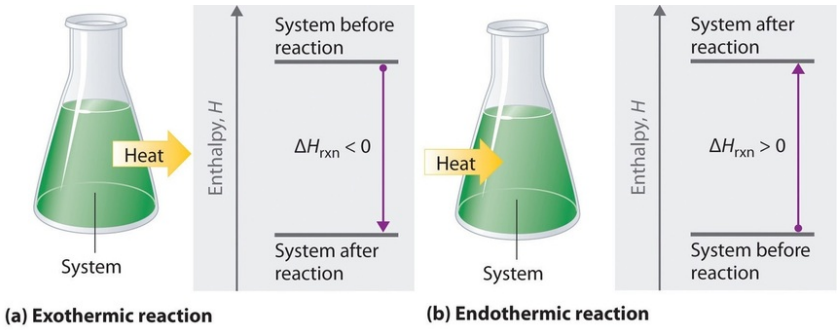


Figure 1.2.1.2: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill. (CC BY-NC-SA; anonymous)

- **Reversing a reaction or a process changes the sign of ΔH.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0$$

$$H_2O(l) \rightarrow H_2O(s) + heat \quad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 1.2.1.10, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$\mathbf{2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2\,Fe\,(s) + Al_2O_3\,(s) + 815.5\ kJ} \tag{1.2.1.10}$$

  Thus ΔH = −851.5 kJ/mol of Fe_2O_3. We can also describe ΔH for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for ΔH, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 1.2.1.11, it is the value of ΔH corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$\mathbf{2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2\,Fe\,(s) + Al_2O_3\,(s) \quad \Delta H_{rxn} = -851.5\ kJ} \tag{1.2.1.11}$$

  If 4 mol of Al and 2 mol of $\mathbf{Fe_2O_3}$ react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{1.2.1.12}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 1.2.1.1.

Example 1.2.1.1: Melting Icebergs

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction at 0°C and constant pressure:

$$\mathbf{H_2O\,(s) \longrightarrow H_2O\,(l)}$$

How much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{\text{metric ton}}\ \text{H}_2\text{O}\left(\frac{1000\ \cancel{kg}}{1\ \cancel{\text{metric ton}}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol\,\text{H}_2\text{O}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown below.

Possible sources of the approximately $3.34 \times 10^{11}\ kJ$ needed to melt a 1.00×10^6 metric ton iceberg

- Combustion of 3.8×10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1×10^8 kilowatt-hours of electricity

Alternatively, we can rely on ambient temperatures to slowly melt the iceberg. The main issue with this idea is the cost of dragging the iceberg to the desired place.

? Exercise 1.2.1.1: Thermite Reaction

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer

273 kJ

Enthalpies of Reaction

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, since enthalpy is a state function, all we have to know is the initial and final states of the reaction. This allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}) The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}) The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.

- Enthalpy of vaporization (ΔH_{vap}) The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln}) The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table **1.2.1.1**: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.



Enthalpy of Reaction: Enthalpy of Reaction, YouTube(opens in new window) [youtu.be]

Summary

For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

Contributors and Attributions

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1.2.2: Constant Pressure Calorimetry- Measuring ΔH for Chemical Reactions

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A "student" version, called a *coffee-cup calorimeter* (Figure **1.2.2.1**), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C). Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{1.2.2.1}$$

The use of a constant-pressure calorimeter is illustrated in Example **1.2.2.3**.

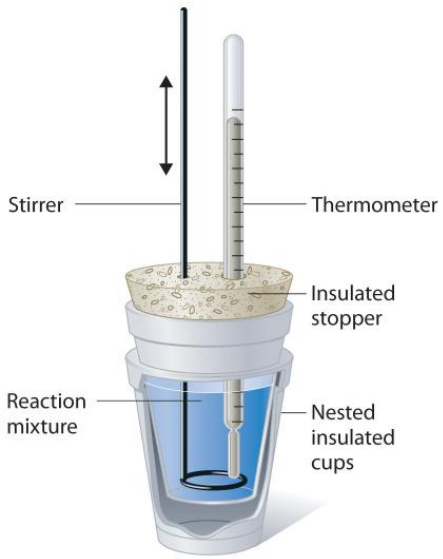


Figure **1.2.2.1**: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants. (CC BY-NC-SA; anonymous)

Example 1.2.2.1

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 5.5.8.
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$(100.0\ mL\ H2O)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g \tag{1.2.2.2}$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$q_{calorimater} = mC_s\Delta T = \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)(11.7\ ^\circ C) = 5130\ J = 5.13\ lJ \tag{1.2.2.3}$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 1.2.2.1, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln}—the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) = -57.2\ kJ/mol \tag{1.2.2.4}$$

Exercise 1.2.2.1

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example **1.2.2.1**, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol

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1.2.3: Relationships Involving Enthalpy of Reactions

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does not depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

> *Hess's Law argues that ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This is nothing more than arguing that ΔH is a state function.*

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 1.2.3.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 5.6.1, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 1.2.3.1); the enthalpy change for this reaction is −732.5 kJ/mol of Fe_2O_3. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 5.6.1); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe). In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 1.2.3.1); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe). As you can see in Figure 5.6.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 5.6.1 gives the overall reaction, shown in part (d):

$$\begin{aligned}
2\,\mathrm{Al(s,25\,^\circ)} + \mathrm{Fe_2O_3(s,25\,^\circ)} &\longrightarrow 2\,\mathrm{Fe(l,1758\,^\circ)} + \mathrm{Al_2O_3(s,1758\,^\circ)} \quad \Delta H = -732.5\ \mathrm{kJ} \quad \text{(a)} \\
2\,\mathrm{Fe(l,1758\,^\circ)} &\longrightarrow 2\,\mathrm{Fe(s,1758\,^\circ)} \quad \Delta H = -27.6\ \mathrm{kJ} \quad \text{(b)} \\
2\,\mathrm{Fe(s,1758\,^\circ)} + \mathrm{Al_2O_3(s,1758\,^\circ)} &\longrightarrow 2\,\mathrm{Fe(s,25\,^\circ)} + \mathrm{Al_2O_3(s,25\,^\circ)} \quad \Delta H = -91.0\ \mathrm{kJ} \\
\hline
2\,\mathrm{Al(s,25\,^\circ)} + \mathrm{Fe_2O_3(s,25\,^\circ)} &\longrightarrow \mathrm{Al_2O_3(s,25\,^\circ)} + 2\,\mathrm{Fe(s,25\,^\circ)}
\end{aligned} \qquad (1.2.3.1)$$

The net reaction in part (d) in Equation 1.2.3.1 is identical to the equation for the thermite reaction that we saw in a previous section. By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 1.2.3.1.

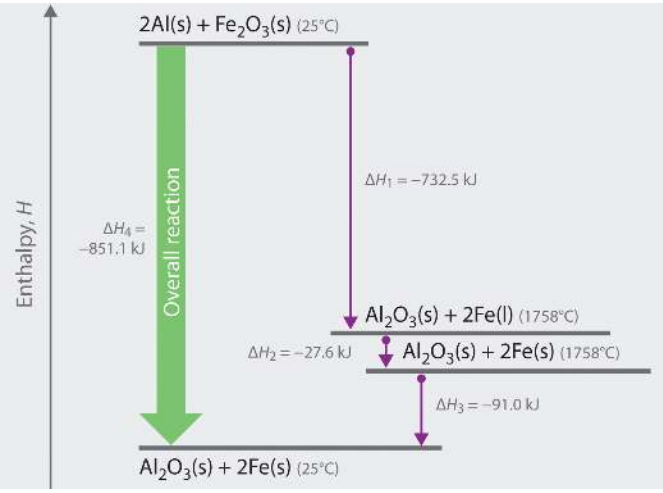


Figure **1.2.3.1**: Energy Changes accompanying the thermite reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.

Comparing parts (a) and (d) in Equation 1.2.3.1 also illustrates an important point: The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution). When the product is liquid iron at its melting point (part (a) in Equation 1.2.3.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 1.2.3.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation. We illustrate how to use this procedure in Example **1.2.3.1**.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

✔ Example 1.2.3.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$(1)\ \ 2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \quad \Delta H = -221.0\ kJ$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ \ C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5\ kJ$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)

B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ \ \mathrm{CO(g)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H_{rxn} = ?$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2\,\mathrm{CO(g)} \longrightarrow 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \quad \Delta H = +221.0\ \mathrm{kJ}$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(s)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(s)} \quad \Delta H = -787.0\ \mathrm{kJ}$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{lll} 2\,\mathrm{CO(g)} \longrightarrow \cancel{2C(s)} + \cancel{O_2(g)} & \Delta H = -\Delta H_1 = +221.0\ \mathrm{kJ} \\ \cancel{2C(s)} + \cancel{2}\ \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H = -2\Delta H_2 = -787.0\ \mathrm{kJ} \\ \hline 2\,\mathrm{CO(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H = -566.0\ \mathrm{kJ} \end{array}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$\mathrm{CO(g)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H = -283.0\ \mathrm{kJ}$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{lll} \text{(A)} & 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \cancel{2CO(g)} & \Delta H_A = \Delta H_1 = +221.0\ \mathrm{kJ} \\ \text{(B)} & \cancel{2CO(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H_B = ? \\ \text{(C)} & 2\,\mathrm{C(s)} + 2\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} & \Delta H = 2\Delta H_2 = 2 \times (-393.5\ \mathrm{kJ}) = -787.0\ \mathrm{kJ} \end{array}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore −566.0 ÷ 2 = −283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, there may be more than one correct way to solve a problem.

Exercise 1.2.3.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer

−136.3 kJ/mol of C_2H_4



Hess's Law: Hess's Law, YouTube(opens in new window) [youtu.be]

Summary

Hess's law is arguing the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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1.2.4: Enthalpies of Reaction from Standard Heats of Formation

Learning Objectives

- To understand Enthalpies of Formation and be able to use them to calculate Enthalpies of Reaction

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements:

$$\textbf{elements} \rightarrow \textbf{compound}$$

which in terms of the the Enthalpy of formation becomes

$$\Delta H_{rxn} = \Delta H_f \tag{1.2.4.1}$$

For example, consider the combustion of carbon:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)}$$

then

$$\Delta H_{rxn} = \Delta H_f\,[CO_2\,(g)]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH_f°) The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

> *The standard enthalpy of formation of any element in its standard state is zero by definition.*

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of

elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 1.2.4.1). Therefore, $O_2(g)$, $H_2(g)$, and graphite have ΔH_f^o values of zero.

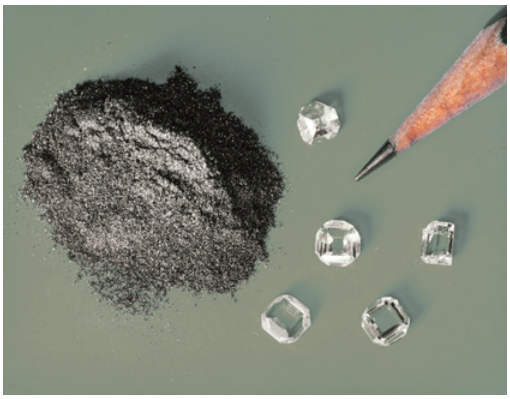


Figure 1.2.4.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ \tag{1.2.4.2}$$

It is not possible to measure the value of $\Delta H^o{}_f$ for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, O_2, and H_2 and measuring the heat evolved as glucose is formed since the reaction shown in Equation 1.2.4.2 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of $\Delta H^o{}_f$ are obtained using **Hess's law** and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH_f^o for an extensive list of compounds are given in Table T1. Note that ΔH_f^o values are always reported in kilojoules per mole of the substance of interest. Also notice in Table T1 that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

✔ Example 1.2.4.1: Enthalpy of Formation

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $HCl\,(g)$
b. $MgCO_3\,(s)$
c. $CH_3(CH_2)_{14}CO_2H\,(s)$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

Use Table T1 to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in Table T1: by a ΔH_f^o value of 0 kJ/mol.

Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2\,(g)$ and $Cl_2\,(g)$, respectively, the unbalanced chemical equation is

$$\mathrm{H_2\,(g) + Cl_2\,(g) \rightarrow HCl\,(g)}$$

Fractional coefficients are required in this case because ΔH^{o}_{f} values are reported for *1 mol* of the product, **HCl**. Multiplying both $\mathrm{H_2\,(g)}$ and $\mathrm{Cl_2\,(g)}$ by 1/2 balances the equation:

$$\mathrm{\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow HCl\,(g)}$$

The standard states of the elements in this compound are $\mathrm{Mg\,(s)}$, $\mathrm{C\,(s,\,graphite)}$, and $\mathrm{O_2\,(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg\,(s) + C\,(s,\,graphite) + O_2\,(g) \rightarrow MgCO_3\,(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg\,(s) + C\,(s,\,graphite) + \tfrac{3}{2}\,O_2\ (g) \rightarrow MgCO_3\,(s)}$$

Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C\,(s,\,graphite) + H_2\,(g) + O_2\,(g) \rightarrow CH_3(CH_2)_{14}CO_2H\,(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

$$\mathrm{16\,C\,(s,\,graphite) + 16\,H_2\,(g) + O_2\,(g) \longrightarrow CH_3(CH_2)_{14}CO_2H\,(s)}$$

? Exercise 1.2.4.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl\,(s)}$
b. $\mathrm{H_2SO_4\,(l)}$
c. $\mathrm{CH_3CO_2H\,(l)}$ (*acetic acid*)

Answer a

$$\mathrm{Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow NaCl\,(s)}$$

Answer b

$$\mathrm{H_2\,(g) + \tfrac{1}{8}\,S_8\,(s) + 2\,O_2\ (\ g) \rightarrow H_2\ SO_4(\ l)}$$

Answer c

$$\mathrm{2\,C\,(s) + O_2\,(g) + 2\,H_2\,(g) \longrightarrow CH_3CO_2H\,(l)}$$



Definition of Heat of Formation Reactions: https://youtu.be/A20k0CK4doI

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction ΔH_{rxn}^o is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{1.2.4.3}$$

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H_{rxn}^o = \underbrace{\left[c\Delta H_f^o\left(C\right) + d\Delta H_f^o\left(D\right)\right]}_{\text{products}} - \underbrace{\left[a\Delta H_f^o\left(A\right) + b\Delta H_f^o\left(B\right)\right]}_{\text{reactants}} \tag{1.2.4.4}$$

More generally, we can write

$$\Delta H_{rxn}^o = \sum m\Delta H_f^o\left(products\right) - \sum n\Delta H_f^o\left(reactants\right) \tag{1.2.4.5}$$

where the symbol $\sum$ means "sum of" and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively. "Products minus reactants" summations such as Equation 1.2.4.5 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, "products minus reactants" summations are very common in chemistry; we will encounter many others in subsequent chapters.

> "Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$\mathrm{C_6H_{12}O_6\left(s\right) + 6\,O_2\left(g\right) \rightarrow 6\,CO_2\left(g\right) + 6\,H_2O\left(l\right)} \tag{1.2.4.6}$$

Using Equation 1.2.4.5, we write

$$\begin{aligned} &\Delta H_f^o \\ &= \left\{6\Delta H_f^o\left[CO_2\left(g\right)\right] + 6\Delta H_f^o\left[H_2O\left(g\right)\right]\right\} - \left\{\Delta H_f^o\left[C_6H_{12}O_6\left(s\right)\right] + 6\Delta H_f^o\left[O_2\left(g\right)\right]\right\} \end{aligned} \tag{1.2.4.7}$$

From Table T1, the relevant ΔH^o_f values are $\Delta H^o_f\,[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f\,[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f\,[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f\,[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 1.2.4.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H_{comb}^o = \left[6\left(-393.5\ kJ/mol\right) + 6\left(-285.8\ kJ/mol\right)\right] - \left[-1273.3 + 6\left(0\ kJ\ mol\right)\right] \tag{1.2.4.8}$$

$$= -2802.5\ kJ/mol \tag{1.2.4.9}$$

As illustrated in Figure **1.2.4.2**, we can use Equation 1.2.4.8 to calculate ΔH_f^o for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH_{comb}^o. The alternative hypothetical pathway consists of **four separate reactions** that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH_f^o values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}\Delta H_1^o &= \Delta H_f^o\,[glucose\,(s)]\\ &= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right)\\ &= +1273.3\ kJ\\ \Delta H_2^o &= 6\Delta H_f^o\,[O_2\,(g)]\\ &= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right)\\ &= 0\ kJ\end{aligned} \tag{1.2.4.10}$$

> *Recall that when we reverse a reaction, we must also reverse the* ***sign*** *of the accompanying enthalpy change (Equation 1.2.4.4 since the products are now reactants and vice versa.*

The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

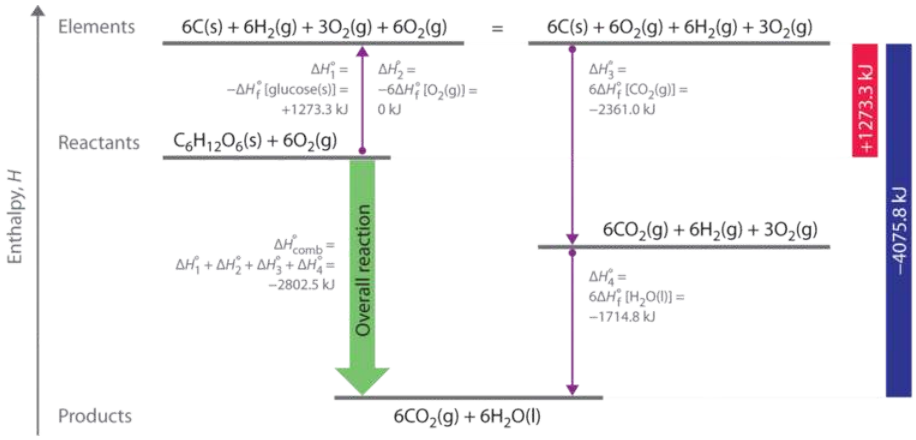


Figure 1.2.4.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 1.2.4.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\begin{aligned}\Delta H_3^o &= \Delta H_f^o\,[CO_2\,(g)] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ\\ \Delta H_4^o &= 6\Delta H_f^o\,[H_2O\,(l)] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ\end{aligned} \tag{1.2.4.11}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H_{comb}^o = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{1.2.4.12}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 1.2.4.5) and ΔH^o_f values. The two results must be the same because Equation 1.2.4.12 is just a more compact way of describing the thermochemical cycle shown in Figure

Example 1.2.4.2: Heat of Combustion

Long-chain fatty acids such as palmitic acid ($CH_3(CH_2)_{14}CO_2H$) are one of the two major sources of energy in our diet (ΔH_f^o =−891.5 kJ/mol). Use the data in Table T1 to calculate ΔH^o_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH_f^o values

Asked for: ΔH^o_{comb} per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 1.2.4.5 and the values from Table T1 to calculate ΔH^o_{comb} the energy released by the combustion of 1 mol of palmitic acid.

B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 1.2.4.8 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH_f^o. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)}$$

Using Equation 1.2.4.5 (“products minus reactants”) with ΔH^o_f values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned}\Delta H^o_{comb} &= \sum m\Delta H_f^o\,(products) - \sum n\Delta H_f^o\,(reactants)\\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\,)]\\ &\quad - [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\,)]\\ &= -9977.3\ kJ/mol\end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 1.2.4.8, \(ΔH^o_f\) of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

Exercise 1.2.4.2: Water–gas shift reaction

Use Table T1 to calculate ΔH^o_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain H_2(g):

$$CO\ (g) + H_2O\ (g) \longrightarrow CO_2\,(g) + H_2\ (g)$$

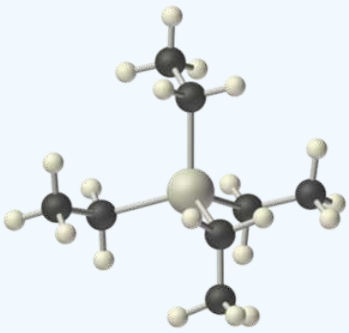
Answer

−41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH_f° which we cannot obtain otherwise. This procedure is illustrated in Example **1.2.4.3**.

Example 1.2.4.3: Tetraethyllead

Beginning in 1923, tetraethyllead [$(C_2H_5)_4Pb$] was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $CO_2(g)$, $H_2O(l)$, and red $PbO(s)$. What is the standard enthalpy of formation of tetraethyllead, given that ΔH_f° is −19.29 kJ/g for the combustion of tetraethyllead and ΔH_f° of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH_{comb}° values

Asked for: ΔH_f° of the reactants

Strategy:

A. Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 1.2.4.5 to get the equation for ΔH°_f of tetraethyl lead.
B. Convert ΔH_{comb}° per gram given in the problem to ΔH_{comb}° per mole by multiplying ΔH_{comb}° per gram by the molar mass of tetraethyllead.
C. Use Table T1 to obtain values of ΔH_f° for the other reactants and products. Insert these values into the equation for ΔH_f° of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2\,(C_2H_5)_4Pb\,(l) + 27\,O_2\,(g) \longrightarrow 2\,PbO\,(s) + 16\,CO_2\,(g) + 20\,H_2O\,(l)$$

Using Equation 1.2.4.5 gives

$$\Delta H_{comb}^\circ = \left[2\Delta H_f^\circ\,(PbO) + 16\Delta H_f^\circ\,(CO_2) + 20\Delta H_f^\circ\,(H_2O)\right] - \left[2\Delta H_f^\circ\,((C_2H_5)_4Pb) + 27\Delta H_f^\circ\,(O_2)\right]$$

Solving for $\Delta H_f^\circ[(C_2H_5)_4Pb]$ gives

$$\Delta H_f^\circ\,((C_2H_5)_4Pb) = \Delta H_f^\circ\,(PbO) + 8\Delta H_f^\circ\,(CO_2) + 10\Delta H_f^\circ\,(H_2O) - \frac{27}{2}\Delta H_f^\circ\,(O_2) - \frac{\Delta H_{comb}^\circ}{2}$$

The values of all terms other than $\Delta H_f^\circ[(C_2H_5)_4Pb]$ are given in Table T1.

B The magnitude of ΔH_{comb}° is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH_{comb}° for 1 mol of tetraethyl lead:

$$\Delta H_{comb}^\circ = \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right)$$
$$= -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^o_{rxn} is

$$\Delta H^o_{rxn} = 2 \ \cancel{mol\ (C_2H5)_4Pb} \left(\frac{-6329\ kJ}{1\ \cancel{mol\ (C_2H5)_4Pb}} \right)$$

$$= -12,480\ kJ$$

C Inserting the appropriate values into the equation for $\Delta H^o_f[(\mathbf{C_2H_5})_4\mathbf{Pb}]$ gives

$$\Delta H^o_f[(C_2H_4)_4 Pb] = [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\ [12,480.2\ kJ/mol\ (C_2H_5)_4Pb]$$

$$= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol$$

? Exercise 1.2.4.3

Ammonium sulfate, $(\mathbf{NH_4})_2\mathbf{SO_4}$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$\mathbf{2\,NH_3\,(g) + H_2SO_4\,(aq)\ \rightarrow (NH_4)_2SO_4\,(s)}$$

The value of ΔH^o_{rxn} is -179.4 kJ/mole $\mathbf{H_2SO_4}$. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer

−1181 kJ/mol



Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

Summary

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 °C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH^o_f) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH^o_{rxn}) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the “products minus reactants” rule. The **enthalpy of solution** (

ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Contributors and Attributions

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SECTION OVERVIEW

1.3: QUANTA

QUANTA

1.3.1: Blackbody Radiation Cannot Be Explained Classically

1.3.2: Quantum Hypothesis Used for Blackbody Radiation Law

1.3.3: Photoelectric Effect Explained with Quantum Hypothesis

1.3.4: The Hydrogen Atomic Spectrum

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1.3.1: Blackbody Radiation Cannot Be Explained Classically

Learning Objectives

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation. Objectives for this section include

- Be familiar with black-body radiators
- Apply Stefan-Boltzmann's Law to estimate total light output from a radiator
- Apply Wien's Displacement Law to estimate the peak wavelength (or frequency) of the output from a black body radiator
- Understand the Rayleigh-Jeans Law and how it fails to properly model black-body radiation

All normal matter at temperatures above absolute zero emits electromagnetic radiation, which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*. Conversely, all normal matter *absorbs* electromagnetic radiation to some degree. An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody. When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called *blackbody radiation*.

A room temperature blackbody appears black, as most of the energy it radiates is infra-red and cannot be perceived by the human eye. Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey, even though its objective physical spectrum peaks in the infrared range. When it becomes a little hotter, it appears dull red. As its temperature increases further it becomes yellow, white, and ultimately blue-white.



Figure 1.1.1 : Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature. In fact, we can be much more precise:

> *A body emits radiation at a given temperature and frequency exactly as well as it absorbs the same radiation.*

This statement was proved by Gustav Kirchhoff: the essential point is that if we *instead* suppose a particular body can absorb better than it emits, then in a room full of objects all at the same temperature, it will absorb radiation from the other bodies better than it radiates energy back to them. This means it will get hotter, and the rest of the room will grow colder, contradicting the second law of thermodynamics. *Thus, a body must emit radiation exactly as well as it absorbs the same radiation at a given temperature and frequency in order to not violate the second law of thermodynamics.*

Any body at any temperature above absolute zero **will** radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter.* So how do we construct a perfect absorber in the laboratory? In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a

lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find (Figure 1.1.2).

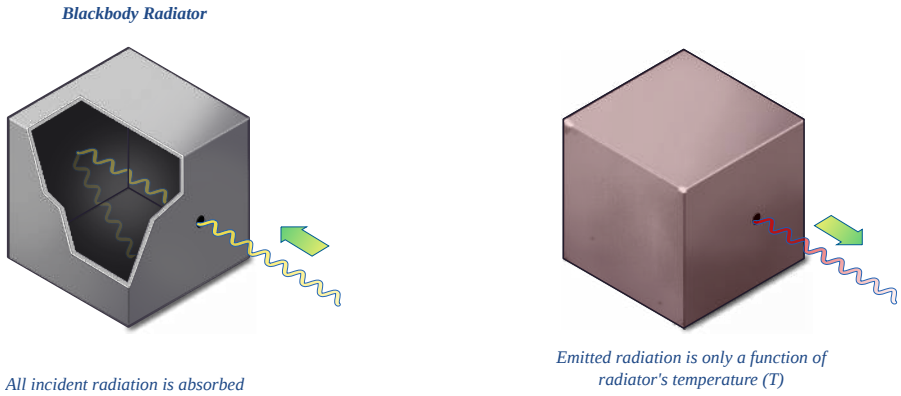


Figure 1.1.2 : Blackbody radiator is any object that is a perfect emitter and a perfect absorber of radiation. (CC BY-NC; Ümit Kaya via LibreTexts)

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution of blackbody radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven, and began to measure the radiation coming out. The beam coming out of the hole was passed through a diffraction grating, which sent the different wavelengths/frequencies in different directions, all towards a screen. A detector was moved up and down along the screen to find how much radiant energy was being emitted in each frequency range. They found a radiation intensity/frequency curve close to the distributions in Figure 1.1.3 .

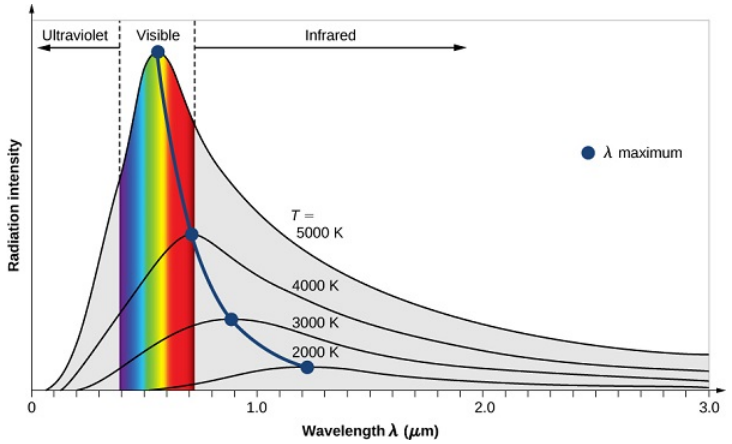
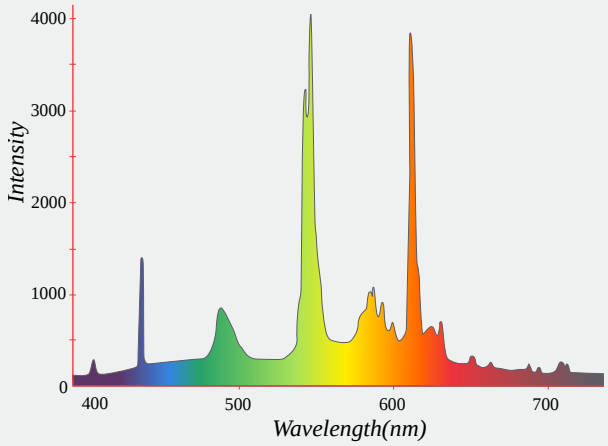


Figure 1.1.3 : Graphic representation of spectral distribution of blackbody radiation at different temperatures. The Stefan-Boltzmann's Law is observed as the increase in the emission amplitude with increasing temperature and the Wien's Displacement Law is observed as the shift to smaller wavelength with increasing temperature. (CC-BY 4.0; OpenStax)

By measuring the blackbody emission curves at different temperatures (Figure 1.1.3), they were also able to construct two important phenomenological Laws (i.e., formulated from experimental observations, not from basic principles of nature): **Stefan-Boltzmann's Law** and **Wien's Displacement Law**.

Not all radiators are blackbody radiators

The radiation of a blackbody radiator is produced by the thermal activity of the material, not the nature of the material, nor how it got thermally excited. Some examples of blackbodies include incandescent light bulbs, stars, and hot stove tops. The emission appears as a continuous spectrum (Figure 1.1.3) with multiple coexisting colors. However, not every radiator is a blackbody radiator. For example, the emission of a fluorescence bulb is not one. The following spectrum show the distribution of light from a fluoresce light tube and is a mixture of discrete bands at different wavelengths of light in contrast to the continuous spectra in Figure 1.1.3 for blackbody radiators.



Fluorescent lighting spectrum with emission peaks. Graph of Intensity (counts) vs. Wavelength (nm) in the visible spectrum. (CC BY-NC; Ümit Kaya via LibreTexts).

Fluorescent light bulbs contain a mixture of inert gases (usually argon and neon) together with a drop of mercury at low pressure. A different mix of visible colors blend to produce a light that appears to us white with different shadings.

The Stefan-Boltzmann Law

The first quantitative conjecture based on experimental observations was the **Stefan-Boltzmann Law** (1879) which states the total power (i.e., integrated over all emitting frequencies in Figure 1.1.3) radiated from one square meter of black surface goes as the *fourth power* of the absolute temperature (Figure 1.1.4):

$$P = \sigma T^4 \tag{1.3.1.1}$$

where

- P is the total amount of radiation emitted by an object per square meter ($Watts/m^2$)
- σ is a constant called the Stefan-Boltzman constant ($5.67 \times 10^{-8}\ Watts\ m^{-2}K^{-4}$)
- T is the absolute temperature of the object (in K)

The Stefan-Boltzmann Law is easily observed by comparing the integrated value (i.e., under the curves) of the experimental black-body radiation distribution in Figure 1.1.3 at different temperatures. In 1884, Boltzmann derived this T^4 behavior from theory by applying classical thermodynamic reasoning to a box filled with electromagnetic radiation, using Maxwell's equations to relate pressure to energy density. That is, the tiny amount of energy coming out of the hole (Figure 1.1.2) would of course have the same temperature dependence as the radiation intensity inside.

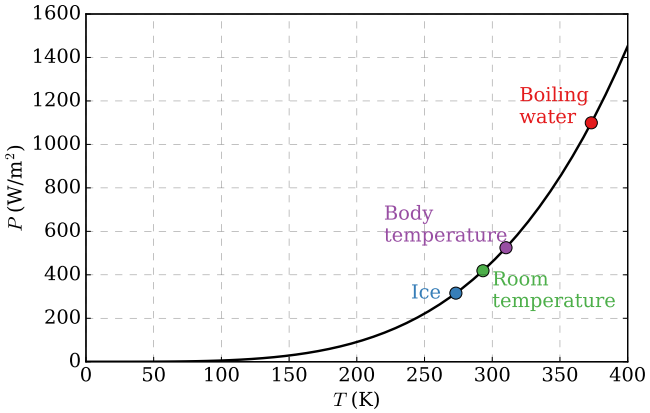


Figure 1.1.4 : Graph of a function of total emitted energy of a blackbody proportional to the fourth power of its thermodynamic temperature T according to the Stefan–Boltzmann law. (CC BY-SA 4.0; Nicoguaro)

Example 1.1.1

The sun's surface temperature is 5700 K.

a. How much power is radiated by the sun?
b. Given that the distance to earth is about 200 sun radii, what is the maximum power possible from a one square kilometer solar energy installation?

Solution

(a) First, we calculate the area of the sun followed by the flux (power). The sun has a radius of $6.96 \times 10^8 m$

The area of the sun is $A = 4\pi R^2$.

$$\begin{aligned} A &= 4(3.1416)(6.96 \times 10^8 m)^2 \\ &= 6.08 \times 10^{18} m^2 \end{aligned}$$

The power radiated from the sun (via Stefan-Boltzmann Law) is $P = \sigma T^4$ (Equation 1.3.1.1).

$$\begin{aligned} P &= (5.67 \times 10^{-8}\, Watts\, m^{-2} K^{-4})(5700K)^4 \\ &= 5.98 \times 10^7 Watts/m^2 \end{aligned}$$

This value is per square meter.

(b) To calculate the total power radiated by the sun is thus:

$$\begin{aligned} P_{total} = PA &= (5.98 \times 10^7 Watts/m^2)(6.08 \times 10^{18} m^2) \\ &= 3.6 \times 10^{26} Watts \end{aligned}$$

Wien's Displacement Law

The second phenomenological observation from experiment was **Wien's Displacement Law**. Wien's law identifies the dominant (peak) wavelength, or color, of light coming from a body at a given temperature. As the oven temperature varies, so does the frequency at which the emitted radiation is most intense (Figure 1.1.3). In fact, that frequency is directly proportional to the absolute temperature:

$$\nu_{max} \propto T \tag{1.3.1.2}$$

where the proportionality constant is $5.879 \times 10^{10} Hz/K$.

Wien himself deduced this law theoretically in 1893, following Boltzmann's thermodynamic reasoning. It had previously been observed, at least semi-quantitatively, by an American astronomer, Langley. This upward shift in ν_{max} with T is familiar to everyone—when an iron is heated in a fire (Figure 1.1.1), the first visible radiation (at around 900 K) is deep red, the lowest frequency visible light. Further increase in T causes the color to change to orange then yellow, and finally blue at very high temperatures (10,000 K or more) for which the peak in radiation intensity has moved beyond the visible into the ultraviolet.

Another representation of Wien's Law (Equation 1.3.1.2) in terms of the peak wavelength of light is

$$\lambda_{max} = \frac{b}{T} \tag{1.3.1.3}$$

where T is the absolute temperature in kelvin and b is a constant of proportionality called **Wien's displacement constant**, equal to $2.89 \times 10^{-3} m\ K$, or more conveniently to obtain wavelength in micrometers, $b \approx 2900\ \mu m \cdot K$. This is an inverse relationship between wavelength and temperature. So the higher the temperature, the shorter or smaller the wavelength of the thermal radiation. The lower the temperature, the longer or larger the wavelength of the thermal radiation. For visible radiation, hot objects emit bluer light than cool objects.

✔ Example 1.1.2

If surface body temperature is 90 °F.

a. How much radiant energy in $W\, m^{-2}$ would your body emit?
b. What is the peak wavelength of emitted radiation?

c. What is the total radiant energy emitted by your body in Watts? Note: The average adult human male has a body surface area of about 1.9 m^2 and the average body surface area for a woman is about 1.6 m^2.

Solution

(a) 90 °F is 305 K. We use Stefan-Boltzmann Law (Equation 1.3.1.1). The total amount of radiation emitted will be $P = \sigma T^4$.

$$\begin{aligned} P &= (5.67 \times 10^{-8}\, Watts\, m^{-2} K^{-4})(305K)^4 \\ &= 491 W\, m^{-2} \end{aligned}$$

The peak wavelength of emitted radiation is found using Wien's Law:

$$\begin{aligned} \lambda_{max} &= \frac{2.898 \times 10^{-3} m \cdot K}{T} \\ &= \frac{2.898 \times 10^{-3} m \cdot K}{305K} \\ &= 9.5 \times 10^{-6} m = 9.5 \mu m \end{aligned}$$

The total radiant energy density in Watts is :

$$\begin{aligned} \text{Energy}_{\text{male}} &= (491 W\, m^{-2})(1.9 m^2) = 933 W \\ \text{Energy}_{\text{female}} &= (491 W\, m^{-2})(1.6 m^2) = 786 W \end{aligned}$$

Example 1.1.3 : The Temperature of the Sun

For example, if the Sun has a surface temperature of 5700 K, what is the wavelength of maximum intensity of solar radiation?

Solution

If we substitute 5700 K for T in Equation 1.3.1.3, we have

$$\begin{aligned} \lambda_{max} &= \frac{0.0029}{5700} \\ &= 5.1 \times 10^{-7}\, m \end{aligned}$$

Knowing that violet light has a wavelength of about 4.0×10^{-7} meters, yellow about 5.6×10^{-7} meters, and red about 6.6×10^{-7} meters, what can we say about the color of the Sun's peak radiation? The peak wavelength of the Sun's radiation is at a slightly shorter wavelength than the color yellow, so it is a slightly greenish yellow. To see this greenish tinge to the Sun, you would have to look at it from space. It turns out that the Earth's atmosphere scatters some of the shorter waves of sunlight, which shifts its peak wavelength to pure yellow.

Remember that thermal radiation always spans a wide range of wavelengths (Figure 1.1.2) and Equation 1.3.1.3 only specifies the single wavelength that is the **peak** of the spectrum. So although the Sun appears yellowish-white, when you disperse sunlight with a prism you see radiation with all the colors of the rainbow. Yellow just represents a characteristic wavelength of the emission.

Exercise 1.1.1

a. At what wavelength does the sun emit most of its radiation if it has a temperature of 5,778 K?
b. At what wavelength does the earth emit most of its radiation if it has a temperature of 288 K?

Answer a

500 nm

Answer b

10.0 microns

The Rayleigh-Jeans Law

Lord Rayleigh and J. H. Jeans developed an equation which explained blackbody radiation at low frequencies. The equation which seemed to express blackbody radiation was built upon all the known assumptions of physics at the time. *The big assumption which Rayleigh and Jean implied was that infinitesimal amounts of energy were continuously added to the system when the frequency was increased*. Classical physics assumed that energy emitted by atomic oscillations could have any continuous value. This was true for anything that had been studied up until that point, including things like acceleration, position, or energy. Their resulting **Rayleigh-Jeans Law** was

$$d\rho\left(\nu,T\right)=\rho_{\nu}\left(T\right)d\nu \tag{1.3.1.4}$$

$$=\frac{8\pi k_{B}T}{c^{3}}\nu^{2}d\nu \tag{1.3.1.5}$$

Experimental data performed on the black box showed slightly different results than what was expected by the Rayleigh-Jeans law (Figure 1.1.5). The law had been studied and widely accepted by many physicists of the day, but the experimental results did not lie, something was different between what was theorized and what actually happens. The experimental results showed a bell type of curve, but according to the Rayleigh-Jeans law the frequency diverged as it neared the ultraviolet region (Equation 1.3.1.5). Ehrenfest later dubbed this the "ultraviolet catastrophe". It is important to emphasizing that Equation 1.3.1.5 is a **classical** result: the only inputs are classical dynamics and Maxwell's electromagnetic theory.

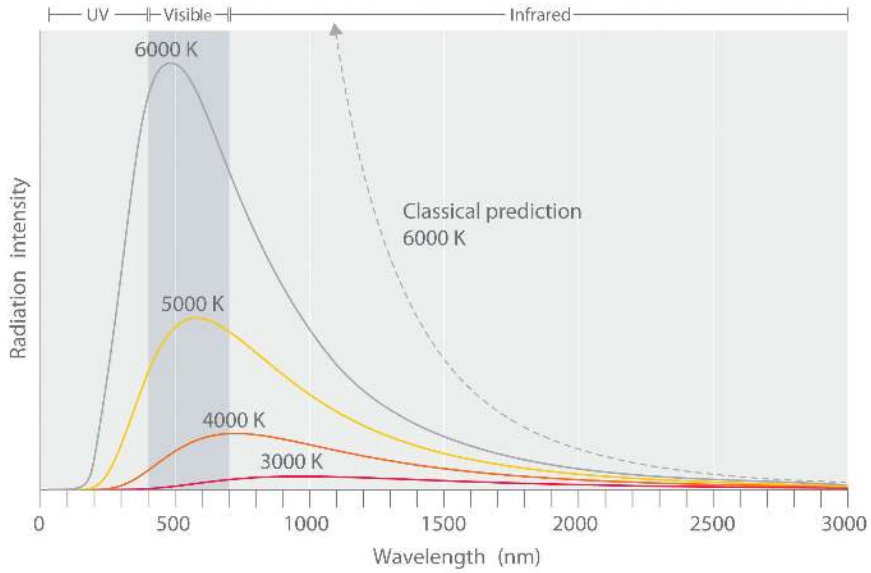


Figure 1.1.5 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the hot metalwork in Figure 1.1.5 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. (CC BY-SA-NC; anonymous)

Differential vs. Integral Representation of the Distribution

Radiation is understood as a continuous distribution of amplitude vs. wavelength or, equivalently, amplitude vs. frequency (Figure 1.1.5). According to Rayleigh-Jeans law, the intensity at a specific frequency ν and temperature is

$$\rho(\nu,T)=\frac{8\pi k_{b}T\nu^{2}}{c^{3}}.$$

However, in practice, we are more interested in frequency intervals. An exact frequency is the limit of a sequence of smaller and smaller intervals. If we make the assumption that, for a sufficiently small interval, $\rho(\nu,T)$ does not vary, we get your definition for the differential $d\rho(\nu,T)$ in Equation 1.3.1.5:

The assumption is fair due to the continuity of $\rho(\nu, T)$. This is the approximation of an integral on a very small interval $d\nu$ by the height of a point inside this interval ($\frac{8\pi k_b T\nu^2}{c^3}$) times its length ($d\nu$). So, if we sum an infinite amount of small intervals like the one above we get an integral. The total radiation between ν_1 and ν_2 will be:

$$\begin{aligned}\int_{\nu_1}^{\nu_2} \mathrm{d}\rho(\nu, T) &= \int_{\nu_1}^{\nu_2} \rho(\nu, T)\,\mathrm{d}\nu \\ &= \int_{\nu_1}^{\nu_2} \frac{8\pi k_b T\nu^2}{c^3}\mathrm{d}\nu \\ &= 8\pi k_b T\frac{v_2^3 - v_1^3}{3c^3}.\end{aligned}$$

Observe that $\rho(\nu, T)$ is quadratic in ν.

Example 1.1.4 : The Ultraviolet Catastrophe

What is the total spectral radiance of a radiator that follows the Rayleigh-Jeans law for its emission spectrum?

Solution

The total spectral radiance $\rho_{tot}(T)$ is the combined emission over all possible wavelengths (or equivalently, frequencies), which is an integral over the relevant distribution (Equation 1.3.1.5 for the Rayleigh-Jeans Law).

$$\begin{aligned}\rho_{tot}(T) &= \int_0^\infty d\rho\,(\nu, T) \\ &= \int_0^\infty \frac{8\pi k_B T}{c^3}\nu^2 d\nu\end{aligned}$$

but the integral

$$\int_0^\infty x^2 \mathrm{d}x$$

does not converge. Worse, it is infinite,

$$\lim_{k\to\infty}\int_0^k x^2 \mathrm{d}x = \infty$$

Hence, the classically derived Rayleigh-Jeans law predicts that the radiance of a blackbody is **infinite**. Since radiance is power per angle and unit area, this also implies that the total power and hence the energy a blackbody emitter gives off is infinite, which is patently absurd. This is called the ultraviolet catastrophe because the absurd prediction is caused by the classical law not predicting the behavior at high frequencies/small wavelengths correctly (Figure 1.1.5).

Contributors and Attributions

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1.3.2: Quantum Hypothesis Used for Blackbody Radiation Law

Learning Objectives

- To understand how energy is quantized in blackbody radiation

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could not be explained by the theories available at the time.

One experimental phenomenon that could not be adequately explained by classical physics was blackbody radiation (Figure 1.2.1). Attempts to explain or calculate this spectral distribution from classical theory were complete failures. A theory developed by Rayleigh and Jeans predicted that the intensity should go to infinity at short wavelengths. Since the intensity actually drops to zero at short wavelengths, the Rayleigh-Jeans result was called the **ultraviolet catastrophe** (Figure 1.2.1 dashed line). There was no agreement between theory and experiment in the ultraviolet region of the blackbody spectrum.

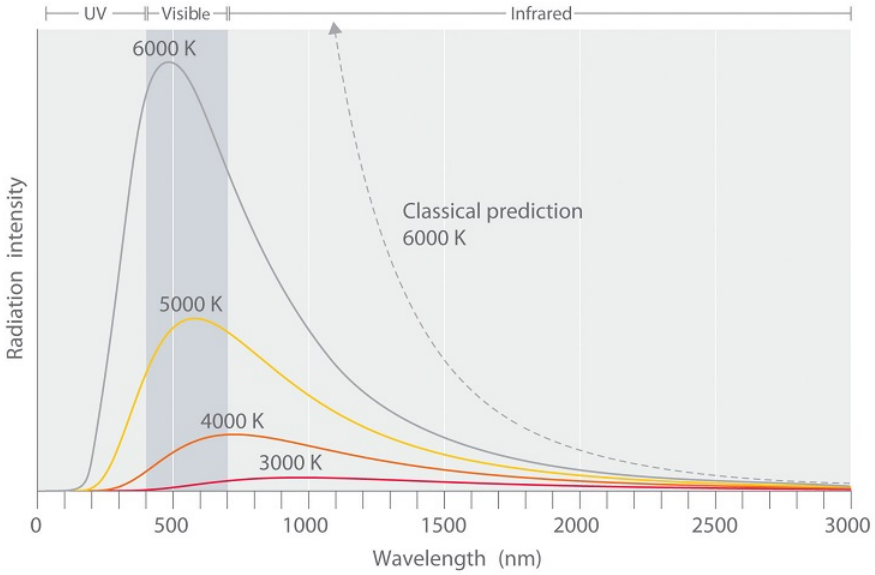


Figure 1.2.1 : Relationship between the temperature of an object and the spectrum of blackbody radiation it emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun. Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity. (CC BY-SA-NC; anonymous).

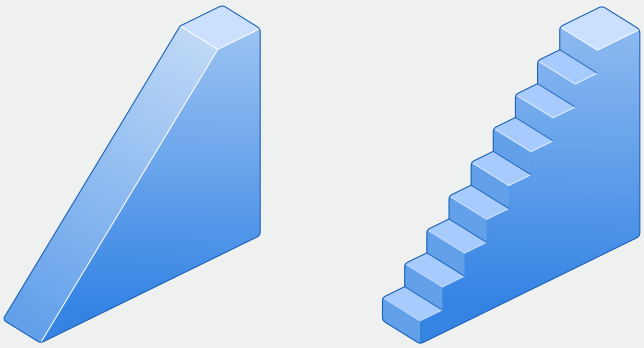
Quantizing Electrons in the Radiator

In 1900, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.2.1 , so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral

multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum.

Quantization

Although quantization may seem to be an unfamiliar concept, we encounter it frequently in quantum mechanics (hence the name). For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. It is also similar to going up and down a hill using discrete stair steps rather than being able to move up and down a continuous slope. Your potential energy takes on discrete values as you move from step to step. Even electrical charge is quantized: an ion may have a charge of −1 or −2, but *not* −1.33 electron charges.



A continuous vs. a quantized (gravitationaly) potential energy system. In the continuous case (left) a system can have any potential energy, but in the quantized case (right), a system can only have certain values (other values are not allowed). (CC BY-NC; Ümit Kaya via LibreTexts)

Planck's quantization of energy is described by the his famous equation:

$$E = h\nu \tag{1.3.2.1}$$

where the proportionality constant h is called **Planck's constant**, one of the most accurately known fundamental constants in science

$$h = 6.626070040(81) \times 10^{-34}\, J \cdot s$$

However, for our purposes, its value to four significant figures is sufficient:

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

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.2.1 . We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.2.1 , and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

Max Planck explain the spectral distribution of blackbody radiation as result from oscillations of electrons. Similarly, oscillations of electrons in an antenna produce radio waves. Max Planck concentrated on modeling the oscillating charges that must exist in the oven walls, radiating heat inwards and—in thermodynamic equilibrium—themselves being driven by the radiation field. He found he could account for the observed curve if he required these oscillators not to radiate energy continuously, as the classical theory would demand, but they could **only** lose or gain energy in chunks, called **quanta**, of size $h\nu$, for an oscillator of frequency ν (Equation 1.3.2.1).

With that assumption, Planck calculated the following formula for the radiation energy density inside the oven:

$$d\rho(\nu,T) = \rho_\nu(T)d\nu \tag{1.3.2.2}$$

$$= \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.3.2.3}$$

with

- $\pi = 3.14159$
- h = $6.626 \times 10^{-34} J \cdot s$
- c = $3.00 \times 10^8\, m/s$
- ν = $1/s$
- k_B = $1.38 \times 10^{-23} J/K$
- T is absolute temperature (in Kelvin)

Planck's radiation energy density (Equation 1.3.2.3) can also be expressed in terms of wavelength λ.

$$\rho(\lambda,T) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda k_BT}-1}\right) \tag{1.3.2.4}$$

With a wavelength of maximum energy density at:

$$\lambda_{max} = \frac{hc}{4.965kT}$$

This can be used to calculate the radiance emitted from surface per unit frequency

$$dB_\nu(\nu,T) = \rho_\nu(T)d\nu$$

$$= \frac{2h\nu^3}{c^2} \cdot \frac{1}{\exp\left(\frac{h\nu}{k_BT}\right)-1}d\nu \tag{1.3.2.5}$$

or

$$B_\lambda(\lambda,T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{hc/(\lambda k_BT)}-1} \tag{1.3.2.6}$$

Planck's equation (Equation 1.3.2.4) gave an excellent agreement with the experimental observations for all temperatures (Figure 1.2.2).

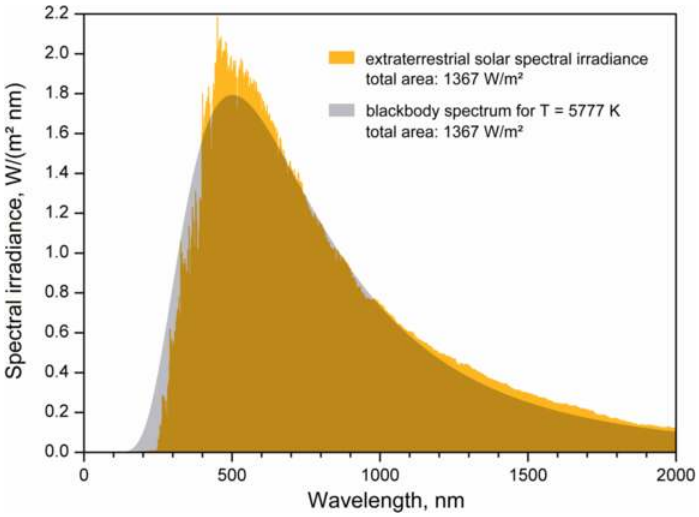
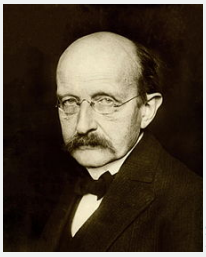


Figure 1.2.2 : The Sun is an excellent approximation of a blackbody. Its effective temperature is ~5777 K. (CC-SA-BY 3.0; Sch).

Max Planck (1858–1947)

Planck made many substantial contributions to theoretical physics, but his fame as a physicist rests primarily on his role as the originator of quantum theory. In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



MAX-PLANCK-GESELLSCHAFT

(left) The German physicist Max Planck had a major influence on the early development of quantum mechanics, being the first to recognize that energy is sometimes quantized. Planck also made important contributions to special relativity and classical physics. (Public Domain; Library of Congress via Wikimedia) (left) The society's logo features Minerva, the Roman goddess of wisdom. (Fair use)

One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the Max Planck Society.

Exercise 1.2.1

Use Equation 1.3.2.4 to show that the units of $\rho(\lambda, T)\, d\lambda$ are J/m^3 as expected for an energy density.

The near perfect agreement of this formula with precise experiments (e.g., Figure 1.2.3), and the consequent necessity of energy quantization, was the most important advance in physics in the century. His blackbody curve was completely accepted as the correct one: more and more accurate experiments confirmed it time and again, yet the radical nature of the quantum assumption did not sink in. Planck was not too upset—he didn't believe it either, he saw it as a technical fix that (he hoped) would eventually prove unnecessary.

> *Part of the problem was that Planck's route to the formula was long, difficult and implausible—he even made contradictory assumptions at different stages, as Einstein pointed out later. However, the result was correct anyway!*

The mathematics implied that the energy given off by a blackbody was not continuous, but given off at certain specific wavelengths, in regular increments. If Planck assumed that the energy of blackbody radiation was in the form

$$E = nh\nu$$

where n is an integer, then he could explain what the mathematics represented. This was indeed difficult for Planck to accept, because at the time, there was no reason to presume that the energy should only be radiated at specific frequencies. Nothing in Maxwell's laws suggested such a thing. It was as if the vibrations of a mass on the end of a spring could only occur at specific energies. Imagine the mass slowly coming to rest due to friction, but not in a continuous manner. Instead, the mass jumps from one fixed quantity of energy to another without passing through the intermediate energies.

> *To use a different analogy, it is as if what we had always imagined as smooth inclined planes were, in fact, a series of closely spaced steps that only presented the illusion of continuity.*

Summary

The agreement between Planck's theory and the experimental observation provided strong evidence that the energy of electron motion in matter is quantized. In the next two sections, we will see that the energy carried by light also is quantized in units of $h\bar{\nu}$. These packets of energy are called "photons."

Contributors and Attributions

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- David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski ("Quantum States of Atoms and Molecules")

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1.3.3: Photoelectric Effect Explained with Quantum Hypothesis

Learning Objectives

- To be familiar with the photoelectron effect for bulk materials
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light wavelength
- Understand how the photoelectron kinetic energy and intensity vary as a function of incident light intensity
- Describe what a workfunction is and relate it to ionization energy
- Describe the photoelectric effect with Einstein's quantized photon model of light

Nature, it seemed, was quantized (non-continuous, or discrete). If this was so, how could Maxwell's equations correctly predict the result of the blackbody radiator? Planck spent a good deal of time attempting to reconcile the behavior of electromagnetic waves with the discrete nature of the blackbody radiation, to no avail. It was not until 1905, with yet another paper published by Albert Einstein, that the wave nature of light was expanded to include the particle interpretation of light which adequately explained Planck's equation.

The photoelectric effect was first documented in 1887 by the German physicist Heinrich Hertz and is therefore sometimes referred to as the Hertz effect. While working with a spark-gap transmitter (a primitive radio-broadcasting device), Hertz discovered that upon absorption of certain frequencies of light, substances would give off a visible spark. In 1899, this spark was identified as light-excited electrons (called **photoelectrons**) leaving the metal's surface by J.J. Thomson (Figure 1.3.1).

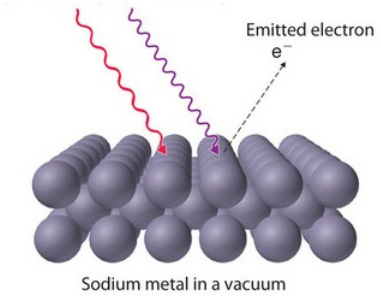


Figure 1.3.1 : The photoelectric effect involves irradiating a metal surface with photons of sufficiently high energy to cause the electrons to be ejected from the metal. (CC BY-SA-NC; anonymous)

The classical picture underlying the photoelectron effect was that the atoms in the metal contained electrons, that were shaken and caused to vibrate by the oscillating electric field of the incident radiation. Eventually some of them would be shaken loose, and would be ejected from the cathode. It is worthwhile considering carefully how the *number* and *speed* of electrons emitted would be expected to vary with the *intensity* and *color* of the incident radiation along with the time needed to observe the photoelectrons.

- Increasing the intensity of radiation would shake the electrons more violently, so one would expect more to be emitted, and they would shoot out at greater speed, on average.
- Increasing the frequency of the radiation would shake the electrons faster, so it might cause the electrons to come out faster. For very dim light, it would take some time for an electron to work up to a sufficient amplitude of vibration to shake loose.

Lenard's Experimental Results (Intensity Dependence)

In 1902, Hertz's student, Philipp Lenard, studied how the energy of the emitted photoelectrons varied with the intensity of the light. He used a carbon arc light and could increase the intensity a thousand-fold. The ejected electrons hit another metal plate, the collector, which was connected to the cathode by a wire with a sensitive ammeter, to measure the current produced by the illumination (Figure 1.3.2). To measure the energy of the ejected electrons, Lenard charged the collector plate negatively, to repel the electrons coming towards it. Thus, only electrons ejected with enough kinetic energy to get up this potential hill would contribute to the current.

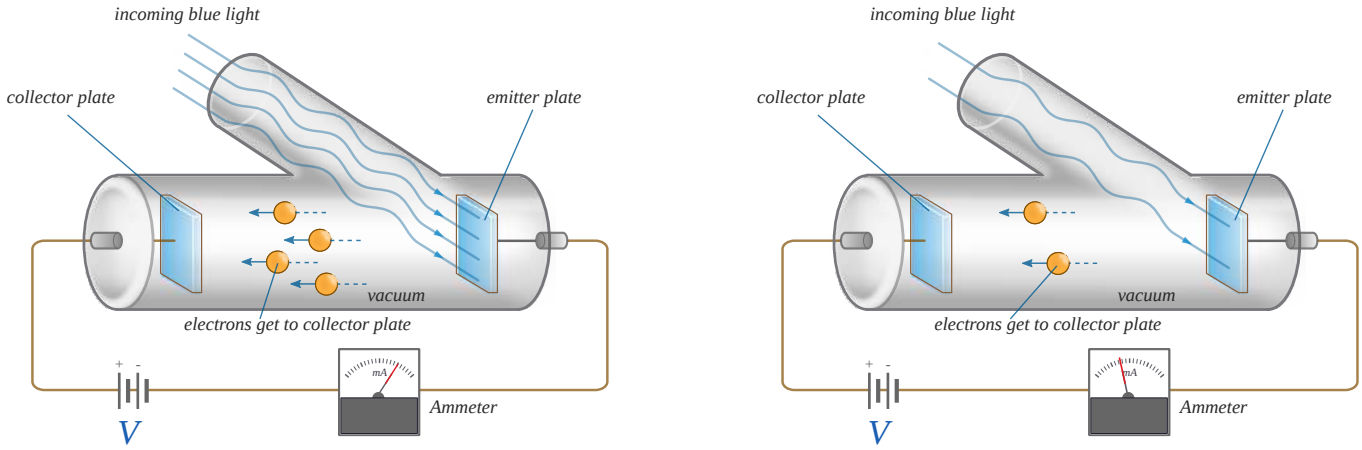


Figure **1.3.3.2**: Lenard's photoelectric experiment. (left) High light intensity increase photocurrent (number of collected photoelectrons). (right) Low light intensity has reduced photocurrent. However, the kinetic energy of the ejected electrons is independent of incident light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Lenard discovered that there was a well defined minimum voltage that stopped any electrons getting through (V_{stop}). To Lenard's surprise, he found that V_{stop} did not depend at all on the intensity of the light! Doubling the light intensity doubled the *number* of electrons emitted, but did not affect the *kinetic energies* of the emitted electrons. The more powerful oscillating field ejected more electrons, but the maximum individual energy of the ejected electrons was the same as for the weaker field (Figure 1.3.2).

Millikan's Experimental Results (Wavelength Dependence)

The American experimental physicist Robert Millikan followed up on Lenard's experiments and using a powerful arc lamp, he was able to generate sufficient light intensity to separate out the colors and check the photoelectric effect using light of different colors. He found that the maximum energy of the ejected electrons *did* depend on the color - the shorter wavelength, higher frequency light eject photoelectrons with greater kinetic energy (Figures 1.3.3).

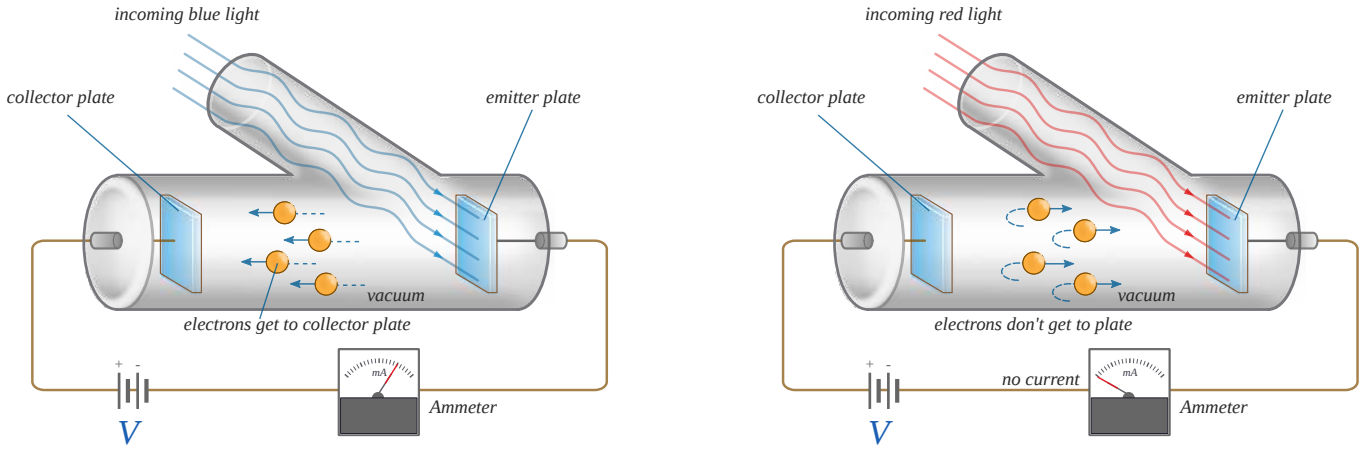


Figure 1.3.3 : Millikan's photoelectric experiment. (left) Incident high-energy blue light. The battery represents the potential Lenard used to charge the collector plate negatively, which would actually be a variable voltage source. Since the electrons ejected by the blue light are getting to the collector plate, the potential supplied by the battery is less than V_{stop}, for blue light. (right) Indicent low-energy red light. Since the electrons ejected by the red light are not getting to the collector plate, the potential supplied by the battery exceeds V_{stop} for red light. (CC BY-NC; Ümit Kaya via LibreTexts)

As shown in Figure 1.3.4 , just the opposite behavior from classical is observed from Lenard's and Millikan's experiments. The intensity affects the number of electrons, and the frequency affects the kinetic energy of the emitted electrons. From these sketches, we see that

- the kinetic energy of the electrons is linearly proportional to the frequency of the incident radiation above a threshold value of ν_0 (no current is observed below ν_0), and the kinetic energy is independent of the intensity of the radiation, and
- the number of electrons (i.e. the electric current) is proportional to the intensity and independent of the frequency of the incident radiation above the threshold value of ν_0 (i.e., no current is observed below ν_0).

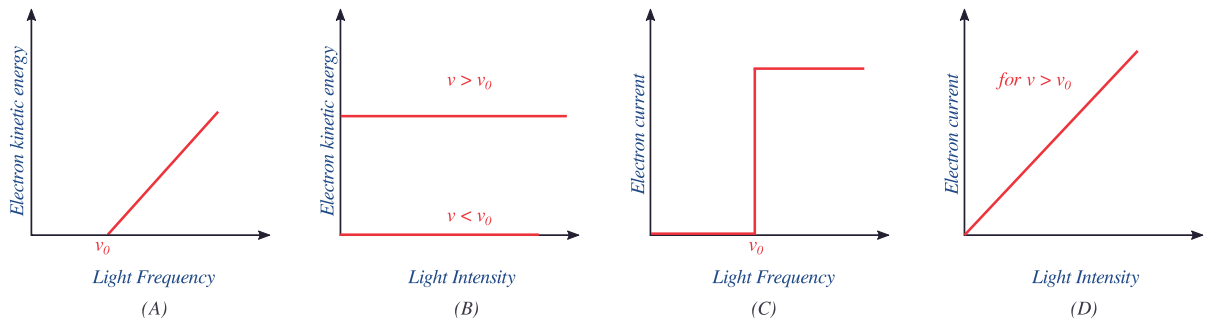


Figure 1.3.4 : Schematic drawings showing the characteristics of the photoelectric effect from Lenard's and Millikan's experiments. (A) The kinetic energy of any single emitted electron increases linearly with frequency above some threshold value (B) The electron kinetic energy is independent of the light intensity above the threshold frequency and zero below. (C) The number of electrons emitted per second (i.e. the electric current) is independent of light frequency above the threshhold frequency and zero below. (D) The number of electrons increases linearly with the light intensity. (CC BY-NC; Ümit Kaya via LibreTexts)

Classical Theory does not Describe Experiment

Classical theory predicts that energy carried by light is proportional to its amplitude independent of its frequency, and this fails to correctly explain the observed wavelength dependence in Lenard's and Millikan's observations.

As with most of the experimental results we discuss in this text, the behavior described above is a simplification of the true experimental results observed in the laboratory. A more complex description involves a greater introduction of more complex physics and instrumentation, which will be ignored for now.

Einstein's Quantum Picture

In 1905 Einstein gave a very simple interpretation of Lenard's results and borrowed Planck's hypothesis about the quantized energy from his blackbody research and assumed that the incoming radiation should be thought of as quanta of energy $h\nu$, with ν the frequency. In photoemission, one such quantum is absorbed by one electron. If the electron is some distance into the material of the cathode, some energy will be lost as it moves towards the surface. There will always be some electrostatic cost as the electron leaves the surface, which is the workfunction, Φ. The most energetic electrons emitted will be those very close to the surface, and they will leave the cathode with kinetic energy

$$KE = h\nu - \Phi \tag{1.3.3.1}$$

On cranking up the negative voltage on the collector plate until the current just stops, that is, to V_{stop}, the highest kinetic energy electrons (KE_e) must have had energy eV_{stop} upon leaving the cathode. Thus,

$$eV_{stop} = h\nu - \Phi \tag{1.3.3.2}$$

Thus, Einstein's theory makes a very definite quantitative prediction: if the frequency of the incident light is varied, and V_{stop} plotted as a function of frequency, the slope of the line should be $\frac{h}{e}$ (Figure **1.3.3.4*A***). It is also clear that there is a minimum light frequency for a given metal ν_o, that for which the quantum of energy is equal to Φ (Equation 1.3.3.1). Light below that frequency, no matter how bright, will not eject electrons.

> *According to both Planck and Einstein, the energy of light is proportional to its frequency rather than its amplitude, there will be a minimum frequency ν_0 needed to eject an electron with no residual energy.*

Since every photon of sufficient energy excites only one electron, increasing the light's intensity (i.e. the number of photons/sec) only increases the *number* of released electrons and not their kinetic energy. In addition, no time is necessary for the atom to be heated to a critical temperature and therefore the release of the electron is nearly instantaneous upon absorption of the light. Finally, because the photons must be above a certain energy to satisfy the workfunction, a threshold frequency exists below which no

photoelectrons are observed. This frequency is measured in units of Hertz (1/second) in honor of the discoverer of the photoelectric effect.

Einstein's Equation 1.3.3.1 explains the properties of the photoelectric effect quantitatively. A strange implication of this experiment is that light can behave as a kind of massless "particle" now known as a *photon* whose energy $E = h\nu$ can be transferred to an actual particle (an electron), imparting kinetic energy to it, just as in an elastic collision between to massive particles such as billiard balls.

> Robert Millikan initially did not accept Einstein's theory, which he saw as an attack on the wave theory of light, and worked for ten years until 1916, on the photoelectric effect. He even devised techniques for scraping clean the metal surfaces inside the vacuum tube. For all his efforts he found disappointing results: he confirmed Einstein's theory after ten years. In what he writes in his paper, Millikan is still desperately struggling to avoid this conclusion. However, by the time of his Nobel Prize acceptance speech, he has changed his mind rather drastically!

Einstein's simple explanation (Equation 1.3.3.1) completely accounted for the observed phenomena in Lenard's and Millikan's experiments (Figure 1.3.4) and began an investigation into the field we now call *quantum mechanics*. This new field seeks to provide a quantum explanation for classical mechanics and create a more unified theory of physics and thermodynamics. The study of the photoelectric effect has also lead to the creation of new field of photoelectron spectroscopy. Einstein's theory of the photoelectron presented a completely different way to measure Planck's constant than from black-body radiation.

The Workfunction (Φ)

The **workfunction** is an intrinsic property of the metal. While the workfunctions and ionization energies appear as similar concepts, they are independent. The workfunction of a metal is the minimum amount of energy (**E**) necessary to remove an electron from the surface of the bulk (*solid*) metal (sometimes referred to as **binding energy**).

$$\mathrm{M(s) + \Phi \rightarrow M^{+}(s) + e^{-}(\text{free with no kinetic energy})}$$

The workfunction is qualitatively similar to ionization energy (**IE**), which is the amount of energy required to remove an electron from an atom or molecule in the *gaseous* state.

$$\mathrm{M(g) + IE \rightarrow M^{+}(g) + e^{-}(\text{free with no kinetic energy})}$$

However, these two energies differ in magnitude (Table 1.3.1). For instance, copper has a workfunction of about 4.7 eV, but has a higher ionization energy of 7.7 eV. Generally, the ionization energies for metals are greater than the corresponding workfunctions (i.e., the electrons are less tightly bound in bulk metal).

Table 1.3.1 : Workfunctions and Ionization Energies of Select Elements

Element	Workfunction Φ (eV)	Ionization Energy (eV)
Lithium (Li)	2.93	5.39
Beryllium (Be)	4.98	9.32
Boron (B)	4.45	8.298
Carbon (C)	5.0	11.26
Sodium (Na)	2.36	5.13
Aluminum (Al)	4.20	5.98
Silicon (Si)	4.85	8.15
Potassium (K)	2.3	4.34
Iron (Fe)	4.67	7.87
Cobalt (Co)	4.89	7.88
Copper (Cu)	4.7	7.7
Gallium (Ga)	4.32	5.99
Germanium (Ge)	5.0	7.89
Arsenic (As)	3.75	9.81
Selenium (Se)	5.9	9.75
Silver (Ag)	4.72	7.57
Tin (Sn)	4.42	7.34
Cesium (Cs)	1.95	3.89
Gold (Au)	5.17	9.22
Mercury $(Hg)_{liquid}$	4.47	10.43
Bismuth (Bi)	4.34	7.29

Example 1.3.1 : Calcium

a. What is the energy in joules and electron volts of a photon of 420-nm violet light?
b. What is the maximum kinetic energy of electrons ejected from calcium by 420-nm violet light, given that the workfunction for calcium metal is 2.71 eV?

Strategy

To solve part (a), note that the energy of a photon is given by $E = h\nu$. For part (b), once the energy of the photon is calculated, it is a straightforward application of Equation 1.3.3.1 to find the ejected electron's maximum kinetic energy, since Φ is given.

Solution for (a)

Photon energy is given by

$$E = h\nu$$

Since we are given the wavelength rather than the frequency, we solve the familiar relationship $c = \nu\lambda$ for the frequency, yielding

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

Combining these two equations gives the useful relationship

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

Now substituting known values yields

$$\begin{aligned} E &= \frac{(6.63 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{420 \times 10^{-9}\ m} \\ &= 4.74 \times 10^{-19}\ J \end{aligned}$$

Converting to eV, the energy of the photon is

$$\begin{aligned} E &= (4.74 \times 10^{-19}\ J)\left(\frac{1\ eV}{1.6 \times 10^{-19}\ J}\right) \\ &= 2.96\ eV. \end{aligned}$$

Solution for (b)

Finding the kinetic energy of the ejected electron is now a simple application of Equation 1.3.3.1. Substituting the photon energy and binding energy yields

$$\begin{aligned} KE_e &= h\nu – \Phi \\ &= 2.96\ eV – 2.71\ eV \\ &= 0.246\ eV. \end{aligned}$$

Discussion

The energy of this 420-nm photon of violet light is a tiny fraction of a joule, and so it is no wonder that a single photon would be difficult for us to sense directly—humans are more attuned to energies on the order of joules. But looking at the energy in electron volts, we can see that this photon has enough energy to affect atoms and molecules. A DNA molecule can be broken with about 1 eV of energy, for example, and typical atomic and molecular energies are on the order of eV, so that the UV photon in this example could have biological effects.

The ejected electron (called a photoelectron) has a rather low energy, and it would not travel far, except in a vacuum. The electron would be stopped by a retarding potential of 0.26 eV. In fact, if the photon wavelength were longer and its energy less than 2.71 eV, then the formula would give a negative kinetic energy, an impossibility. This simply means that the 420-nm photons with their 2.96-eV energy are not much above the frequency threshold. You can show for yourself that the threshold wavelength is 459 nm (blue light). This means that if calcium metal is used in a light meter, the meter will be insensitive to wavelengths longer than those of blue light. Such a light meter would be insensitive to red light, for example.

? Exercise 1.3.1 : Silver

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver? Is this in the visible range?

Answer

Given that the workfunction is 4.72 eV from Table 1.3.1 , then only photons with wavelengths lower than 263 nm will induce photoelectrons (calculated via $E = h\nu$). This is ultraviolet and not in the visible range.

? Exercise 1.3.2

Why is the workfunction of an element generally lower than the ionization energy of that element?

Answer

The workfunction of a metal refers to the minimum energy required to extract an electron from the surface of a (**bulk**) metal by the absorption a photon of light. The workfunction will vary from metal to metal. In contrast, ionization energy is

the energy needed to detach electrons from **atoms** and also varies with each particular atom, with the valence electrons require less energy to extract than core electrons (i.e., from lower shells) that are more closely bound to the nuclei. The electrons in the metal lattice there less bound (i.e., free to move within the metal) and removing one of these electrons is much easier than removing an electron from an atom because the metallic bonds of the bulk metal reduces their binding energy. As we will show in subsequent chapters, the more delocalized a particle is, the lower its energy.

Summary

Although Hertz discovered the photoelectron in 1887, it was not until 1905 that a theory was proposed that explained the effect completely. The theory was proposed by Einstein and it made the claim that electromagnetic radiation had to be thought of as a series of particles, called photons, which collide with the electrons on the surface and emit them. This theory ran contrary to the belief that electromagnetic radiation was a wave and thus it was not recognized as correct until 1916 when Robert Millikan experimentally confirmed the theory

The photoelectric effect is the process in which electromagnetic radiation ejects electrons from a material. Einstein proposed photons to be quanta of electromagnetic radiation having energy $E = h\nu$ is the frequency of the radiation. All electromagnetic radiation is composed of photons. As Einstein explained, all characteristics of the photoelectric effect are due to the interaction of individual photons with individual electrons. The maximum kinetic energy KE_e of ejected electrons (photoelectrons) is given by $KE_e = h\nu - \Phi$, where $h\nu$ is the photon energy and Φ is the workfunction (or binding energy) of the electron to the particular material.

Conceptual Questions

1. Is visible light the only type of electromagnetic radiation that can cause the photoelectric effect?
2. Which aspects of the photoelectric effect cannot be explained without photons? Which can be explained without photons? Are the latter inconsistent with the existence of photons?
3. Is the photoelectric effect a direct consequence of the wave character of electromagnetic radiation or of the particle character of electromagnetic radiation? Explain briefly.
4. Insulators (nonmetals) have a higher Φ than metals, and it is more difficult for photons to eject electrons from insulators. Discuss how this relates to the free charges in metals that make them good conductors.
5. If you pick up and shake a piece of metal that has electrons in it free to move as a current, no electrons fall out. Yet if you heat the metal, electrons can be boiled off. Explain both of these facts as they relate to the amount and distribution of energy involved with shaking the object as compared with heating it.

Contributors and Attributions

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1.3.4: The Hydrogen Atomic Spectrum

Overview

- To introduce the concept of absorption and emission line spectra and describe the Balmer equation to describe the visible lines of atomic hydrogen.

The first person to realize that white light was made up of the colors of the rainbow was Isaac Newton, who in 1666 passed sunlight through a narrow slit, then a prism, to project the colored spectrum on to a wall. This effect had been noticed previously, of course, not least in the sky, but previous attempts to explain it, by Descartes and others, had suggested that the white light became colored when it was refracted, the color depending on the angle of refraction. Newton clarified the situation by using a second prism to reconstitute the white light, making much more plausible the idea that the white light was composed of the separate colors. He then took a monochromatic component from the spectrum generated by one prism and passed it through a second prism, establishing that no further colors were generated. That is, light of a single color did not change color on refraction. He concluded that white light was made up of all the colors of the rainbow, and that on passing through a prism, these different colors were refracted through slightly different angles, thus separating them into the observed spectrum.

Atomic Line Spectra

The spectrum of hydrogen *atoms*, which turned out to be crucial in providing the first insight into atomic structure over half a century later, was first observed by Anders Ångström in Uppsala, Sweden, in 1853. His communication was translated into English in 1855. Ångström, the son of a country minister, was a reserved person, not interested in the social life that centered around the court. Consequently, it was many years before his achievements were recognized, at home or abroad (most of his results were published in Swedish).

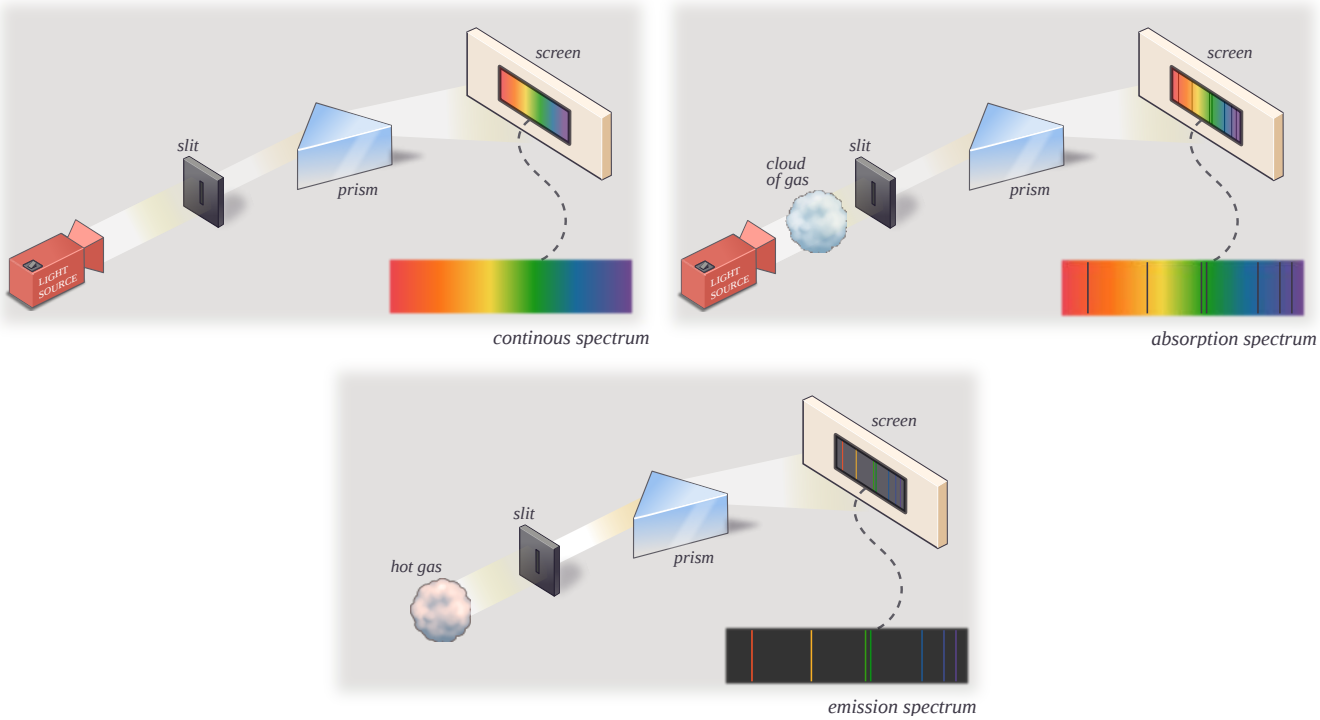


Figure 1.4.1 : Three Kinds of Spectra. When we see a lightbulb or other source of continuous radiation, all the colors are present. When the continuous spectrum is seen through a thinner gas cloud, the cloud's atoms produce absorption lines in the continuous spectrum. When the excited cloud is seen without the continuous source behind it, its atoms produce emission lines. We can learn which types of atoms are in the gas cloud from the pattern of absorption or emission lines. (CC BY-NC; Ümit Kaya via LibreTexts).

Most of what is known about atomic (and molecular) structure and mechanics has been deduced from spectroscopy. Figure 1.4.1 shows two different types of spectra. A continuous spectrum can be produced by an incandescent solid or gas at high pressure (e.g., blackbody radiation is a continuum). An emission spectrum can be produced by a gas at low pressure excited by heat or by collisions with electrons. An absorption spectrum results when light from a continuous source passes through a cooler gas, consisting of a series of dark lines characteristic of the composition of the gas.

Fraunhofer Lines

In 1802, William Wollaston in England had discovered that the solar spectrum had tiny gaps - there were many thin dark lines in the rainbow of colors. These were investigated much more systematically by Joseph von Fraunhofer, beginning in 1814. He increased the dispersion by using more than one prism. He found an "almost countless number" of lines. He labeled the strongest dark lines A, B, C, D, etc. Frauenhofer between 1814 and 1823 discovered nearly 600 dark lines in the solar spectrum viewed at high resolution and designated the principal features with the letters A through K, and weaker lines with other letters (Table 1.4.1). Modern observations of sunlight can detect many thousands of lines. It is now understood that these lines are caused by absorption by the outer layers of the Sun.

Table 1.4.1 : Major Fraunhofer lines and the elements they are associated with.

Designation	Element	Wavelength (nm)
y	O_2	898.765
Z	O_2	822.696
A	O_2	759.370
B	O_2	686.719
C	H	656.281
a	O_2	627.661
D_1	Na	589.592
D_2	Na	588.995
D_3 or d	He	587.5618

The Fraunhofer lines are typical spectral absorption lines. These dark lines are produced whenever a cold gas is between a broad spectrum photon source and the detector. In this case, a decrease in the intensity of light in the frequency of the incident photon is seen as the photons are absorbed, then re-emitted in random directions, which are mostly in directions different from the original one. This results in an *absorption line*, since the narrow frequency band of light initially traveling toward the detector, has been turned into heat or re-emitted in other directions.

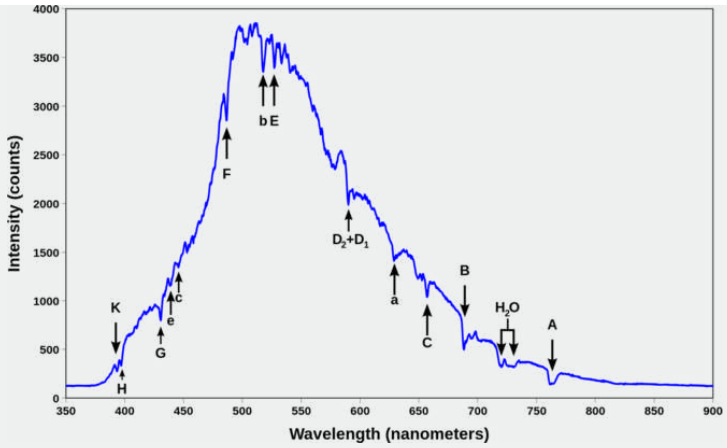


Figure 1.4.2 : Spectrum of blue sky. Dips are present at the Fraunhofer line wavelengths. (CC BY-SA 4.0; Eric Bajart via Wikipedia).

By contrast, if the detector sees photons emitted directly from a glowing gas, then the detector often sees photons emitted in a narrow frequency range by quantum emission processes in atoms in the hot gas, resulting in an *emission line*. In the Sun, Fraunhofer lines are seen from gas in the outer regions of the Sun, which are too cold to directly produce emission lines of the elements they represent.

Gases heated to incandescence were found by Bunsen, Kirkhoff and others to emit light with a series of sharp wavelengths. The emitted light analyzed by a spectrometer (or even a simple prism) appears as a multitude of narrow bands of color. These so called *line spectra* are characteristic of the atomic composition of the gas. The line spectra of several elements are shown in Figure 1.4.3 .

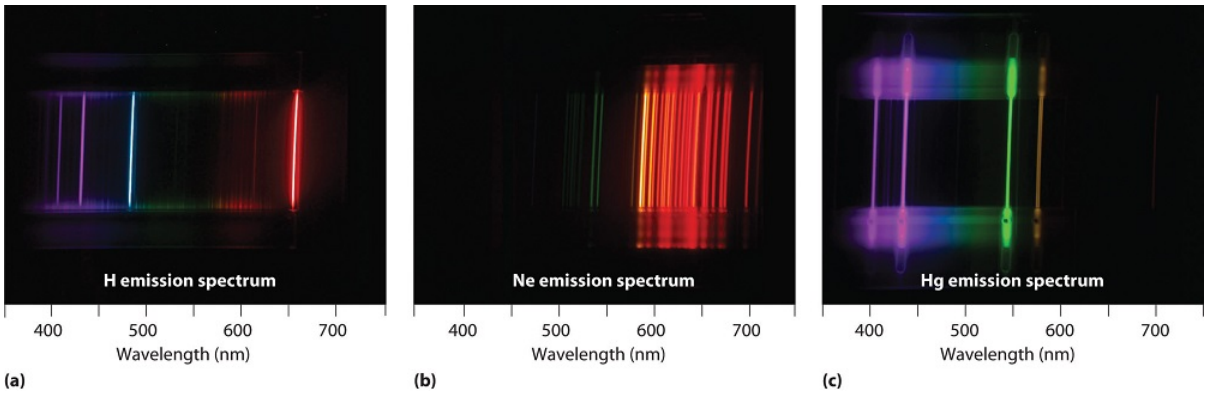


Figure 1.4.3 : The Emission Spectra of Elements Compared with Hydrogen. These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV; these are not shown. (CC BY-SA-NC; Anonymous by request).

The Balmer Series of Hydrogen

Obviously, if any pattern could be discerned in the spectral lines for a specific atom (in contract to the mixture that Fraunhofer lines represent), that might be a clue as to the internal structure of the atom. One might be able to build a model. A great deal of effort went into analyzing the spectral data from the 1860's on. The big breakthrough was made by Johann Balmer, a math and Latin teacher at a girls' school in Basel, Switzerland. Balmer had done no physics before and made his great discovery when he was almost sixty.

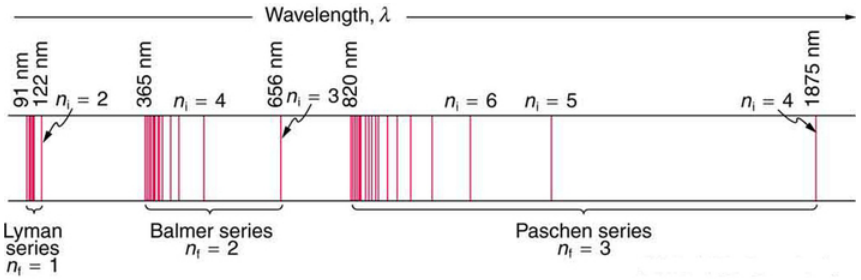


Figure 1.4.4 : A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and n_i are shown for some of the lines (CC BY-SA; OpenStax).

Balmer decided that the most likely atom to show simple spectral patterns was the lightest atom, hydrogen. Ångström had measured the four visible spectral lines to have wavelengths 656.21, 486.07, 434.01 and 410.12 nm (Figure 1.4.4). Balmer concentrated on just these four numbers, and found they were represented by the phenomenological formula:

$$\lambda = b\left(\frac{n_2^2}{n_2^2 - 4}\right) \tag{1.3.4.1}$$

where b = 364.56 nm and $n_2 = 3, 4, 5, 6$.

The first four wavelengths of Equation 1.3.4.1 (with n_2 = 3, 4, 5, 6) were in excellent agreement with the experimental lines from Ångström (Table 1.4.2). Balmer predicted that other lines exist in the ultraviolet that correspond to $n_2 \geq 7$ and in fact some of them had already been observed, unbeknown to Balmer.

Table 1.4.2 : The Balmer Series of Hydrogen Emission Lines

n_2	3	4	5	6	7	8	9	10
λ	*656*	*486*	*434*	*410*	397	389	383	380
color	*red*	*teal*	*blue*	*indigo*	violet	not visible	not visible	not visible

The n_2 integer in the Balmer series extends theoretically to infinity and the series represents a monotonically increasing energy (and frequency) of the absorption lines with increasing n_2 values. Moreover, the energy difference between successive lines decreased as n_2 increases (1.4.4). This behavior converges to a highest possible energy as Example 1.4.1 demonstrates. If the lines are plot according to their λ on a linear scale, you will get the appearance of the spectrum in Figure 1.4.4 ; these lines are called the **Balmer series**.

Balmer's general formula (Equation 1.3.4.1) can be rewritten in terms of the inverse wavelength typically called the *wavenumber* ($\tilde{\nu}$).

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.3.4.2}$$

$$= R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \tag{1.3.4.3}$$

where $n_2 = 3, 4, 5, 6$ and R_H is the Rydberg constant (discussed in the next section) equal to 109,737 cm^{-1}.

He further conjectured that the 4 could be replaced by 9, 16, 25, … and this also turned out to be true - but these lines, further into the infrared, were not detected until the early twentieth century, along with the ultraviolet lines.

The Wavenumber as a Unit of Frequency

The relation between wavelength and frequency for electromagnetic radiation is

$$\lambda\nu = c$$

In the SI system of units the wavelength, (λ) is measured in meters (m) and since wavelengths are usually very small one often uses the nanometer (nm) which is $10^{-9}\ m$. The frequency (ν) in the SI system is measured in reciprocal seconds 1/s − which is called a Hertz (after the discover of the photoelectron effect) and is represented by Hz.

It is common to use the reciprocal of the wavelength in centimeters as a measure of the frequency of radiation. This unit is called a wavenumber and is represented by ($\tilde{\nu}$) and is defined by

$$\begin{aligned}\tilde{\nu} &= \frac{1}{\lambda} \\ &= \frac{\nu}{c}\end{aligned}$$

Wavenumbers is a convenient unit in spectroscopy because it is directly proportional to energy.

$$\begin{aligned}E &= \frac{hc}{\lambda} \\ &= hc \times \frac{1}{\lambda} \\ &= hc\tilde{\nu} \\ &\propto \tilde{\nu}\end{aligned}$$

Example 1.4.1 : Balmer Series

Calculate the longest and shortest wavelengths (in nm) emitted in the Balmer series of the hydrogen atom emission spectrum.

Solution

From the behavior of the Balmer equation (Equation 1.3.4.1 and Table 1.4.2), the value of n_2 that gives the longest (i.e., greatest) wavelength (λ) is the smallest value possible of n_2, which is (n_2=3) for this series. This results in

$$\begin{aligned}\lambda_{longest} &= (364.56\ nm)\left(\frac{9}{9-4}\right) \\ &= (364.56\ nm)\,(1.8) \\ &= 656.2\ nm\end{aligned}$$

This is also known as the H_α line of atomic hydrogen and is bright red (Figure **1.3.4.3***a*).

For the shortest wavelength, it should be recognized that the shortest wavelength (greatest energy) is obtained at the limit of greatest (n_2):

$$\lambda_{shortest} = \lim_{n_2 \to \infty} (364.56\ nm)\left(\frac{n_2^2}{n_2^2-4}\right)$$

This can be solved via L'Hôpital's Rule, or alternatively the limit can be expressed via the equally useful energy expression (Equation 1.3.4.3) and simply solved:

$$\begin{aligned}\tilde{\nu}_{greatest} &= \lim_{n_2 \to \infty} R_H\left(\frac{1}{4} - \frac{1}{n_2^2}\right) \\ &= \lim_{n_2 \to \infty} R_H\left(\frac{1}{4}\right) \\ &= 27,434\ cm^{-1}\end{aligned}$$

Since $\frac{1}{\tilde{\nu}} = \lambda$ in units of cm, this converts to 364 nm as the shortest wavelength possible for the Balmer series.

The Balmer series is particularly useful in astronomy because the Balmer lines appear in numerous stellar objects due to the abundance of hydrogen in the universe, and therefore are commonly seen and relatively strong compared to lines from other elements.

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1.3.5: The Rydberg Formula and the Hydrogen Atomic Spectrum

Learning Objectives

- Describe Rydberg's theory for the hydrogen spectra.
- Interpret the hydrogen spectrum in terms of the energy states of electrons.

In an amazing demonstration of mathematical insight, in 1885 Balmer came up with a simple formula for predicting the wavelength of any of the lines in atomic hydrogen in what we now know as the Balmer series. Three years later, Rydberg generalized this so that it was possible to determine the wavelengths of any of the lines in the hydrogen emission spectrum. Rydberg suggested that all atomic spectra formed families with this pattern (he was unaware of Balmer's work). It turns out that there are families of spectra following Rydberg's pattern, notably in the alkali metals, sodium, potassium, etc., but not with the precision the hydrogen atom lines fit the Balmer formula, and low values of n_2 predicted wavelengths that deviate considerably.

Rydberg's phenomenological equation is as follows:

$$\tilde{\nu} = \frac{1}{\lambda} \tag{1.3.5.1}$$

$$= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{1.3.5.2}$$

where R_H is the **Rydberg constant** and is equal to 109,737 cm^{-1} ($2.18 \times 10^{-18}\ J$) and n_1 and n_2 are integers (whole numbers) with $n_2 > n_1$.

For the Balmer lines, $n_1 = 2$ and n_2 can be any whole number between 3 and infinity. The various combinations of numbers that can be substituted into this formula allow the calculation the wavelength of any of the lines in the hydrogen emission spectrum; there is close agreement between the wavelengths generated by this formula and those observed in a real spectrum.

Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic radiation start with $n_2 = 3$, and $n_1 = 2$. Is there a different series with the following formula (e.g., $n_1 = 1$)?

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{1.3.5.3}$$

The values for n_2 and wavenumber $\tilde{\nu}$ for this series would be:

Table 1.5.1 : The Lyman Series of Hydrogen Emission Lines ($n_1 = 1$)

n_2	2	3	4	5	...
λ (nm)	121	102	97	94	...
$\tilde{\nu}$ (cm^{-1})	82,2291	97,530	102,864	105,332	...

Do you know in what region of the electromagnetic radiation these lines are? Of course, these lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_1 = 3$ and $n_2 = 4, 5, 6, 7, \ldots$ is called **Paschen series**.

Other Series

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series, using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly-α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa-δ). The first six series have specific names:

- Lyman series with $n_1 = 1$

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$

Example 1.5.1 : The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the *n* = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy

A. Substitute the appropriate values into Equation 1.3.5.2 (the Rydberg equation) and solve for λ.
B. Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution

We can use the Rydberg equation (Equation 1.3.5.2) to calculate the wavelength:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Solution A

For the Lyman series, $n_1 = 1$.

$$\begin{aligned} \frac{1}{\lambda} &= R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= 1.097 \times 10^7 \, m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) \\ &= 8.228 \times 10^6 \, m^{-1} \end{aligned}$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit (wavenumbers) is particularly convenient. We can convert the answer in part A to cm^{-1}.

$$\begin{aligned} \tilde{\nu} &= \frac{1}{\lambda} \\ &= 8.228 \times 10^6 \, \cancel{m^{-1}} \left(\frac{\cancel{m}}{100 \, cm} \right) \\ &= 82,280 \, cm^{-1} \end{aligned}$$

and

$$\lambda = 1.215 \times 10^{-7} \, m = 122 \, nm$$

This emission line is called Lyman alpha and is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

Solution B

his wavelength is in the ultraviolet region of the spectrum.

Exercise 1.5.1 : The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n_1 = 5$. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer

$4.65 \times 10^3\ nm$; infrared

The above discussion presents only a phenomenological description of hydrogen emission lines and fails to provide a probe of the nature of the atom itself. Clearly a continuum model based on classical mechanics is not applicable, and as the next Section demonstrates, a simple connection between spectra and atomic structure can be formulated.

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SECTION OVERVIEW

1.4: ATOMIC ORBITALS

ATOMIC ORBITALS

1.4.1: Matter Has Wavelike Properties

1.4.2: de Broglie Waves can be Experimentally Observed

1.4.3: The Bohr Theory of the Hydrogen Atom

1.4.4: The Heisenberg Uncertainty Principle

1.4.E: The Dawn of the Quantum Theory (Exercises)

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1.4.1: Matter Has Wavelike Properties

Learning Objectives

- To introduce the wave-particle duality of light extends to matter
- To describe how matter (e.g., electrons and protons) can exhibit wavelike properties, e.g., interference and diffraction patterns
- To use algebra to find the de Broglie wavelength or momentum of a particle when either one of these quantities is given

The next real advance in understanding the atom came from an unlikely quarter - a student prince in Paris. Prince Louis de Broglie was a member of an illustrious family, prominent in politics and the military since the 1600's. Louis began his university studies with history, but his elder brother Maurice studied x-rays in his own laboratory, and Louis became interested in physics. After World War I, de Broglie focused his attention on Einstein's two major achievements, the theory of special relativity and the quantization of light waves. He wondered if there could be some connection between them. Perhaps the quantum of radiation really should be thought of as a particle. De Broglie suggested that if waves (photons) could behave as particles, as demonstrated by the photoelectric effect, then the converse, namely that particles could behave as waves, should be true. He associated a wavelength λ to a particle with momentum p using Planck's constant as the constant of proportionality:

$$\lambda = \frac{h}{p} \tag{1.4.1.1}$$

which is called the **de Broglie wavelength**. The fact that particles can behave as waves but also as particles, depending on which experiment you perform on them, is known as the **wave-particle duality**.

Deriving the de Broglie Wavelength

From the discussion of the photoelectric effect, we have the first part of the particle-wave duality, namely, that electromagnetic waves can behave like particles. These particles are known as *photons*, and they move at the speed of light. Any particle that moves at or near the speed of light has kinetic energy given by Einstein's special theory of relatively. In general, a particle of mass m and momentum p has an energy

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{1.4.1.2}$$

Note that if $p = 0$, this reduces to the famous rest-energy expression $E = mc^2$. However, photons are massless particles (technically rest-massless) that always have a finite momentum p. In this case, Equation 1.4.1.2 becomes

$$E = pc.$$

From Planck's hypothesis, one quantum of electromagnetic radiation has energy $E = h\nu$. Thus, equating these two expressions for the kinetic energy of a photon, we have

$$h\nu = \frac{hc}{\lambda} = pc \tag{1.4.1.3}$$

Solving for the wavelength λ gives Equation 1.4.1.1:

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

where v is the velocity of the particle. Hence, de Broglie argued that if particles can behave as waves, then a relationship like this, which pertains particularly to waves, should also apply to particles.

Equation 1.4.1.1 allows us to associate a wavelength λ to a particle with momentum p. As the momentum increases, the wavelength decreases. In both cases, this means the energy becomes larger. i.e., short wavelengths *and* high momenta correspond to high energies.

> *It is a common feature of quantum mechanics that particles and waves with short wavelengths correspond to high energies and vice versa.*

Having decided that the photon might well be a particle with a rest mass, even if very small, it dawned on de Broglie that in other respects it might not be too different from other particles, especially the very light electron. In particular, maybe the electron also had an associated wave. The obvious objection was that if the electron was wavelike, why had no diffraction or interference effects been observed? But there was an answer. If de Broglie's relation between momentum and wavelength also held for electrons, the wavelength was sufficiently short that these effects would be easy to miss. As de Broglie himself pointed out, the wave nature of light is not very evident in everyday life. As the next section will demonstrate, the validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both electrons (i.e., matter) and electromagnetic radiation (i.e., light).

Example 1.6.1 : Electron Waves

Calculate the de Broglie wavelength for an electron with a kinetic energy of 1000 eV.

Solution

To calculate the de Broglie wavelength (Equation 1.4.1.1), the momentum of the particle must be established and requires knowledge of both the mass and velocity of the particle. The mass of an electron is $9.109383 \times 10^{-28}\ g$ and the velocity is obtained from the given kinetic energy of 1000 eV:

$$\begin{aligned} KE &= \frac{mv^2}{2} \\ &= \frac{p^2}{2m} = 1000\ eV \end{aligned}$$

Solve for momentum

$$p = \sqrt{2mKE}$$

convert to SI units

$$p = \sqrt{(1000\ \cancel{eV})\left(\frac{1.6 \times 10^{-19}\ J}{1\ \cancel{eV}}\right)(2)(9.109383 \times 10^{-31}\ kg)}$$

expanding definition of joule into base SI units and cancel

$$\begin{aligned} p &= \sqrt{(3.1 \times 10^{-16}\ kg \cdot m^2/s^2)(9.109383 \times 10^{-31}\ kg)} \\ &= \sqrt{2.9 \times 10^{-40}\ kg^2\ m^2/s^2} \\ &= 1.7 \times 10^{-23} kg \cdot m/s \end{aligned}$$

Now substitute the momentum into the equation for de Broglie's wavelength (Equation 1.4.1.1) with Planck's constant ($h = 6.626069 \times 10^{-34}\ J \cdot s$). After expanding units in Plank's constant

$$\begin{aligned} \lambda &= \frac{h}{p} \\ &= \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{1.7 \times 10^{-23} kg \cdot m/s} \\ &= 3.87 \times 10^{-11}\ m \\ &= 38.9\ pm \end{aligned}$$

Exercise 1.6.1 : Baseball Waves

Calculate the de Broglie wavelength for a fast ball thrown at 100 miles per hour and weighing 4 ounces. Comment on whether the wave properties of baseballs could be experimentally observed.

Answer

Following the unit conversions below, a 4 oz baseball has a mass of 0.11 kg. The velocity of a fast ball thrown at 100 miles per hour in m/s is 44.7 m/s.

$$m = (4\ \cancel{oz})\left(\frac{0.0283\ kg}{1\ \cancel{oz}}\right) = 0.11 kg$$

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{hr}}\right)\left(\frac{1609.34\ m}{\cancel{mi}}\right)\left(\frac{1\ \cancel{hr}}{3600\ s}\right) = 44.7\ m/s$$

The de Broglie wavelength of this fast ball is:

$$\lambda = \frac{h}{mv} = \frac{6.626069 \times 10^{-34}\ kg \cdot m^2/s}{(0.11\ kg)(44.7\ m/s)} = 1.3 \times 10^{-34} m$$

Exercise 1.6.2 : Electrons vs. Protons

If an electron and a proton have the same velocity, which would have the longer de Broglie wavelength?

a. The electron
b. The proton
c. They would have the same wavelength

Answer

Equation 1.4.1.1 shows that the de Broglie wavelength of a particle's matter wave is inversely proportional to its momentum (mass times velocity). Therefore the smaller mass particle will have a smaller momentum and longer wavelength. The electron is the lightest and will have the longest wavelength.

This was the prince's Ph.D. thesis, presented in 1924. His thesis advisor was somewhat taken aback, and was not sure if this was sound work. He asked de Broglie for an extra copy of the thesis, which he sent to Einstein. Einstein wrote shortly afterwards: *"I believe it is a first feeble ray of light on this worst of our physics enigmas*" and the prince got his Ph.D.

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1.4.2: de Broglie Waves can be Experimentally Observed

Learning Objectives

- To present the experimental evidence behind the wave-particle duality of matter

The validity of de Broglie's proposal was confirmed by electron diffraction experiments of G.P. Thomson in 1926 and of C. Davisson and L. H. Germer in 1927. In these experiments it was found that electrons were scattered from atoms in a crystal and that these scattered electrons produced an interference pattern. The interference pattern was just like that produced when water waves pass through two holes in a barrier to generate separate wave fronts that combine and interfere with each other. These diffraction patterns are characteristic of wave-like behavior and are exhibited by both matter (e.g., electrons and neutrons) and electromagnetic radiation. Diffraction patterns are obtained if the wavelength is comparable to the spacing between scattering centers.

> *Diffraction occurs when waves encounter obstacles whose size is **comparable** with its wavelength.*

Continuing with our analysis of experiments that lead to the new quantum theory, we now look at the phenomenon of electron diffraction.

Diffraction of Light (Light as a Wave)

It is well-known that *light* has the ability to diffract around objects in its path, leading to an interference pattern that is particular to the object. This is, in fact, how holography works (the interference pattern is created by allowing the diffracted light to interfere with the original beam so that the hologram can be viewed by shining the original beam on the image). A simple illustration of light diffraction is the Young double slit experiment (Figure 1.7.1). Here, light as waves (pictured as waves in a plane parallel to the double slit apparatus) impinge on the two slits. Each slit then becomes a point source for spherical waves that subsequently interfere with each other, giving rise to the light and dark fringes on the screen at the right.

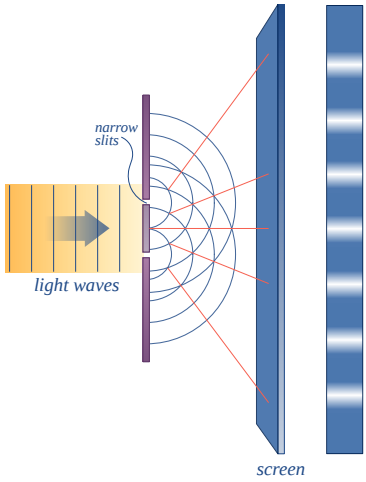


Figure 1.7.1 : Young double slit experiment. Two slits are illuminated by a plane light waves. (CC BY-NC; Ümit Kaya via LibreTexts)

The double-slit experiments are direct demonstration of wave phenomena via observed interference. These types of experiment were first performed by Thomas Young in 1801, as a demonstration of the wave behavior of light. In the basic version of this experiment, light is illuminated only a plate pierced by two parallel slits, and the light passing through the two slits is observed on a screen behind the plate (Figures 1.7.1 and 1.7.2).

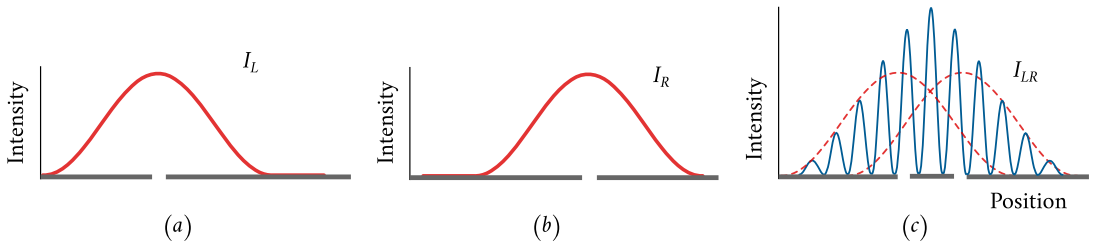


Figure 1.7.2 : Amplitude of particles through (a) left slit, (b) right slit, (c) through both slits. In absence of wavelength interference behavior, the intensity will be the sum of each single slit results (red) and when there is interference, pronounced oscillations in intensity is observed (blue curve). (CC BY; Ümit Kaya via LibreTexts)

The wave nature of light causes the light waves passing through the two slits to interfere, producing bright and dark bands on the screen – a result that would not be expected if light consisted of classical particles (Figure **1.4.2.0*c***). However, the light is always found to be absorbed at the screen at discrete points, as individual particles (not waves); the interference pattern appears via the varying density of these particle hits on the screen. Furthermore, versions of the experiment that include detectors at the slits find that each detected photon passes through one slit (as would a classical particle), and not through both slits (as would a wave).

> *Interference is a wave phenomenon in which two (or more) waves superimpose to form a resultant wave of greater or lower amplitude. It is the primary property used to identify wave behavior.*

Diffraction of Electrons (Electrons as Waves)

According to classical physics, electrons should behave like particles - they travel in straight lines and do not curve in flight unless acted on by an external agent, like a magnetic field. In this model, if we fire a beam of electrons through a double slit onto a detector, we should get two bands of "hits", much as you would get if you fired a machine gun at the side of a house with two windows - you would get two areas of bullet-marked wall inside, and the rest would be intact (Figure 1.7.3 (left) and Figure 1.7.2).

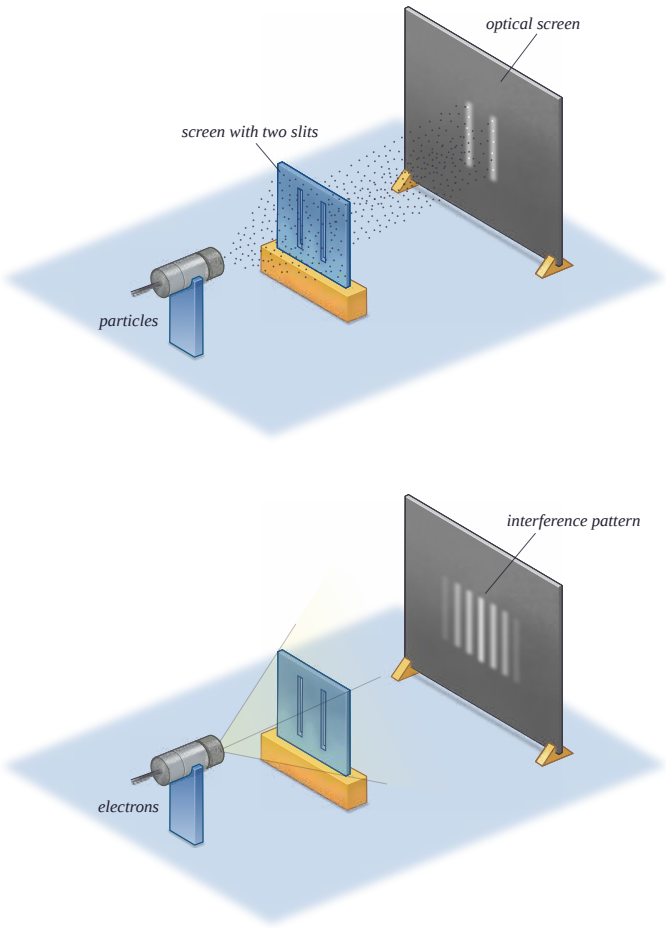


Figure 1.7.3 : (left) classical model of electrons. (right) wave property of electrons. (CC BY-NC; Ümit Kaya via LibreTexts)

However, if the slits are made small enough and close enough together, we actually observe the electrons are *diffracting* through the slits and *interfering* with each other just like waves (Figure 1.7.3 (right) and Figure 1.7.2 a,b). This means that the electrons have **wave-particle duality**, just like photons, in agreement with de Broglie's hypothesis discussed previously. In this case, they must have properties like wavelength and frequency. We can deduce the properties from the behavior of the electrons as they pass through our diffraction grating.

This was a pivotal result in the development of quantum mechanics. Just as the photoelectric effect demonstrated the particle nature of light, the Davisson–Germer experiment showed the wave-nature of matter, and completed the theory of wave-particle duality. For physicists this idea was important because it meant that not only could any particle exhibit wave characteristics, but that one could use wave equations to describe phenomena in matter if one used the de Broglie wavelength.



Figure 1.7.4 : An image of an ant in a scanning electron microscope based on the wave properties of electrons. (Public Domain; United States Geological Survey, an agency of the United States Department of the Interior)

An electron microscope use a beam of accelerated electrons as a source of illumination. Since the wavelength of electrons can be up to 100,000 times shorter than that of visible light photons, electron microscopes have a higher resolving power than light microscopes and can reveal the structure of smaller objects. A transmission electron microscope can achieve better than 50 pm resolution and magnifications of up to about 10,000,000x whereas most light microscopes are limited by diffraction to about 200 nm resolution and useful magnifications below 2000x (Figure 1.7.4).

Is Matter a Particle or a Wave?

An electron, indeed any particle, is neither a *particle* nor a *wave*. Describing the electron as a particle is a mathematical model that works well in some circumstances while describing it as a wave is a different mathematical model that works well in other circumstances. When you choose to do some calculation of the electron's behavior that treats it either as a particle or as a wave, you're not saying the electron **is** a particle or **is** a wave: you're just choosing the mathematical model that makes it easiest to do the calculation.

Neutron Diffraction (Neutrons as Waves)

Like all quantum particles, neutrons can also exhibit wave phenomena and if that wavelength is short enough, atoms or their nuclei can serve as diffraction obstacles. When a beam of neutrons emanating from a reactor is slowed down and selected properly by their speed, their wavelength lies near one angstrom (0.1 nanometer), the typical separation between atoms in a solid material. Such a beam can then be used to perform a diffraction experiment. Neutrons interact directly with the nucleus of the atom, and the contribution to the diffracted intensity depends on each isotope; for example, regular hydrogen and deuterium contribute differently. It is also often the case that light (low Z) atoms contribute strongly to the diffracted intensity even in the presence of large Z atoms.

Example 1.7.1 : Neutron Diffraction

Neutrons have no electric charge, so they do not interact with the atomic electrons. Hence, they are very penetrating (e.g., typically 10 cm in lead). Neutron diffraction was proposed in 1934, to exploit de Broglie's hypothesis about the wave nature of matter. Calculate the momentum and kinetic energy of a neutron whose wavelength is comparable to atomic spacing ($1.8 \times 10^{-10}\, m$).

Solution

This is a simple use of de Broglie's equation

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

where we recognize that the wavelength of the neutron must be comparable to atomic spacing (let's assumed equal for convenience, so $\lambda = 1.8 \times 10^{-10}\, m$). Rearranging the de Broglie wavelength relationship above to solve for momentum (p):

$$\begin{aligned} p &= \frac{h}{\lambda} \\ &= \frac{6.6 \times 10^{-34} Js}{1.8 \times 10^{-10} m} \\ &= 3.7 \times 10^{-24}\, kg\ m\ s^{-1} \end{aligned}$$

The relationship for kinetic energy is

$$KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

where v is the velocity of the particle. From the reference table of physical constants, the mass of a neutron is $1.6749273 \times 10^{-27}$ kg, so

$$KE = \frac{(3.7 \times 10^{-24}\ kg\ m\ s^{-1})^2}{2(1.6749273 \times 10^{-27}\ kg)}$$
$$= 4.0 \times 10^{-21} J$$

The neutrons released in nuclear fission are ‘fast’ neutrons, i.e. much more energetic than this. Their wavelengths be much smaller than atomic dimensions and will not be useful for neutron diffraction. We slow down these fast neutrons by introducing a "moderator", which is a material (e.g., graphite) that neutrons can penetrate, but will slow down appreciably.

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1.4.3: The Bohr Theory of the Hydrogen Atom

Learning Objectives

- Introduce the fundamentals behind the Bohr Atom and demonstrate it can predict the Rydberg's equation for the atomic spectrum of hydrogen

Rutherford's Failed Planetary Atom

Ernest Rutherford had proposed a model of atoms based on the α-particle scattering experiments of Hans Geiger and Ernest Marsden. In these experiments helium nuclei (α-particles) were shot at thin gold metal foils. Most of the particles were not scattered; they passed unchanged through the thin metal foil. Some of the few that were scattered were scattered in the backward direction; i.e. they recoiled. This backward scattering requires that the foil contain heavy particles. When an α-particle hits one of these heavy particles it simply recoils backward, just like a ball thrown at a brick wall. Since most of the α-particles don't get scattered, the heavy particles (the nuclei of the atoms) must occupy only a very small region of the total space of the atom. Most of the space must be empty or occupied by very low-mass particles. These low-mass particles are the electrons that surround the nucleus.

There are some basic problems with the Rutherford model. The Coulomb force that exists between oppositely charge particles means that a positive nucleus and negative electrons should attract each other, and the atom should collapse. To prevent the collapse, the electron was postulated to be orbiting the positive nucleus. The Coulomb force (discussed below) is used to change the direction of the velocity, just as a string pulls a ball in a circular orbit around your head or the gravitational force holds the moon in orbit around the Earth. The origin for this hypothesis that suggests this perspective is plausible is the similarity of gravity and Coulombic interactions. The expression for the force of gravity between two masses (Newton's Law of gravity) is

$$F_{gravity} \propto \frac{m_1 m_2}{r^2} \tag{1.4.3.1}$$

with m_1 and m_2 representing the **mass** of object 1 and 2, respectively and r representing the distance between the objects centers

The expression for the Coulomb force between two charged species is

$$F_{Coulomb} \propto \frac{Q_1 Q_2}{r^2} \tag{1.4.3.2}$$

with Q_1 and Q_2 representing the **charge** of object 1 and 2, respectively and r representing the distance between the objects centers.

However, this analogy has a problem too. An electron going around in a circle is constantly being accelerated because its velocity vector is changing. A charged particle that is being accelerated emits radiation. This property is essentially how a radio transmitter works. A power supply drives electrons up and down a wire and thus transmits energy (electromagnetic radiation) that your radio receiver picks up. The radio then plays the music for you that is encoded in the waveform of the radiated energy.

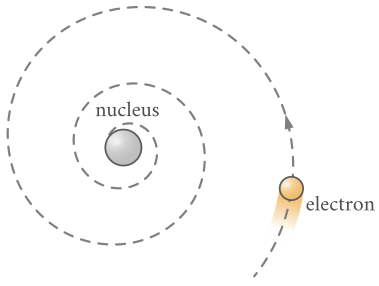


Figure 1.8.1 : The classical death spiral of an electron around a nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

If the orbiting electron is generating radiation, it is losing energy. If an orbiting particle loses energy, the radius of the orbit decreases. To conserve angular momentum, the frequency of the orbiting electron increases. The frequency increases continuously as the electron collapses toward the nucleus. Since the frequency of the rotating electron and the frequency of the radiation that is

emitted are the same, both change continuously to produce a continuous spectrum and not the observed discrete lines. Furthermore, if one calculates how long it takes for this collapse to occur, one finds that it takes about 10^{-11} seconds. This means that nothing in the world based on the structure of atoms could exist for longer than about 10^{-11} seconds. Clearly something is terribly wrong with this classical picture, which means that something was missing at that time from the known laws of physics.

Conservative Forces can be explained with Potentials

A conservative force is dependent only on the position of the object. If a force is conservative, it is possible to assign a numerical value for the potential at any point. When an object moves from one location to another, the force changes the potential energy of the object by an amount that does not depend on the path taken. The potential can be constructed as simple derivatives for 1-D forces:

$$F = -\frac{dV}{dx}$$

or as gradients in 3-D forces

$$F = -\nabla V$$

where ∇ is the vector of partial derivatives

$$\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

The most familiar conservative forces are gravity and Coulombic forces.

The Coulomb force law (Equation 1.4.3.2) comes from the corresponding Coulomb potential (sometimes call electrostatic potential)

$$V(r) = \frac{kQ_1Q_2}{r} \tag{1.4.3.3}$$

and it can be easily verified that the Coulombic force from this interaction ($F(r)$) is

$$F(r) = -\frac{dV}{dr} \tag{1.4.3.4}$$

As r is varied, the energy will change, so that we have an example of a potential energy curve $V(r)$ (Figure 1.4.3.2;). If Q_1 and Q_2 are the same sign, then the curve which is a purely **repulsive potential**, i.e., the energy increases monotonically as the charges are brought together and decreases monotonically as they are separated. From this, it is easy to see that like charges (charges of the same sign) repel each other.

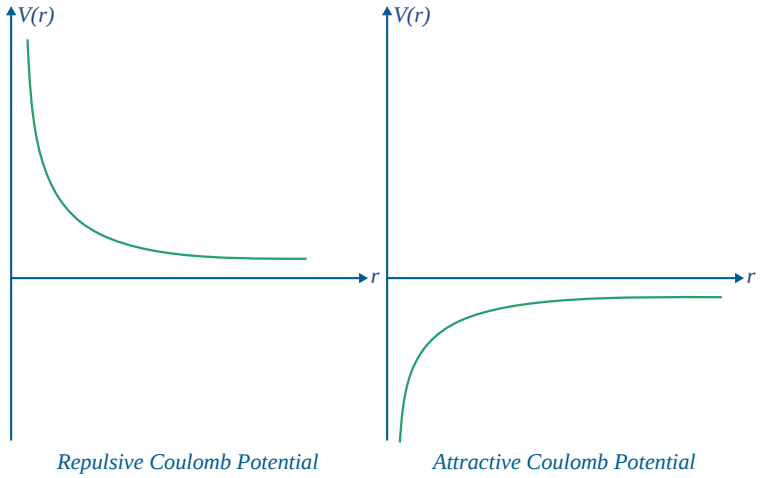


Figure 1.8.2 : Potential energy curve for the Coulomb interactions between two charges of same sign (left) and opposite signs (right). (CC BY-NC; Ümit Kaya via LibreTexts)

If the charges are of opposite sign, then the curve appears roughly Figure **1.4.3.2;** and this is a purely **attractive potential**. Thus, the energy decreases as the charges are brought together, implying that opposite charges attract

The Bohr Model

It is observed that line spectra discussed in the previous sections show that hydrogen atoms absorb and emit light at only discrete wavelengths. This observation is connected to the discrete nature of the allowed energies of a quantum mechanical system. Quantum mechanics postulates that, in contrast to classical mechanics, the energy of a system can only take on certain discrete values. This leaves us with the question: How do we determine what these allowed discrete energy values are? After all, it seems that Planck's formula for the allowed energies came out of nowhere.

The model we will describe here, due to Niels Bohr in 1913, is an early attempt to predict the allowed energies for single-electron atoms such as **H**, $\mathbf{He^{+}}$, $\mathbf{Li^{2+}}$, $\mathbf{Be^{3+}}$, etc. Although Bohr's reasoning relies on classical concepts and hence, is not a correct explanation, the reasoning is interesting, and so we examine this model for its historical significance.

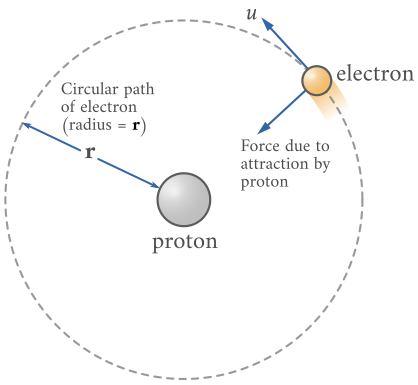


Figure 1.8.3 : Bohr atom with an electron revolving around a fixed nucleus. (CC BY-NC; Ümit Kaya via LibreTexts)

Consider a nucleus with charge $+Ze$ and one electron orbiting the nucleus. In this analysis, we will use another representation of the constant k in Coulomb's law (Equation 1.4.3.3), which is more commonly represented in the form:

$$k = \frac{1}{4\pi\epsilon_0} \tag{1.4.3.5}$$

where ϵ_0 is known as the **permittivity of free space** with the numerical value $\epsilon_0 = 8.8541878 \times 10^{-12}\ C^2 J^{-1} m^{-1}$.

The total energy of the electron (the nucleus is assumed to be fixed in space at the origin) is the sum of kinetic and potential energies:

$$E_{total} = \underbrace{\frac{p^2}{2m_e}}_{\text{kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{potential energy}}$$

The force on the electron is

$$\vec{F} = -\frac{Ze^2}{4\pi\epsilon_0 r^3} r$$

and its magnitude is

$$F = |\vec{F}| = \frac{Ze^2}{4\pi\epsilon_0 r^3}|r| = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

since $\vec{F} = m_e\vec{a}$, the magnitude, it follows that $|\vec{F}| = m_e|\vec{a}|$. If we assume that the orbit is circular, then the acceleration is *purely centripetal*, so

$$|a| = \frac{v^2}{r}$$

where v is the velocity of the electron. Equating force $|F|$ to $m_e|a|$, we obtain

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = m_e\frac{v^2}{r}$$

or

$$\frac{Ze^2}{4\pi\epsilon_0} = m_e v^2 r$$

or

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = (m_e v r)^2 \tag{1.4.3.6}$$

The reason for writing the equation this way is that the quantity $m_e vr$ is the classical orbital angular momentum of the electron. Bohr was familiar with Maxwell's theory of classical electromagnetism and knew that in a classical theory, the orbiting electron should radiate energy away and eventually collapse into the nucleus (Figure 1.8.1). He circumvented this problem by following Planck's idea underlying blackbody radiation and positing that the orbital angular momentum $m_e vr$ of the electron could only take on specific values

$$m_e vr = n\hbar \tag{1.4.3.7}$$

with $n = 1, 2, 3, \ldots$.

> *Note that the electron must be in motion, so $n = 0$ is not allowed.*

Substituting Equation 1.4.3.7 into the Equation 1.4.3.6, we find

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2(\hbar)^2 \tag{1.4.3.8}$$

Equation 1.4.3.8 implies that orbits could only have certain allowed radii

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{Ze^2 m_e}n^2 \tag{1.4.3.9}$$

$$= \frac{a_0}{Z}n^2 \tag{1.4.3.10}$$

with $n = 1, 2, 3, \ldots$. The collection of constants has been defined to be a_0

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2 m_e}$$

a quantity that is known as the **Bohr radius**.

We can also calculate the allowed momenta since $m_e vr = n\hbar$, and $p = m_e v$. Thus,

$$p_n r_n = n\hbar$$

$$p_n = \frac{n\hbar}{r_n}$$

$$= \frac{\hbar Z}{a_0 n}$$

$$= \frac{Ze^2 m_e}{4\pi\epsilon_0\hbar n}$$

From p_n and r_n, we can calculate the allowed energies from

$$E_n = \frac{p_n^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

Substituting in the expressions for p_n and r_n and simplifying gives

$$E_n = -\frac{Z^2 e^4 m_e}{32\pi^2 \epsilon_0^2 \hbar^2}\frac{1}{n^2} = -\frac{e^4 m_e}{8\epsilon_0^2 h^2}\frac{Z^2}{n^2} \tag{1.4.3.11}$$

We can redefine a new energy scale by defining **the Rydberg** as

$$1\ Ry = \frac{e^4 m_e}{8\epsilon_0^2 h^2} = 2.18 \times 10^{-18}\ J.$$

and this simplifies the allowed energies predicted by the Bohr model (Equation 1.4.3.11) as

$$E_n = -(2.18 \times 10^{-18})\frac{Z^2}{n^2}\ J = -\frac{Z^2}{n^2}\ R_y \tag{1.4.3.12}$$

Hence, the energy of the electron in an atom also is quantized. Equation 1.4.3.12 gives the energies of the electronic states of the hydrogen atom. It is very useful in analyzing spectra to represent these energies graphically in an energy-level diagram. An energy-level diagram has energy plotted on the vertical axis with a horizontal line drawn to locate each energy level (Figure 1.8.4).

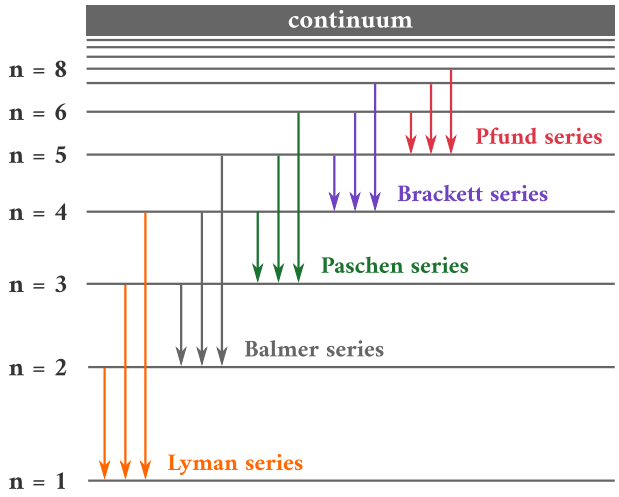


Figure 1.8.4 : Energy levels predicted by the Bohr model of hydrogen ($Z = 1$). (CC BY-NC; Ümit Kaya via LibreTexts)

These turn out to be the correct energy levels, apart from small corrections that cannot be accounted for in this pseudo-classical treatment. Despite the fact that the energies are essentially correct, the Bohr model masks the true quantum nature of the electron, which only emerges from a fully quantum mechanical analysis.

? Exercise 1.8.1

Calculate a value for the Bohr radius using Equation 1.4.3.8 to check that this equation is consistent with the value 52.9 pm. What would the radius be for $n = 1$ in the Li^{2+} ion?

Answer

Starting from Equation 1.4.3.8 and solving for r:

$$\frac{Ze^2 m_e r}{4\pi\epsilon_0} = n^2\hbar^2$$

$$r = \frac{4n^2\hbar^2\pi\epsilon_0}{Ze^2 m_e}$$

with

- e is the fundamental charge: $e = 1.60217662 \times 10^{-19} C^2$
- m_e is the mass of an electron: $m_e = 9.10938356 \times 10^{-31} kg$

- ϵ_o is the permittivity of free space: $\epsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$
- $\hbar$ is the reduced planks constant: $\hbar = 1.0546 \times 10^{-34} m^2 kg/s$

For the ground-state of the hydrogen atom: $Z = 1$ and $n = 1$.

$$\begin{aligned} r &= \frac{4\hbar^2 \pi \epsilon_0}{e^2 m_e} \\ &= \frac{4(1.0546 \times 10^{-34} m^2 kg/s)^2 \times \pi \times 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}}{(1.60217662 \times 10^{-19} C)^2 (9.10938356 \times 10^{-31} kg)} \\ &= 5.29 \times 10^{-11} m = 52.9\, pm \end{aligned}$$

For the ground-state of the lithium +2 ion: $Z = 3$ and $n = 1$

$$\begin{aligned} r &= \frac{4\hbar^2 \pi \epsilon_0}{3e^2 m_e} \\ &= \frac{4(1.0546 \times 10^{-34} m^2 kg/s)^2 \times \pi \times 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}}{3(1.60217662 \times 10^{-19} C)^2 (9.10938356 \times 10^{-31} kg)} \\ &= 1.76 \times 10^{-11} m = 17.6\, pm \end{aligned}$$

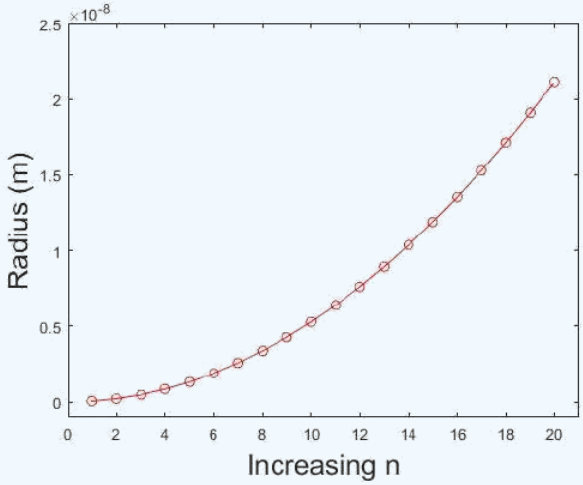
As expected, the $\mathbf{Li^{2+}}$ has a smaller radius than the $\mathbf{H}$ atoms because of the increased nuclear charge.

? Exercise 1.8.2 : Rydberg states

How do the radii of the hydrogen orbits vary with n? Prepare a graph showing r as a function of n. States of hydrogen atoms with $n = 200$ have been prepared (called Rydberg states). What is the diameter of the atoms in these states?

Answer

This is a straightforward application of Equation of 1.4.3.10. The hydrogen atom has only certain allowable radii and these radii can be predicted from the equation that relates them with each n. Note that the electron must be in motion so $n = 0$ is not allowed.



This plot shows the relationship of radius as a function of n. Note that at $n = 1$ the radius is not zero. (CC BY-NC; Ümit Kaya via LibreTexts)

$4\pi\epsilon_0 = 1.113 \times 10^{-10} \mathrm{C^2 J^{-1} m^{-1}}$ and $\hbar = 1.054 \times 10^{-34} \mathrm{Js}$, also knowing

$$e = 1.602 \times 10^{-19} \mathrm{C\ with}$$
$$m_e = 9.109 \times 10^{-31} \mathrm{kg}$$

and Z is the nuclear charge, we use this equation directly. A simplification can be made by taking advantage of the fact that

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e}$$

resulting in

$$r_n = \frac{a_0}{Z} n^2$$

where $a_0 = 5.292 \times 10^{-11}\text{m}$ which is the Bohr Radius.

Suppose we want to find the radius where $n = 200. n^2 = 40000$ so plugging in directly we have

$$r_n = \frac{(5.292 \times 10^{-11})}{(1)}(40000)$$
$$= 2.117 \times 10^{-6} m$$

for the radius of a hydrogen atom with an electron excited to the $\text{n} = 200$ state. The diameter is then $4.234 \times 10^{-6}\text{m}$.

The Wave Argument for Quantization

The above discussion is based off of a classical picture of an orbiting electron with the quantization from the angular momentum (Equation 1.4.3.7) requirement lifted from Planck's quantization arguments. Hence, only allows certain trajectories are stable (with differing radii). However, as discussed previously, the electron will have a wavelike property also with a de Broglie wavelength λ

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

Hence, a larger momentum p implies a shorter wavelength. That means as n increases (Equation 1.4.3.12), the wavelength must also increase; this is a common feature in quantum mechanics and will be often observed. In the Bohr atom, the circular symmetry and the wave property of the electron requires that the electron waves have an integer number of wavelengths (Figure 1.4.3.1*A*). If not, then the waves will overlap imperfectly and cancel out (i.e., the electron will cease to exist) as demonstrated in Figure 1.4.3.1*B*.

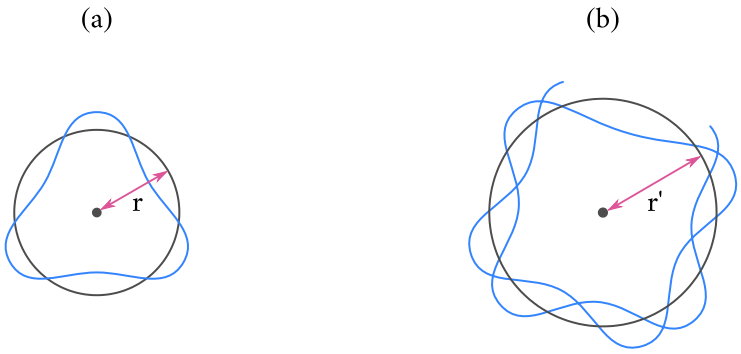


Figure 1.8.5 : Waves on a string have a wavelength related to the length of the string, allowing them to interfere constructively. (A) If we imagine the string bent into a closed circle, we get a rough idea of how electrons in circular orbits can interfere constructively. (B) If the wavelength does not fit into the circumference, the electron interferes destructively; it cannot exist in such an orbit. (CC BY-NC; Ümit Kaya via LibreTexts)

A more detailed discussion of the effect of electron waves in atoms will be discuss in the following chapters.

Derivation of the Rydberg Equation from Bohr Model

Given a prediction of the allowed energies of a system, how could we go about verifying them? The general experimental technique known as *spectroscopy* permits us to probe the various differences between the allowed energies. Thus, if the prediction of the actual energies, themselves, is correct, we should also be able to predict these differences. Let us assume that we are able to place the electron in Bohr's hydrogen atom into an energy state E_n for $n > 1$, i.e. one of its so-called *excited states*. The electron will rapidly return to its lowest energy state, known as the *ground state* and, in doing so, emit light. The energy carried away by the light is determined by the condition that the total energy is conserved (Figure 1.8.6).

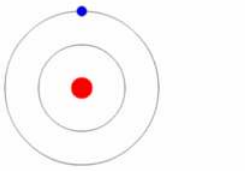


Figure 1.8.6 : A simple illustration of Bohr's model of the atom, with an electron making quantum leaps. (CC BY-SA 3.0 unported; Kurzon via Wikipedia)

Thus, if n_i is the integer that characterizes the initial (excited) state of the electron, and n_f is the final state (here we imagine that $n_f = 1$, but is applicable in cases that $n_f < n_i$, i.e., emission)

$$E_{nf} = E_{ni} - h\nu$$

or

$$\nu = \frac{E_{ni} - E_{nf}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{1.4.3.13}$$

We can now identify the Rydberg constant R_H with the ratio of constants on the right hand side of Equation 1.4.3.13

$$R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3}$$

Evaluating R_H from the fundamental constants in this formula gives a value within 0.5% of that obtained experimentally from the hydrogen atom spectrum.

Thus, by observing the emitted light, we can determine the energy difference between the initial and final energy levels, which results in the emission spectra discussed in Sections 1.4 and 1.5. Different values of n_f determine which emission spectrum is observed, and the examples shown in the figure are named after the individuals who first observed them. The figure below shows some of the transitions possible for different n_f and n_i values discussed previously.

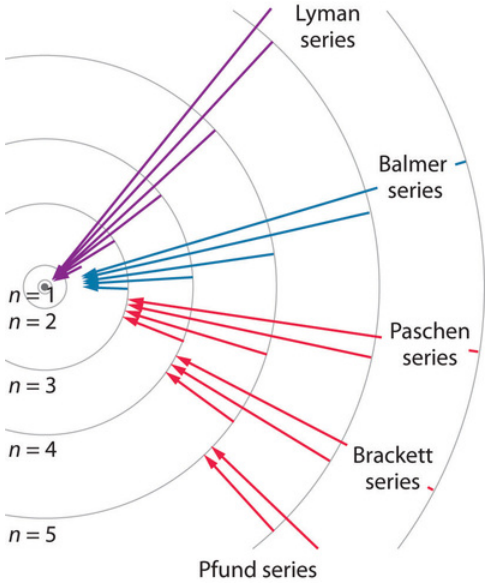


Figure 1.8.7 : Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. Orbits are not drawn to scale. (CC BY-NC-SA 3.0; anonymous)

If the atom absorbs light it ends up in an excited state as a result of the absorption. The absorption is only possible for light of certain frequencies, and again, conservation of energy determines what these frequencies are. If light is absorbed, then the final

energy E_{nf} will be related to the initial energy E_{ni} with $n_f > n_i$ by

$$E_{nf} = E_{ni} + h\nu$$

or

$$\nu = \frac{E_{nf} - E_{ni}}{h} = \frac{Z^2 e^4 m_e}{8\epsilon_0^2 h^3}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Exercise 1.8.3

a. Calculate the energy of a photon that is produced when an electron in a hydrogen atom goes from an orbit with $n = 4$ to an orbit with $n = 1$.

b. What happens to the energy of the photon as the initial value of n approaches infinity?

Answer

a:

$$\begin{aligned} E_{nf} &= E_{ni} - h\nu \\ E_{photon} = h\nu &= E_{nf} - E_{ni} \\ &= \frac{Z^2 e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\ &= \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{1^2} - \frac{1}{4^2}\right) \\ &= 2.18 \times 10^{-18}\left(1 - \frac{1}{16}\right) \\ &= 2.04 \times 10^{-18} J \end{aligned}$$

b:

As $n_i \to \infty$

$$E_{photon} = \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\frac{1}{n_i^2} \to 0$$

$$E_{photon} \to \frac{e^4 m_e}{8\epsilon_o^2 h^2}\left(\frac{1}{n_f^2}\right)$$

Bohr's proposal explained the hydrogen atom spectrum, the origin of the Rydberg formula, and the value of the Rydberg constant. Specifically it demonstrated that the integers in the Rydberg formula are a manifestation of quantization. The energy, the angular momentum, and the radius of the orbiting electron all are quantized. This quantization also parallels the concept of stable orbits in the Bohr model. Only certain values of E, M, and r are possible, and therefore the electron cannot collapse onto the nucleus by continuously radiating energy because it can only have certain energies, and it cannot be in certain regions of space. The electron can only jump from one orbit (quantum state) to another. The quantization means that the orbits are stable, and the electron cannot spiral into the nucleus in spite of the attractive Coulomb force.

Although Bohr's ideas successfully explained the hydrogen spectrum, they failed when applied to the spectra of other atoms. In addition a profound question remained. Why is angular momentum quantized in units of $\hbar$? As we shall see, de Broglie had an answer to this question, and this answer led Schrödinger to a general postulate that produces the quantization of angular momentum as a consequence. This quantization is not quite as simple as proposed by Bohr, and we will see that it is not possible to determine the distance of the electron from the nucleus as precisely as Bohr thought. In fact, since the position of the electron in the hydrogen atom is not at all as well defined as a classical orbit (such as the moon orbiting the earth) it is called an orbital. An electron orbital represents or describes the position of the electron around the nucleus in terms of a mathematical function called a wavefunction that yields the **probability** of positions of the electron.

Contributors and Attributions

- Mark Tuckerman (New York University)
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1.4.4: The Heisenberg Uncertainty Principle

Learning Objectives

- To understand that sometime you cannot know everything about a quantum system as demonstrated by the Heisenberg uncertainly principle.

In classical physics, studying the behavior of a physical system is often a simple task due to the fact that several physical qualities can be measured simultaneously. However, this possibility is absent in the quantum world. In 1927 the German physicist Werner Heisenberg described such limitations as the Heisenberg Uncertainty Principle, or simply the Uncertainty Principle, stating that it is not possible to measure both the momentum and position of a particle simultaneously.

The Heisenberg Uncertainty Principle is a fundamental theory in quantum mechanics that defines why a scientist cannot measure multiple quantum variables simultaneously. Until the dawn of quantum mechanics, it was held as a fact that all variables of an object could be known to exact precision simultaneously for a given moment. Newtonian physics placed no limits on how better procedures and techniques could reduce measurement uncertainty so that it was conceivable that with proper care and accuracy all information could be defined. Heisenberg made the bold proposition that there is a lower limit to this precision making our knowledge of a particle inherently uncertain.

Probability

Matter and photons are waves, implying they are spread out over some distance. What is the position of a particle, such as an electron? Is it at the center of the wave? The answer lies in how you measure the position of an electron. Experiments show that you will find the electron at some definite location, unlike a wave. But if you set up exactly the same situation and measure it again, you will find the electron in a different location, often far outside any experimental uncertainty in your measurement. Repeated measurements will display a statistical distribution of locations that appears wavelike (Figure 1.9.1).

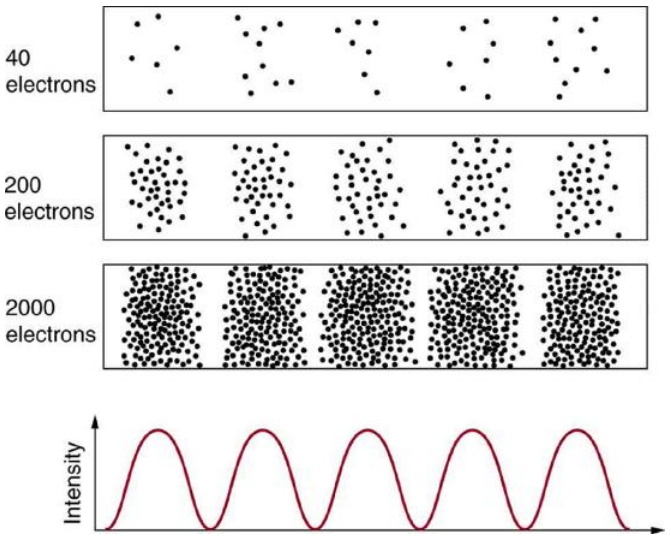


Figure 1.9.1 : The building up of the diffraction pattern of electrons scattered from a crystal surface. Each electron arrives at a definite location, which cannot be precisely predicted. The overall distribution shown at the bottom can be predicted as the diffraction of waves having the de Broglie wavelength of the electrons (CC BY 4.0; OpenStax).

After de Broglie proposed the wave nature of matter, many physicists, including Schrödinger and Heisenberg, explored the consequences. The idea quickly emerged that, *because of its wave character, a particle's trajectory and destination cannot be precisely predicted for each particle individually*. However, each particle goes to a definite place (Figure 1.9.1). After compiling enough data, you get a distribution related to the particle's wavelength and diffraction pattern. There is a certain *probability* of finding the particle at a given location, and the overall pattern is called a **probability distribution**. Those who developed quantum mechanics devised equations that predicted the probability distribution in various circumstances.

It is somewhat disquieting to think that you cannot predict exactly where an individual particle will go, or even follow it to its destination. Let us explore what happens if we try to follow a particle. Consider the double-slit patterns obtained for electrons and photons in Figure 1.9.2 . The interferrence patterns build up statistically as individual particles fall on the detector. This can be observed for photons or electrons—for now, let us concentrate on electrons. You might imagine that the electrons are interfering with one another as any waves do. To test this, you can lower the intensity until there is never more than one electron between the slits and the screen. The same interference pattern builds up!

This implies that a particle's probability distribution spans both slits, and the particles actually interfere with themselves. Does this also mean that the electron goes through both slits? An electron is a basic unit of matter that is not divisible. But it is a fair question, and so we should look to see if the electron traverses one slit or the other, or both. One possibility is to have coils around the slits that detect charges moving through them. What is observed is that an electron always goes through one slit or the other; it does not split to go through both.

But there is a catch. If you determine that the electron went through one of the slits, you no longer get a double slit pattern—instead, you get single slit interference. There is no escape by using another method of determining which slit the electron went through. Knowing the particle went through one slit forces a single-slit pattern. If you do not observe which slit the electron goes through, you obtain a double-slit pattern. How does knowing which slit the electron passed through change the pattern? The answer is fundamentally important—*measurement affects the system being observed*. Information can be lost, and in some cases it is impossible to measure two physical quantities simultaneously to exact precision. For example, you can measure the position of a moving electron by scattering light or other electrons from it. Those probes have momentum themselves, and by scattering from the electron, they change its momentum *in a manner that loses information*. There is a limit to absolute knowledge, even in principle.

Heisenberg's Uncertainty Principle

It is mathematically possible to express the uncertainty that, Heisenberg concluded, always exists if one attempts to measure the momentum and position of particles. First, we must define the variable "x" as the position of the particle, and define "p" as the momentum of the particle. The momentum of a photon of light is known to simply be its frequency, expressed by the ratio h/λ, where h represents Planck's constant and λ represents the wavelength of the photon. The position of a photon of light is simply its wavelength (λ). To represent finite change in quantities, the Greek uppercase letter delta, or Δ, is placed in front of the quantity. Therefore,

$$\Delta p = \frac{h}{\lambda} \tag{1.4.4.1}$$

$$\Delta x = \lambda \tag{1.4.4.2}$$

By substituting Δx for λ into Equation 1.4.4.1, we derive

$$\Delta p = \frac{h}{\Delta x} \tag{1.4.4.3}$$

or,

$$\Delta p \Delta x = h \tag{1.4.4.4}$$

early form of uncertainty principle

A Common Trend in Quantum Systems

Equation 1.4.4.4 can be derived by assuming the particle of interest is behaving as a particle, and not as a wave. Simply let $\Delta p = mv$, and $\Delta x = h/(mv)$ (from De Broglie's expression for the wavelength of a particle). Substituting in Δp for mv in the second equation leads to Equation 1.4.4.4.

Equation 1.4.4.4 was further refined by Heisenberg and his colleague Niels Bohr, and was eventually rewritten as

$$\Delta p_x \Delta x \geq \frac{h}{4\pi} = \frac{\hbar}{2} \tag{1.4.4.5}$$

with $\hbar = \frac{h}{2\pi} = 1.0545718 \times 10^{-34}\ m^2 \cdot kg/s$.

Equation 1.4.4.5 reveals that the more accurately a particle's position is known (the smaller Δx is), the less accurately the momentum of the particle in the x direction (Δp_x) is known. Mathematically, this occurs because the smaller Δx becomes, the larger Δp_x must become in order to satisfy the inequality. However, the more accurately momentum is known the less accurately position is known (Figure 1.9.2).

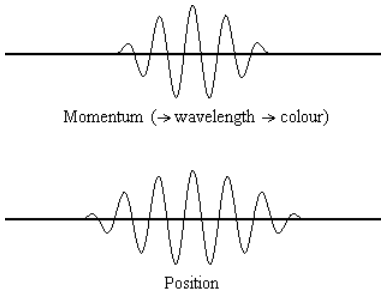


Figure 1.9.2 : The animation shows the relevant spreads in the uncertainty for position and momentum of light/photons (light wave's corresponding photon particle). From the result of de Broglie, we know that for a particle with known momentum, p will have a precise value for its de Broglie wavelength can be determined (and hence a specific color of the light).

What is the Proper Definition of Uncertainty?

Equation 1.4.4.5 relates the uncertainty of momentum and position. An immediate questions that arise is if Δx represents the full range of possible x values or if it is half (e.g., $\langle x \rangle \pm \Delta x$). Δx is the standard deviation and is a statistic measure of the spread of x values. The use of half the possible range is more accurate estimate of Δx. As we will demonstrated later, once we construct a wavefunction to describe the system, then both x and Δx can be explicitly derived. However for now, Equation 1.4.4.5 will work.

For example: If a problem argues a particle is trapped in a box of length, L, then the uncertainly of it position is $\pm L/2$. So the value of Δx used in Equation 1.4.4.5 should be $L/2$, not L.

Example 1.9.1

An electron is confined to the size of a magnesium atom with a 150 pm radius. What is the **minimum** uncertainty in its velocity?

Solution

The uncertainty principle (Equation 1.4.4.5):

$$\Delta p \Delta x \geq \frac{\hbar}{2}$$

can be written

$$\Delta p \geq \frac{\hbar}{2 \Delta x}$$

and substituting $\Delta p = m \Delta v$ since the mass is not uncertain.

$$\Delta v \geq \frac{\hbar}{2\, m\, \Delta x}$$

the relevant parameters are

- mass of electron $m = m_e = 9.109383 \times 10^{-31}\ kg$
- uncertainty in position: $\Delta x = 150 \times 10^{-12} m$

$$\Delta v \geq \frac{1.0545718 \times 10^{-34}\ \cancel{kg}\, m^2/s}{(2)\,(9.109383 \times 10^{-31}\ \cancel{kg})\,(150 \times 10^{-12}\ \cancel{m})}$$

$$= 3.9 \times 10^5\ m/s$$

Exercise 1.9.1

What is the maximum uncertainty of velocity the electron described in Example 1.9.1 ?

Answer

Infinity. There is no limit in the maximum uncertainty, just the minimum uncertainty.

Understanding the Uncertainty Principle through Wave Packets and the Slit Experiment

It is hard for most people to accept the uncertainty principle, because in classical physics the velocity and position of an object can be calculated with certainty and accuracy. However, in quantum mechanics, the wave-particle duality of electrons does not allow us to accurately calculate both the momentum and position because the wave is not in one exact location but is spread out over space. A "wave packet" can be used to demonstrate how either the momentum or position of a particle can be precisely calculated, but not both of them simultaneously. An accumulation of waves of varying wavelengths can be combined to create an average wavelength through an interference pattern: this average wavelength is called the "wave packet". The more waves that are combined in the "wave packet", the more precise the position of the particle becomes and the more uncertain the momentum becomes because more wavelengths of varying momenta are added. Conversely, if we want a more precise momentum, we would add less wavelengths to the "wave packet" and then the position would become more uncertain. Therefore, there is no way to find both the position and momentum of a particle simultaneously.



Several scientists have debated the Uncertainty Principle, including Einstein. Einstein created a slit experiment to try and disprove the Uncertainty Principle. He had light passing through a slit, which causes an uncertainty of momentum because the light behaves like a particle and a wave as it passes through the slit. Therefore, the momentum is unknown, but the initial position of the particle is known. Here is a video that demonstrates particles of light passing through a slit and as the slit becomes smaller, the final possible array of directions of the particles becomes wider. As the position of the particle becomes more precise when the slit is narrowed, the direction, or therefore the momentum, of the particle becomes less known as seen by a wider horizontal distribution of the light.

Example 1.9.2

The speed of a 1.0 g projectile is known to within $10^{-6}\ m/s$.

a. Calculate the *minimum* uncertainty in its position.
b. What is the *maximum* uncertainty of its position?

Solution a

From Equation 1.4.4.5, the $\Delta p_x = m\Delta v_x$ with $m = 1.0\ g$. Solving for Δx to get

$$\begin{aligned}\Delta x &= \frac{\hbar}{2m\Delta v} \\ &= \frac{1.0545718 \times 10^{-34}\ m^2 \cdot kg/s}{(2)(0.001\ kg)(10^{-6}\ m/s)} \\ &= 5.3 \times 10^{-26}\ m\end{aligned}$$

This negligible for all intents and purpose as expected for any macroscopic object.

Solution b

Unlimited (or the size of the universe). The Heisenberg uncertainty principles does not quantify the maximum uncertainty.

Exercise 1.9.2

Estimate the minimum uncertainty in the speed of an electron confined to a hydrogen atom within a diameter of $1 \times 10^{-10} m$?

Answer

We need to quantify the uncertainty of the electron in position. We can estimate that as $\pm 5 \times 10^{-10} m$. Hence, substituting the relavant numbers into Equation 1.4.4.5 and solving for Δv we get

$$\Delta v = 1.15 \times 10^{6}\ km/s$$

Notice that the uncertainty is significantly greater for the electron in a hydrogen atom than in the magnesium atom (Example 1.9.1) as expected since the magnesium atom is appreciably bigger.

Heisenberg's Uncertainty Principle not only helped shape the new school of thought known today as quantum mechanics, but it also helped discredit older theories. Most importantly, the Heisenberg Uncertainty Principle made it obvious that there was a fundamental error in the Bohr model of the atom. Since the position and momentum of a particle cannot be known simultaneously, Bohr's theory that the electron traveled in a circular path of a fixed radius orbiting the nucleus was obsolete. Furthermore, Heisenberg's uncertainty principle, when combined with other revolutionary theories in quantum mechanics, helped shape wave mechanics and the current scientific understanding of the atom.

Humor: Heisenberg and the Police

- Heisenberg get pulled over for speeding by the police. The officer asks him "Do you know how fast you were going?"
- Heisenberg replies, "No, but we know exactly where we are!"
- The officer looks at him confused and says "you were going 108 miles per hour!"
- Heisenberg throws his arms up and cries, "Great! Now we're lost!"

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1.4.E: The Dawn of the Quantum Theory (Exercises)

Solutions to select questions can be found online.

1.1A

Sodium metal has a threshold frequency of 4.40×10^{14} Hz. What is the kinetic energy of a photoelectron ejected from the surface of a piece of sodium when the ejecting photon is 6.20×10^{14} Hz? What is the velocity of this photoelectron? From which region of the electromagnetic spectrum is this photon?

1.1B

What is the longest-wavelength electromagnetic radiation that can eject a photoelectron from silver, given that the work function is 4.73 eV? Is this in the visible range?

Solution

263 nm

1.1C

Find the longest-wavelength photon that can eject an electron from potassium, given that the work function is 2.24 eV. Is this visible electromagnetic radiation?

1.1C

What is the work function in eV of electrons in magnesium, if the longest-wavelength photon that can eject electrons is 337 nm?

Solution

3.69 eV

1.1D

Calculate the work function in eV of electrons in aluminum, if the longest-wavelength photon that can eject the electromagnetic is 304 nm.

1.1E

What is the maximum kinetic energy in eV of electrons ejected from sodium metal by 450-nm electromagnetic radiation, given that the work function is 2.28 eV?

Solution

0.483 eV

1.1F

UV radiation having a wavelength of 120 nm falls on gold metal, to which electrons are bound by 4.82 eV. What is the maximum kinetic energy of the ejected photoelectrons?

1.1G

Violet light of wavelength 400 nm ejects electrons with a maximum kinetic energy of 0.860 eV from sodium metal. What is the work function of electrons to sodium metal?

Solution

2.25 eV

1.1H

UV radiation having a 300-nm wavelength falls on uranium metal, ejecting 0.500-eV electrons. What is the work function of electrons to uranium metal?

1.1I

What is the wavelength of electromagnetic radiation that ejects 2.00-eV electrons from calcium metal, given that the work function is 2.71 eV? What type of electromagnetic radiation is this?

Solution

(a) 264 nm

(b) Ultraviolet

1.1J

Find the wavelength of photons that eject 0.100-eV electrons from potassium, given that the work function is 2.24 eV. Are these photons visible?

1.1K

What is the maximum velocity of electrons ejected from a material by 80-nm photons, if they are bound to the material by 4.73 eV?

Solution

1.95×10^{6} m/s

1.1L

Photoelectrons from a material with a work function of 2.71 eV are ejected by 420-nm photons. Once ejected, how long does it take these electrons to travel 2.50 cm to a detection device?

1.1M

A laser with a power output of 2.00 mW at a wavelength of 400 nm is projected onto calcium metal. (a) How many electrons per second are ejected? (b) What power is carried away by the electrons, given that the work function is 2.71 eV?

Solution

(a) $\mathbf{4.02 \times 10^{15}/s}$

(b) 0.256 mW

1.1N

(a) Calculate the number of photoelectrons per second ejected from a 1.00-mm 2 area of sodium metal by 500-nm electromagnetic radiation having an intensity of $\mathbf{1.30\ kW/m^2}$ (the intensity of sunlight above the Earth's atmosphere). (b) Given that the work function is 2.28 eV, what power is carried away by the electrons? (c) The electrons carry away less power than brought in by the photons. Where does the other power go? How can it be recovered?

1.1O

Red light having a wavelength of 700 nm is projected onto magnesium metal to which electrons are bound by 3.68 eV. (a) Use $\boldsymbol{KE_e = h\nu - \Phi}$ to calculate the kinetic energy of the ejected electrons. (b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

Solution

(a) –1.90 eV–1.90 eV

(b) Negative kinetic energy

(c) That the electrons would be knocked free.

Unreasonable Results

1.1P

(a) What is the work function of electrons to a material from which 4.00-eV electrons are ejected by 400-nm electromagnetic radiation? (b) What is unreasonable about this result? (c) Which assumptions are unreasonable or inconsistent?

1.2A

a. Suppose the electron in a hydrogen atom is in the circular Bohr orbit with n = 30. How many times per second does it go around?
b. Suppose now the electron drops to the n = 29 state, emitting a single photon. What is the frequency of this photon, in cycles per second?
c. Comment on the relation between your answers in (a), (b) above. What would you guess the relation to be for n = 300?

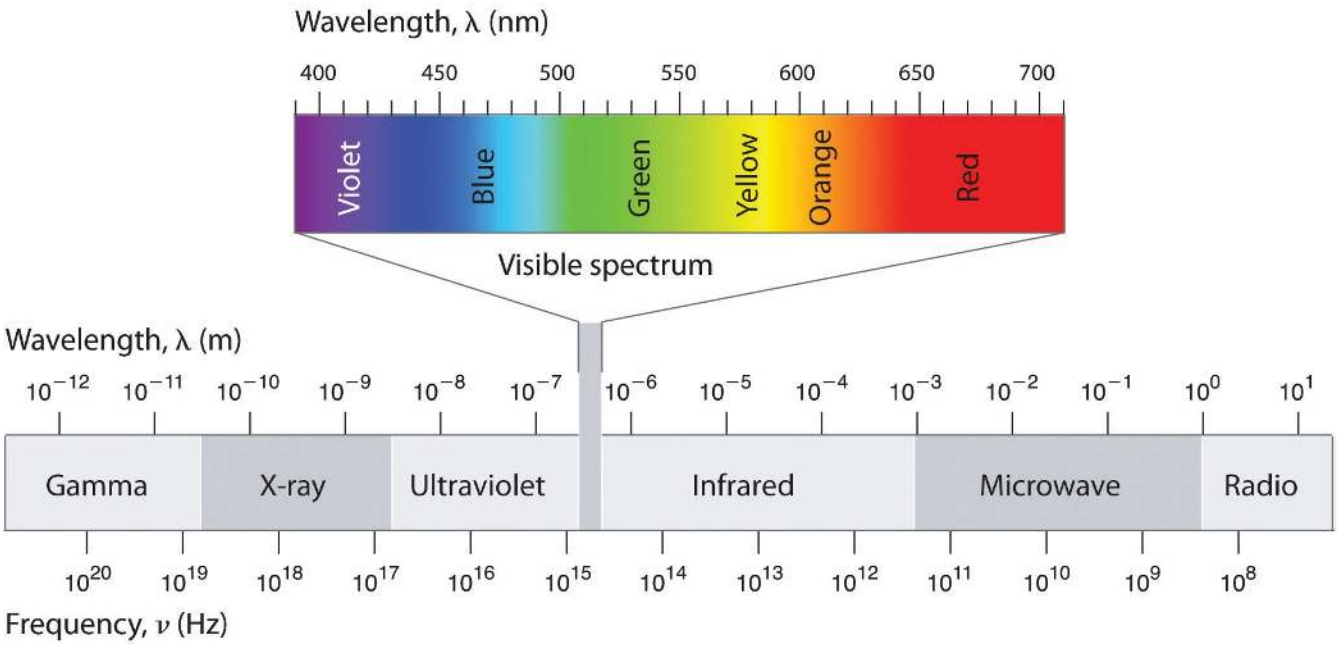
1.2B

The μ (muon) is a cousin of the electron, the only difference being its mass is 207 times greater. The μ has a lifetime of about 2 ms. If a beam of muons is directed at a solid, the muons will go into orbit around nuclei. The Bohr atom, with a muon replacing the electron, is a useful model for picturing this.

1. For a nucleus of charge Ze, how large is the n = 1 μ orbit compared with the electron orbit?
2. What is the frequency of the photon emitted by the μ in the n = 2 to n = 1 transition?
3. For the gold nucleus, the $n = 1$ μ orbit is inside the nucleus. Find the frequency of the emitted photon for $n = 2$ to $n = 1$ in this case. (Hint: you'll need the radius of the gold nucleus. Assume here that the positive charge is uniformly spread throughout the nucleus.)

1.3

Past Infrared region, in direction of the lower energies, the microwave region is located. In this region, radiation usually is characterized by frequency (ν) which is expressed in units of **MHz**, where **Hz** is a cycle per second. Given a microwave frequency of 2.0×10^4 **MHz**, calculate v, λ, and energy per photon for this radiation and then compare the results with figure below.



Solution

The frequency(v) of the microwave radiation is given and once convert to Hz get the following

$$v=2.0e^{4}MHz(1e^{6}Hz/1MHz)= 2.0e^{10}s^{-1}\,Hz$$

now we find the wavelength using formula and get

$$\lambda = \frac{c}{v} = \frac{2.998 \times 10^8 m\,s^{-1}}{2.0 \times 10^{10}\,s^{-1}} = 1.5 \times 10^{-2}\,m$$

finally we use E=hv to calculate the energy

$$E=hv=(6.626e^{-34}J*s)(2.0e^{10}s^{-1})= 1.3e^{-23}J$$

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1.4

Compare the Planck Distribution and the Rayleigh-Jean Distributions. For large values of ν, which one would be greater?

Solution

The Planck Distribution is

$$d\rho = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{\frac{h\nu}{k_B T}} - 1} d\nu$$

And the Rayleigh Jean Distribution is

$$d\rho = \frac{8\pi \rho^2 k_B T}{c^3} d\nu$$

For larger ν, the Rayleigh Jean Distribution increases, while the Planck Distribution decreases because of the exponential term in the denominator outweighing the ν^3 term.

1.4

Plancks principal assumption was that energies of electronic oscillator can only have values $E = nh\nu$ and $\Delta E = h\nu$. In fact, as v→0 then ΔE→0 and E becomes continuous. It should be expected that the nonclassical Plank distribution to go over to the classical Rayleigh-Jeans distribution at low frequencies, where ΔE →0. Prove that Equation 1.2 reduces to Equation 1.1 as v→0.

Note: The Taylor expansion of an exponential

$$e^x \approx 1 + x + \left(\frac{x^2}{2!}\right) + \ldots$$

can truncated to $e^x \approx 1 + x$ when x is small.

Solution

Important to know Planks equation and put it into use:

$$dp(v,T)=P_v(T)dv=(8\pi h/c^3)(v^3 dv/e^{hv/k_bT}-1)$$

Note: $P_v(T)dv \Rightarrow$ is the radiant energy density between frequencies v and v+dv

Now for small x we have $e^x \approx 1+x$

and as v→0, $hv/k_bT \rightarrow 0$ once we have this we get the following

$$dp(v,T)=(8\pi h/c^3)*((v^3 dv)/(1+(hv/k_bT)-1))= 8\pi h v^3 k_B T dv/c^3 hv = 8\pi v^2 k_B T dv/c^3$$

and this is the classical Rayleigh-Jeans distribution.

1.5

The visible spectrum is in the 400-700 nm range, and contains about 40% of the sun's radiation intensity. Using the Planck Distribution, write an integral expression that can be evaluated to give this result (do not evaluate the integral).

Solution

The Planck Blackbody distribution in terms of wavelength is

$$\rho_\lambda(\lambda,T)d\lambda = \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

And so the intensity contained in the visible spectrum (from 400 nm and 700 nm) is

$$\int_{400}^{700}\rho_\lambda(\lambda,T)d\lambda = \int_{400\,nm}^{700\,nm}\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

The intensity contained in the whole spectrum can be given by

$$\int_0^{\infty}\rho_\lambda(\lambda,T)d\lambda = \int_0^{\infty}\frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}}-1}d\lambda$$

And thus

$$40\% = 100\% \times \frac{\rho_{visible}}{\rho_{total}} = 100\% \times \frac{\int_{400}^{700}\frac{8phc}{\lambda^5\left(e^{\frac{hc}{\lambda k_b T}}-1\right)}d\lambda}{\int_0^{\infty}\frac{8phc}{\lambda^5\left(e^{\frac{hc}{\lambda k_b T}}-1\right)}d\lambda}$$

1.13

What is the frequency and energy of a single 310 nm photon?

Solution

Given: λ = 310 nm.

To find the frequency:

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

]

$$\nu = \frac{2.99\times10^8\frac{m}{s}}{310\ nm}$$

$$\nu = 9.67\times10^{14}s^{-1}$$

To find the energy:

$$E = h\nu$$

$$E = (6.626\times10^{-34})\times\nu$$

$$E = 6.41\times10^{-19}J$$

1.14

A laser emits 3.3×10^{17}photons per second. If the energy per photon is $6.4 \times 10^{-20} J$ per photon, find the a) wattage and b) wavelength of the laser. in what electromagnetic spectra is the laser in?

Solution

a)

$$W = (6.4 \times 10^{-20} J)(3.3 \times 10^{17} \frac{1}{s})$$

$$W = 0.02112 \frac{J}{s}$$

b)

$$E = h\frac{c}{\lambda}$$

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

$$\lambda = \frac{(3 \times 10^{8} \frac{m}{s})(6.626 \times 10^{-34} Js)}{6.4 \times 10^{-20} J}$$

$$\lambda = 3.106 \times 10^{-6} m$$

c)

infrared spectrum

1.15

What is the max wavelength with a given temperature of 7500K?

Solution

For a given temperature, the maximum wavelength allowed is given by:

$$T = \frac{2.9 \times 10^{-3} \text{mK}}{\lambda_{max}}$$

Given: T = 7500K

$$7500 = \frac{2.9 \times 10^{-3} \text{mK}}{\lambda_{max}}$$

$$\lambda_{max} = \frac{2.9 \times 10^{-3} \text{mK}}{7500 \text{K}}$$

$$\lambda_{max} = 3.8 \times 10^{-7} \text{m}$$

Q1.15

A light bulb is a blackbody radiator. What temperature is required such that $\lambda_{max} = 400nm$?

Solution

$$T = \frac{(2.90 \times 10^{-3}\ m \cdot K)}{400 \times 10^{-9}\ m} = 7250\ K.$$

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1.16

An unknown elemental metal has work function of $\Phi = 8.01 \times 10^{-19} J$. Upon illumination with UV light of wavelength 162 nm, electrons are ejected with velocity of at $2.95 \times 10^3 \frac{m}{s}$. What is the threshold wavelength? What is the work function in units of eV? What metal does this correspond to (you will need to consult Table B1)?

Solution

This question involves a bit of a trick in that neither the wavelength of radiation nor the velocity of electrons are necessary to solve for the threshold wavelength or material as requested. To solve for the threshold wavelength, we employ the concept that kinetic energy is 0 at threshold frequency and then use a relation equation to solve for threshold wavelength.

$$\frac{1}{2}mv^2 = h\nu - \Phi$$

So,

$$\nu_{threshold} = \frac{\Phi}{h} = 1.21 \times 10^{15} s^{-1}$$

and

$$\lambda_{threshold} = \frac{c}{\nu_{threshold}} = 248nm$$

With a basic conversion of

$$1\ J = 6.242 \times 10^{18} eV$$

we see that the work function is 5 eV. Using Table B1, we see that this value corresponds to Cobalt (discovered by Georg Brandt).

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1.16

Given the work function of sodium is 1.87 eV, find the kinetic energy of the ejected electrons when light of frequency 2.3 times greater than the threshold frequency is used to excite the electrons.

Solution

step 1: convert work function from electron volts to joules

$$\phi = 1.87\ eV$$

1 eV = $1.602 \times 10^{-19} J$

$$\phi = 1.87 eV \times \frac{1.602 \times 10^{-19} J}{1\ eV} = 2.995 \times 10^{-19} J$$

Step 2: Solve for the threshold frequency

$$\phi = hf$$

$$\frac{\phi}{h} = f$$

$$\frac{2.995 \times 10^{-19} J}{6.626 \times 10^{-34} Js} = f$$

$$4.5 \times 10^{14} Hz = f$$

Step 3: Use threshold frequency to solve for kinetic energy at desired conditions

$$KE = h(2.3f - f)$$

$$KE = h(1.3f)$$

$$KE = (6.626 \times 10^{-34} Js)(1.3(4.5 \times 10^{14} Hz))$$

$$KE = 3.87 \times 10^{-19} J$$

Q1.17

Find kinetic energy emitted off surface of tungsten that is radiated with radiation of 250 nm. Work function of tungsten 4.50 eV.

Solution

Kinetic energy is represented by

$$E = h\nu$$

we then use $c = \nu\lambda$ for the frequency to find

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

Then substitute values to get

$$E = \frac{(6.626 \times 10^{-34}\ J \cdot s)(3.00 \times 10^{8} m/s)}{250 \times 10^{-9}\ m} = 7.95 \times 10^{-19}\ J$$

Convert to eV, to get

$$E = (7.95 \times 10^{-19}\ J)\frac{1\ eV}{1.6 \times 10^{-19}\ J} = 4.97\ eV.$$

Use $KE_e = h\nu - \Phi$ to finally get

$$KE_e = h\nu - \Phi = 4.97\ eV - 4.50\ eV = 0.47\ eV.$$

1.18

A smooth silver Thanksgiving platter and serving spoon (the pilgrims had knives and spoons but no forks) are irradiated with light of wavelength 317 nm. The work function is $\Phi = 6.825 \times 10^{-19} J$. What is the kinetic energy of the ejected electrons [eV]? The threshold frequency?

Solution

We first solve for the threshold frequency.

$$\frac{hc}{\lambda} = \Phi \ = h\nu$$

Rearrange to solve for ν

$$\nu = \frac{\Phi}{h}$$
$$= 1.03 \times 10^{15} s^{-1}$$

Now we solve for kinetic energy.

$$\frac{1}{2} m v^2 = h\nu - \Phi$$

where

$$\nu = \nu_{radiation}$$

and we recall that

$$\nu = \frac{c}{\lambda_{radiation}}$$

Using the right hand side of that kinetic energy equation, we find the result to be

$$KE = 2.55 \times 10^{-19}$$

Q1.18

When a clean surface of silver is irradiated with light of wavelength 255 nm, the work function of ejected electrons is 4.18 eV. Calculate the kinetic energy in eV of the silver and the threshold frequency.

Solution

Kinetic Energy of the electrons can be represented with the formula

$$KE = h\nu - \Phi$$

We have to solve for the Kinetic energy in eV

$$KE = h\nu - \Phi$$

substituting known values gives

$$KE = (6.626 \times 10^{-}34 Js)(\frac{3 \times 10^{8} m/s}{255 \times 10^{-}9m}) - 6.69 * 10^{-}19J$$

$$KE = 1.105 \times 10^{-}19J \approx .690eV$$

The second part of the question asks us to solve for the threshold frequency

$$\nu_o = \frac{\Phi}{h}$$
$$\nu_o = \frac{6.69 \times 10^{-}19J}{6.626 \times 10^{-}34J * s}$$
$$= 1.01 \times 10^{15} Hz$$

Q1.21

A line in the Paschen series of hydrogen has a wavelength of 1.01 x 10^{-6} m. Find the original energy of the electron.

Solution

For the Paschen series n_1= 3. To find n_2 we have to use the Rhydberg formula:

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$$\frac{1}{\lambda} = R_H \times \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

substituting our known values will give us

$$\frac{1}{1.01 \times 10^{-6} m} = 109677 cm^{-1} \left(\frac{1}{3^2} + \frac{1}{n_2^2}\right)$$

converting our units and using algebra gives us

$$0.0903 = \left(\frac{1}{9} - \frac{1}{n_2^2}\right)$$

where

$$n_2 = 6.93 \approx 7$$

We approximate to 7 since n is an integer.

1.22

How does the energy change when a particle absorbs and releases a photon? Show the effects on the state that the particle is in and the energy itself.

Solution

The energy would increase when a photon is absorbed and decrease when a photon is released. We have two equations

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

$$\frac{1}{\lambda} = 109680 \left(\frac{1}{n_1} - \frac{1}{n_2}\right)$$

When a photon is absorbed, λ is positive and when a photon is released λ is negative. From the first equation, we can see that E only depends on the sign of λ. So when a photon is absorbed, energy is positive (increases) and when it is released, energy is negative (decreases).

The second equation shows that when λ is negative, n_1 must be greater than n_2 so the final state is at a lower quantum number than the initial and vice versa for when a photon is absorbed.

1.23

Show that the (a) wavelength of 100 nm occurs within the Lyman series, that (b) wavelength of 500 nm occurs within the Balmer series, and that (c) wavelength of 1000 nm occurs within the Paschen series. Identify the spectral regions to which these wavelengths correspond.

Solution

We can show the where the wavelengths occurs by calculate the maximum and minimum wavelengths of each series using the Rydberg formula.

a) Lyman Series:

$$Max: \frac{1}{\lambda} = 109680\left(1 - \frac{1}{2^2}\right) cm^{-1}$$

$$\lambda = 121.6nm$$

$$Min: \frac{1}{\lambda} = 109680\left(1 - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 91.2nm$$

The range for the Lyman series from 91.2 nm to 121.6 nm, therefore a wavelength of 100 nm occurs within the Lyman series. This corresponds to the ultraviolent region of the spectrum.

b) Balmer Series:

$$Max: \frac{1}{\lambda} = 109680\left(\frac{1}{2^2} - \frac{1}{3^2}\right) cm^{-1}$$

$$\lambda = 656.5nm$$

$$Min: \frac{1}{\lambda} = 109680\left(\frac{1}{2^2} - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 364.7nm$$

The range for the Balmer series from 364.7 nm to 656.5 nm, therefore a wavelength of 500 nm occurs within the Balmer series. This corresponds to the near ultraviolent region of the spectrum.

c) Paschen Series:

$$Max: \frac{1}{\lambda} = 109680\left(\frac{1}{3^2} - \frac{1}{4^2}\right) cm^{-1}$$

$$\lambda = 1875.6nm$$

$$Min: \frac{1}{\lambda} = 109680\left(\frac{1}{3^2} - \frac{1}{\infty}\right) cm^{-1}$$

$$\lambda = 820.6nm$$

The range for the Paschen series from 820.6 nm to 1875.6 nm, therefore a wavelength of 1000 nm occurs within the Paschen series. This corresponds to the near infrared region of the spectrum.

1.24

Calculate the wavelength and the energy of a photon associated with the series limit of the Balmer series.

Solution

First find the minimum wavelength for the Balmer series.

$$\frac{1}{\lambda} = 109,680 cm^{-1}\left(\frac{1}{2^2} - \frac{1}{\infty}\right)$$

$$\lambda = 364.7\, nm$$

Now we can use the wavelength to find the energy.

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

$$= \frac{(6.626 \times 10^{-34})(3 \times 10^{8})}{364.7 \times 10^{-9}}$$

$$= 5.45 \times 10^{-19}\, J$$

1.25

For the following particles (a) an electron with a kinetic energy of 50eV, (b) a proton with a kinetic energy of 50eV , and (c) an electron in the second Bohr orbit of a hydrogen atom, calculate the de Broglie wavelength of each.

Solution

We use $\lambda = \frac{h}{p}$ in all cases to find λ.

a.

$$KE = \frac{mv^2}{2}$$

$$50eV\left(\frac{1.602 \times 10^{-19} J}{1eV}\right) = \frac{(v^2)(9.109 \times 10^{-31} kg)}{2}$$

$$v = 4.19 \times 10^6\, m \cdot s^{-1}$$

So

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$
$$= \frac{6.626 \times 10^{-34} J \cdot s}{(9.109 \times 10^{-31} kg)(4.19 \times 10^6 m \cdot s^{-1})}$$
$$= 1.23 \times 10^{-10} m = 0.123\, nm$$

b. Replace m_e with m_p in (a) to find $\lambda = 2.86 \times 10^{-3} nm$.

c. We must first determine the velocity of an electron in the second Bohr orbit of a hydrogen atom. The velocity of an electron is given by the following equation:

$$v = \frac{nh}{2(\pi)m_e r}$$

and we know

$$r = \frac{\epsilon_0 h^2 n^2}{(\pi)m_e e^2}$$

substituting the two equations we find that

$$v = \frac{e^2}{2nh\epsilon_0}$$

For $n = 2$, because we are talking about the second orbit

$$v = \frac{(1.602 \times 10^{-19} C)^2}{2(2)(6.626 \times 10^{-34} J \cdot s)(8.854 \times 10^{-12} C^2 J^{-1} m^{-1})}$$
$$= 1.09 \times 10^6 m \cdot s^{-1}$$

So

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$
$$= \frac{6.626 \times 10^{-34} J \cdot s}{(9.109 \times 10^{-31} kg)(1.09 \times 10^6 m \cdot s^{-1}}$$
$$= 6.64 \times 10^{-10} m = 0.664\, nm$$

Q1.26

a. What is the velocity and wavelength of an electron with a voltage increase of 75 V?
b. What is the momentum of an electron with a de Broglie wavelength of 20 nm?(mass of an electron is $9.109 \times 10^{-31}\, kg$)

Solution

a.

$$\begin{aligned} KE &= (\text{electron charge}) \times (\text{potential}) \\ &= (1.602 \times 10^{-19}\, C)(75\, V) \\ &= 1.2 \times 10^{-17}\, J \\ &= (1/2)mv^2 \end{aligned}$$

$$v = \sqrt{\frac{2(KE)}{m}} = \sqrt{\frac{2(1.2 \times 10^{-17} J)}{(9.109 \times 10^{-31} kg)}} = 5.133 \times 10^{6} m * s^{-1}$$

$$\begin{aligned} \lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} J * S}{(9.109 \times 10^{-31} kg)(5.133 \times 10^{6} m * s^{-1})} \\ &= 1.2267\, m \end{aligned}$$

b.

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

$$\begin{aligned} p &= \frac{h}{\lambda} \\ &= \frac{6.626 \times 10^{-34} J * S}{20 \times 10^{-6} m} \\ &= 3.313 \times 10^{-29} kg * m * s^{-1} \end{aligned}$$

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1.27

Through what potential a proton must initially at rest fall so its de Broglie wavelength is $1.83 \times 10^{-10}\,m$?

Q1.28

Calculate the energy and wavelength associated with a β particle that has fallen through a potential difference of 3.2 V. Take the mass of a β particle to be $9.1 \times 10^{-31}\text{kg}$.

Solution

A beta particle is an electron, so it has a -1 charge.

$$KE = (\beta \text{ particle charge}) \times \text{Potential} = |-1.602 \times 10^{-19}\text{C}| \times 3.2\text{V}$$

$$KE = 5.126 \times 10^{-19}\text{J per } \beta \text{ particle}$$

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

$$KE = \frac{mv^2}{2} = \frac{p^2}{2m}$$

$$p = \sqrt{2\,KE\,m} = \sqrt{2 \times 5.126 \times 10^{-19}\text{J} \times 9.1 \times 10^{-31}\text{kg}}$$

$$p = 5.66 \times 10^{-25}\text{kg m } s^{-1}$$

$$\lambda = \frac{6.626 \times 10^{-34}\text{J s}}{5.66 \times 10^{-25}\text{kg m s}^{-1}} = 6.86 \times 10^{-10}\text{m}$$

Q1.28

If a proton is going through a potential difference of 3.0V, what is the momentum and wavelength associated with this proton? (mass of a proton is equal to $1.6726 \times 10^{-27}\,kg$)

Solution

$$(charge) * (potential) = KE$$

$$charge = 1.602 \times 10^{-19}C$$

$$(1.602 \times 10^{-19}C) * (3.0V) = KE$$

$$KE = 4.806 \times 10^{-19}J$$

$$KE = \frac{p^2}{2m}$$

$$p = \sqrt{2(KE)m} = \sqrt{2(4.806 \times 10^{-19}J)(1.6726 \times 10^{-27}kg)} = 4.01 \times 10^{-23}kg * m * s^{-1}$$

$$\lambda = h/p = \frac{6.626 \times 10^{-34}J * S}{4.01 \times 10^{-23}kg * m * s^{-1}} = 1.65 \times 10^{-11}m = 0.165\,pm$$

1.29

Neutron diffraction is a modern technique to study structure. In the neutron diffraction, a collimated beam of neutrons was generated at some temperature from high-energy neutron source. This is achieved at several accelerator facilities around the world. If the speed of neutron is $v_n = (3k_BT/m)^{1/2}$ with m as the mass of neutron. What is the required temperature so that neutrons have a de Broglie wavelength of 200 pm? The mass of a neutron to be $1.67 \times 10^{-27}\,kg$.

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1.29

While studying quantum mechanics one day, you wondered what temperature would be required for the Jumbo Jawbreaker you were about to eat to have a de Broglie wavelength of 1.9×10^{-24} meters? Assuming that the speed of a Jumbo Jawbreaker can be calculated from the equation $\nu_n = (\frac{3k_BT}{m})\frac{1}{2}$. You quickly measure the mass of your Jumbo Jawbreaker and found it to be $0.1kg$.

Solution

Knowing that the de Broglie wavelength has the form,

$$\lambda = \frac{h}{m\nu_n}$$

we can substitute the given equation for speed into the de Broglie wavelength equation

$$\lambda = \frac{h}{\sqrt{3mk_BT}}$$

rearrange to solve for temperature

$$T = \frac{h^2}{3mk_B\lambda^2}$$

Substituting in constants we can solve for temperature in Kelvin. Using $h = 6.626 \times 10^{-34} J * s$, $m = 0.1kg$, $k_B = 1.381 \times 10^{-21} J * K^{-1}$, and $\lambda = 1.9 \times 10^{-24}$ meters.

We find that

$$T = \frac{(6.626 \times 10^{-34} J * s)^2}{3(0.1kg)(1.381 \times 10^{-21} J * K^{-1})(1.9 \times 10^{-24})^2}$$

Therefore

$$T = 293.5K$$
$$= 20.35°C$$

1.30

For linear motion, show that a small change in the momentum, $\Delta \mathrm{p}$, changes a change in kinetic energy, $\Delta \mathrm{KE}$, of

$$\Delta \mathrm{KE} = \frac{p_0}{m}\Delta \mathrm{p}$$

where p_0 is initial momentum.

Solution

Since $\Delta \mathrm{p} = dp$ and $\Delta \mathrm{KE} = dKE$,

$$KE = \frac{p^2}{2m}$$

$$dKE = \frac{p_0}{m}dp$$

$$\Delta \mathrm{KE} = \frac{p_0}{m}\Delta \mathrm{p}$$

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1.31

Derive the Bohr formula for $\frac{1}{\lambda_{vac}}$ for a multi-proton and single electron atom such as $\mathbf{He^{+}}$ or $\mathbf{Li^{2+}}$.

Solution

The number of protons (Z) in the nucleus interact with the single electron with the same coulomb force (f). The total force of a nucleus with charge Z can be written as the sum of each proton individually interacting with the electron.

$$f_{Total} = \sum_{i=0}^{Z} \frac{e^2}{4r^2\pi\epsilon_o}$$

Simplifying this expression we find that

$$f_{Total} = \frac{Ze^2}{4r^2\pi\epsilon_o}$$

To prevent the electron from spiraling into or away from the nucleus, the centrifugal force $f = \frac{m_e v^2}{r}$ is equal to the Coulombic force. Therefore

$$\frac{Ze^2}{4r^2\pi\epsilon_o} = \frac{m_e\nu^2}{r}$$

For stability purposes a condition requires electrons to have a set number of complete wavelengths around the circumference of the orbit or

$$2\pi r = n\lambda \text{ , } where\ n = 1, 2, 3..$$

using the de Broglie wavelength formula $\lambda = \frac{h}{p} = \frac{h}{m\nu}$ we find that

$$m_e\nu r = \frac{nh}{2\pi}$$

Solving for ν and substituting into our force relationship $\frac{Ze^2}{4r^2\pi\epsilon_o} = \frac{m_e\nu^2}{r}$ We find that

$$r = \frac{n^2h^2\epsilon_o}{m_e e^2 Z\pi}$$

Now solving for the total energy of the system

$$E = KE + V(r)$$
$$= \frac{1}{2}m_e\nu^2 - \frac{Ze^2}{4r\pi\epsilon_o}$$

Substituting in $m_e\nu^2$ found above into the kinetic energy portion we find

$$E = \frac{Ze^2}{8r\pi\epsilon_o} - \frac{Ze^2}{4r\pi\epsilon_o} = -\frac{Ze^2}{8r\pi\epsilon_o}$$

Substituting r from above we quantize the energy such that

$$E_n = \frac{-Z^2m_e e^4}{8n^2h^2\epsilon_o^2}$$

Since this energy is quantized, the change in energy states will occur where electrons are excited by light or $h\nu$ into higher quantum states. Therefore

$$\Delta E = \frac{-Z^2m_e e^4}{8h^2\epsilon_o^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = h\nu$$

Finally solve for $\frac{1}{\lambda_{vac}}$ remembering that $h\nu = \frac{hc}{\lambda_{vac}}$ where c is the speed of light. We obtain our final solution

$$\boxed{\frac{1}{\lambda_{vac}} = \frac{-Z^2m_e e^4}{8h^3c\epsilon_o^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

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1.32

The series in the $\mathbf{He^+}$ spectrum that corresponds to the set of transitions where the electron falls from a higher level into the n = 4 state is called the Pickering series, an important series in solar astronomy. Derive the formula for the wavelengths of the observed lines in this series. In what region of the spectrum does it occur?

Solution

If we derive the Bohr formula for $\tilde{v} = Z^2 R_H \left(\frac{1}{(n^2)_1} - \frac{1}{(n^2)_2} \right)$

In the Pickering series, the helium spectrum is in $Z = 2$ and $n_2 = 4$

$$\tilde{v} = 4(109,680 cm^{-1}) \left(\frac{1}{4^2} - \frac{1}{n_1^2} \right) \tag{1.4.E.1}$$

where \(n_1 = 5, 6, 7, 8.... \]).

$$n_1 = 5, \tilde{v} \ = 9871 \, \mathrm{cm}^{-1}$$

or

$$\lambda = 1.013 * 10^{-6} meters$$

1.33A

Using the Bohr model, find the third ionization energy for the Lithium atom in eV and in J.

Solution

Energy transitions for a hydrogen like atom are given by $\Delta E = Z^2 R_y (1/n_i^2 - 1/n_f^2)$

where Z is the atomic number and R_y is 13.6 eV

When a hydrogen like atom is ionized, the electron transitions to its highest bound state, at n = infinity,so its quantum number nf goes to infinity, making $1/n_f^2 = 0$.

So $E_{ionization} = (3)^2(13.6)(1/(1)^2 - 0) = 122.9$ eV.

122.9 eV * 1.6 $*10^{-19} = 1.96*10^{-17}$ J

1.33B

Find the ionization energy in eV and $kJ \cdot mol^{-1}$ of singly ionized helium in the $n = 3$ state using Bohr theory

Solution

To find the ionization energy of helium, consider the case where we move an electron from the $n = 3$ state to an infinite distance from the nucleus.

Using the Bohr formula for $\tilde{v}$.

$$\tilde{v} = Z^2 R_H (\frac{1}{n_1^2} - \frac{1}{n_2^2})$$

$$\tilde{v} = 2^2 (109680 \, cm^{-1}) \left(\frac{1}{3^2} - \frac{1}{\infty^2} \right)$$

$$\tilde{v} = 4.87467 \times 10^4 cm^{-1}$$

Then plugging into $E = hc\tilde{v}$

$$E = (6.626 \times 10^{-34} J \cdot s)(2.998 \times 10^8 m \cdot s^{-1})(4.87467 \times 10^6 m^{-1})$$

$$E = 9.68 \times 10^{-19} J = 583 kJ \cdot mol^{-1} = 6eV$$

1.34A

The speed of electron in an *n*th Bohr orbit is given by the equation:

$$v = \frac{e^2}{2\epsilon_0 nh}$$

The force acting between an electron and proton a distance r from one another is given by Coulomb's law:

$$f = \frac{e^2}{4\pi\epsilon_0 r^2}$$

The centrifugal force acts in opposition to the Coulombic force and is given by the equation:

$$f = \frac{mv^2}{r}$$

Find the values of v for the Bohr orbits of n = 4, n = 5, and n = 6, and find the total force in an atom between a proton and electron a distance of 5 x 10^{-11} m away from one another, with the electron moving at a speed of 2 x 10^6 m/s.

Solution

To find v simply substitute the values for n into the equation:

$$v = \frac{e^2}{2\epsilon_0 nh}$$

For the values of v at n = 4, n = 5, n = 6, we get

n = 1

$$v_1 = 546,923\, m \cdot s^{-1}$$

n = 2

$$v_2 = 437,538\, m \cdot s^{-1}$$

n = 3

$$v_3 = 364,615\, m \cdot s^{-1}$$

To find the force between a proton and electron, simply subtract the Coulombic force from the Centrifugal force and substitute appropriate values for the constants:

$$f = \frac{mv^2}{r} - \frac{e^2}{4\pi\epsilon_0 r^2}$$

For which we attain:

$$f = 7.2875 \times 10^{-8} N$$

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1.34B

Prove that the speed of electron in an nth Bohr orbit is $v = \frac{e^2}{2\epsilon_0 nh}$

Then find the first few values of v the Bohr orbit.

Solution

First we have to know that the angular moment of the electron revolving in the nth Bohr orbit is quantized then

$$mvr = \frac{nh}{2\pi}$$

where r is the radius of the nth Bohr orbit.

Kinetic energy of the electron is given as $\frac{mv^2}{2} = \frac{e^2}{2(4\pi\epsilon_0)r}$

So the radius, r must equal $r = \frac{e^2}{(4\pi\epsilon_0)mv^2}$

Now after substituting the value above into the first equation, we get

$mv(\frac{e^2}{(4\pi\epsilon_0)mv^2} = \frac{nh}{2\pi}$

Thus the speed of the electron in the n Bohr orbit is

$v = \frac{e^2}{2\epsilon_0 nh}$

For the first few values of v in the nth Bohr orbit, we get

n = 1

$v = 2.188 \times 10^6 m * s^{-}1$

n = 2

$v_2 = 1.094 \times 10^6 m * s^{-}1$

n = 3

$v_3 = 7.292 \times 10^5 m * s^{-}1$

1.35

What is the uncertainty in an electron's position if the uncertainty in measuring its velocity is 5 $m \cdot s^{-1}$.

Solution

According to the Heisenburg Uncertainty Principle

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

$$\Delta x \geq \frac{\hbar}{2\Delta p}$$

Then by definition $\Delta p = m\Delta v$

$$\Delta x \geq \frac{\hbar}{2m\Delta v}$$

$$\Delta x \geq \frac{6.626 \times 10^{-34} J \cdot s}{4\pi(9.109 \times 10^{-31} kg)(5m \cdot s^{-1})}$$

$$\Delta x \geq 1.16 \times 10^{-5} m$$

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1.35

What is the *uncertainty* in the speed of an electron if we locate it to within 50 pm?

Solution

It is known that the uncertainty of momentum is given by the expression

$$\Delta p = m\Delta v$$

and Heisenberg's Uncertainty Principle states that

$$\Delta x \Delta p \geq h$$

Then

$$\begin{aligned} \Delta x(m\Delta v) &\geq h \\ \Delta v &\geq \frac{h}{m\Delta x} \\ &\geq \frac{6.626 \cdot 10^{-34} J \cdot s}{(9.109 \cdot 10^{-31} kg)(50 \cdot 10^{-12} m)} \\ &\geq 1.45 \cdot 10^{7} m \cdot s \end{aligned}$$

1.35

If we know the velocity of an electron to within $3.5 \times 10^{7} \frac{m}{s}$, then what is the uncertainty in its position?

Solution

Using the Heisenberg Uncertainty Principle,

$$\Delta x \Delta p \geq h = \Delta x \times m\Delta v \geq h$$

and rearranging to solve for uncertainty in velocity,

$$\Delta x \geq \frac{h}{m\Delta v}$$

we can use $h = 6.626 \times 10^{-34} J \cdot s$, $m = 9.109 \times 10^{-31} kg$, and $\Delta v = 3.5 \times 10^{7} \frac{m}{s}$ and find that

$$\Delta x \geq \frac{(6.626 \times 10^{-34} J \cdot s)}{(9.109 \times 10^{-31} kg)(3.5 \times 10^{7} \frac{m}{s})}$$

and thus

$$\Delta x \geq 2.078 \times 10^{-11} meters$$

1.35

If a proton is located to within 1 angstrom, what is its uncertainty in velocity?

Solution

The Heisenberg uncertainty principle states

$\Delta x \Delta p = h/4\pi$

$\Delta x m \Delta v = h/4\pi$

$\Delta v = h/(4m_p \pi \Delta x)$ where m_p is the mass of a proton

$x \sim \Delta x$ the uncertainty in position is on the same order as the location it is confined to, here 1 angstrom

$\Delta v = h/(4m_p \pi x) = (6.626*10^{-34})/(4*(1.67*10^{-27})*3.14*10^{-10})$

= 315.7 m/s

1.36

If the position of an electron is within the 10 pm interval, what is the uncertainty of the momentum? Is this value similar to that of an electron in the first Bohr orbit?

Solution

According to the uncertainty principle for position and momentum,

$$\Delta x \, \Delta p \geq h$$

$$\Delta p \geq \frac{h}{\Delta x}$$

by substituting the respective values we get,

$$\Delta p \geq \frac{6.626 \times 10^{-34} J.s}{10.0 \times 10^{-12} m}$$

$$\geq 2.9 \times 10^{-23} kg.m.s^{-}1$$

Therefore, uncertainty in the momentum of an electron will be $2.9 \times 10^{-23} kg.m.s^{-}1$.

We can calculate the momentum of an electron in the first Bohr radius by using v since we know that,

$$p = m_e v$$

$$= (9.109 \times 10^{-31} kg)(2.188 \times 10^{6} m \cdot s^{-1})$$

$$= (1.992 \times 10^{-24} kg \cdot m \cdot s^{-1})$$

The uncertainty of the momentum of an electron somewhere in a 10 pm interval is greater that the momentum of an electron in the first Bohr radius.

1.37

The Heisenberg Uncertainty Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Show both sides have the same units

Solution

$$\Delta x = meters$$

$$\Delta p = m \Delta v$$

Planck's Constant has units of

$$J \cdot s$$

and

$$J = \frac{kg \cdot m^2}{s^2}$$

so apply these equations we get

$$m \frac{kg \cdot m}{s} \geq \frac{kg \cdot m^2 \cdot s}{s^2}$$

and simplify

$$\frac{kg \cdot m^2}{s} \geq \frac{kg \cdot m^2}{s}$$

Therefore Both sides have same units

1.38

The relationship between energy and time can be seen through the following uncertainty principle: $\Delta E\,\Delta t \geq h$. Through this relationship, it can be interpreted that a particle of mass m, the energy (E=mc^2) can come from nothing and return to nothing within a time $\Delta t \leq h/(mc^2)$. A real particle is one that lasts for time (Δt) or more; likewise, a particle that lasts for less than time (Δt) are called virtual particles. For a charged subatomic particle, a pion, the mass is $2.5 \times 10^{-28} kg$. For a pion to be considered a real particle, what is its minimum lifetime?

Solution

Based on the uncertainty principle for energy and time:

$$\Delta E\,\Delta t \geq h$$

$$\Delta t \geq \frac{h}{mc^2}$$

therefore $E = mc^2$. By plugging in the values, you get

$$\Delta t \geq \frac{6.626 \times 10^{-34} Js}{(2.5 \times 10^{-28} kg)(2.998 \times 10^{8} ms^{-1})^2}$$

$$\geq 2.9 \times 10^{-23} s$$

Therefore, the minimum lifetime if the pion is to be considered a real particle will be $2.9 \times 10^{-23} s$.

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SECTION OVERVIEW

2.1: CONFIGURATION

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2.1.1: Electron Configurations- How Electrons Occupy Orbitals

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2.1.4: Periodic Trends in the Size of Atoms and Effective Nuclear Charge

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2.1.1: Electron Configurations- How Electrons Occupy Orbitals

Learning Objectives

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- 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 **2.1.1.1** depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* 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 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

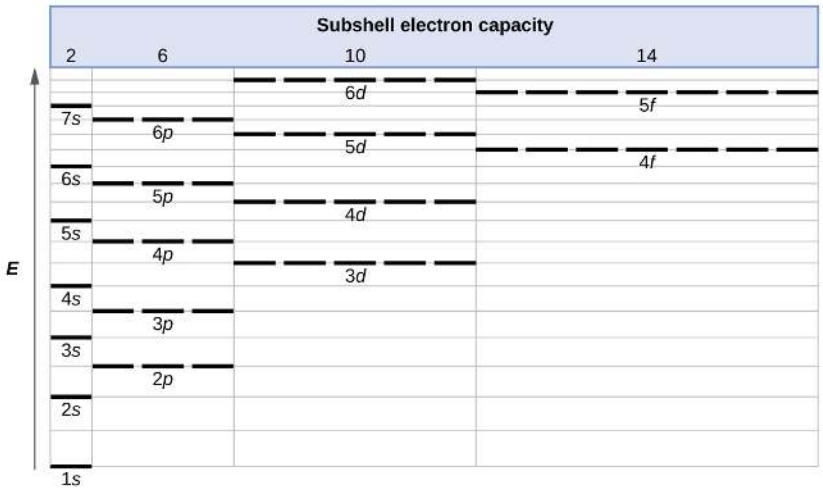


Figure **2.1.1.1**: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

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 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. 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). But 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 (1*s* through 3*p*), 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 (Figure **2.1.1.2**):

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.

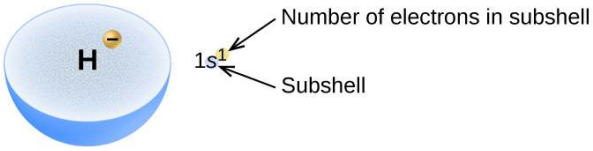


Figure **2.1.1.2**: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

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 (in the order shown in Figure **2.1.1.3**), 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 **2.1.1.3** illustrates the traditional way to remember the filling order for atomic orbitals.

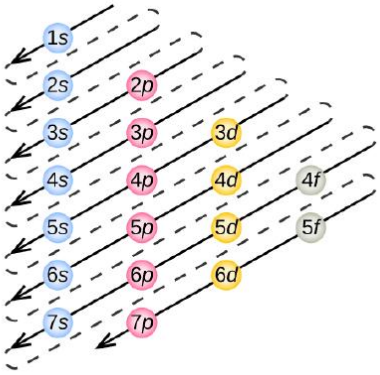


Figure **2.1.1.3**: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

Since the arrangement of the periodic table is based on the electron configurations, Figure **2.1.1.4** 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 3p block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3d orbitals.

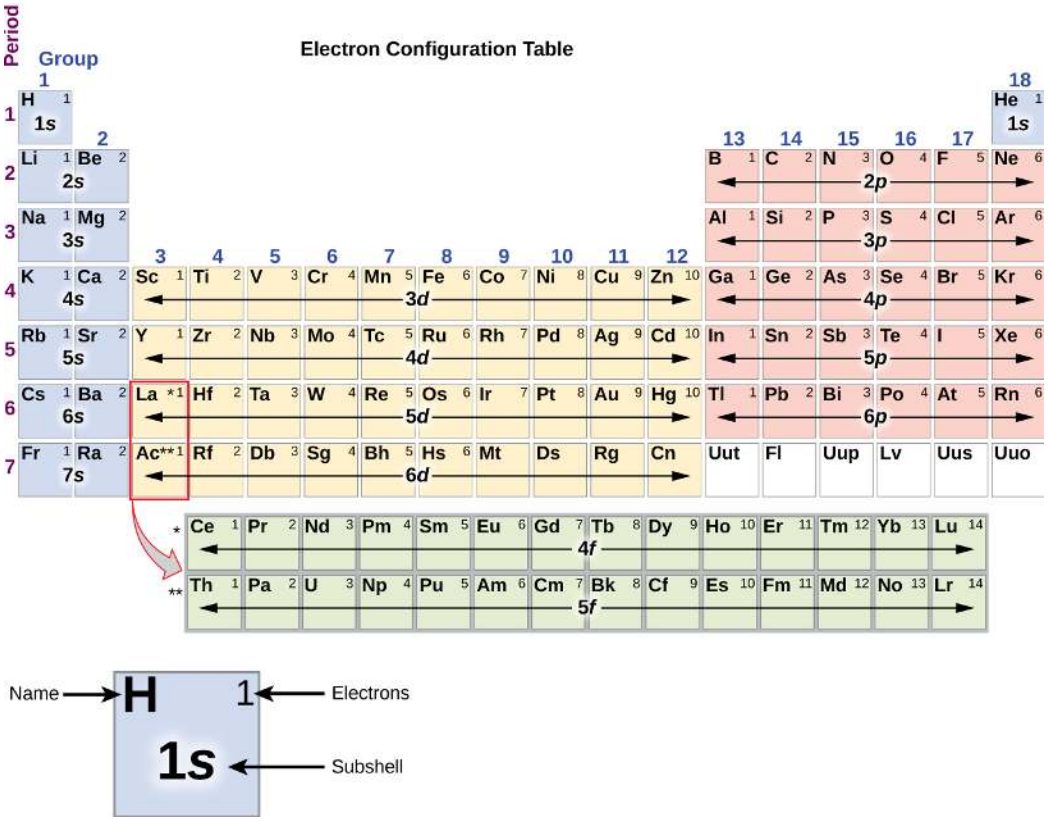
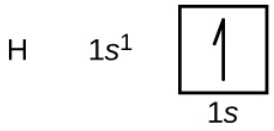
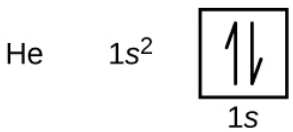


Figure **2.1.1.4**: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure **2.1.1.3** or **2.1.1.4**, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:



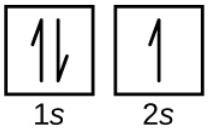
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:



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

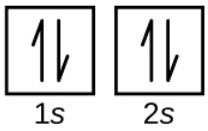
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (Figure **2.1.1.3** or **2.1.1.4**). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$



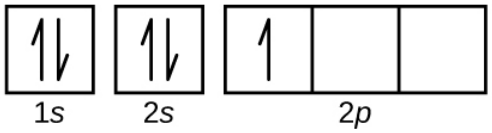
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.

Be $1s^2 2s^2$



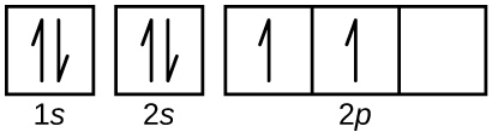
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* 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.

B $1s^2 2s^2 2p^1$



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

C $1s^2 2s^2 2p^2$



Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

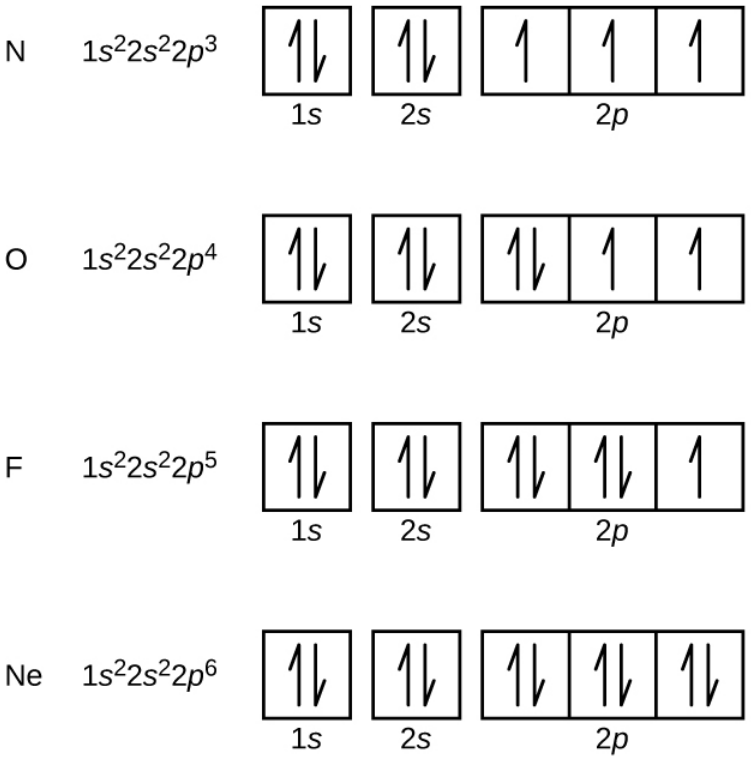


Figure **2.1.1.5**: Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

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 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ 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 (Figure \PageIndex5\PageIndex5). 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, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

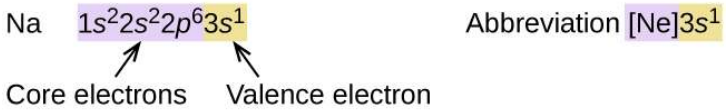


Figure **2.1.1.5**: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [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.

$$\textbf{Li : [He]}\ 2s^1$$
$$\textbf{Na : [Ne]}\ 3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [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 [Ne]$3s^2 3p^1$, is analogous to its family member boron, [He]$2s^2 2p^1$.

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 $n = 3$. Figure **2.1.1.6** shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

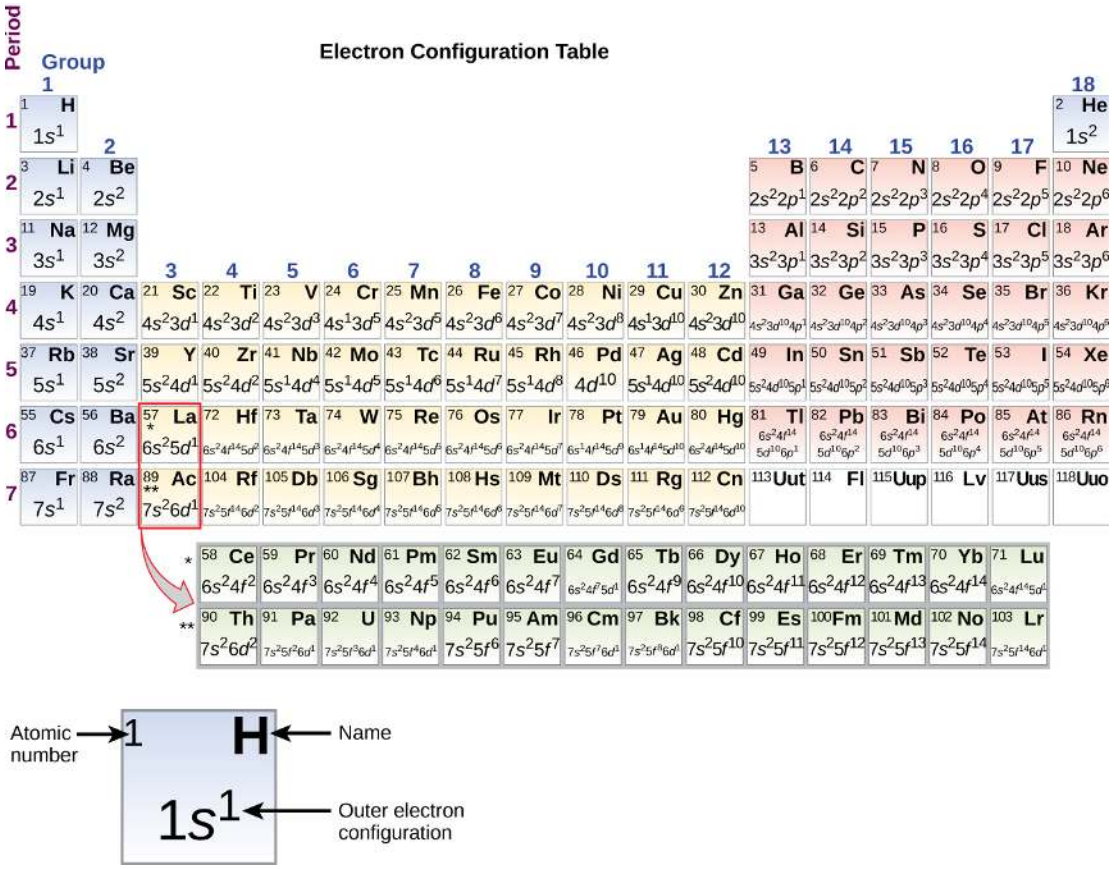


Figure **2.1.1.6**: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

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 3*d* 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 3*d* level but is, instead, added to the 4*s* level (Figure **2.1.1.3** or **2.1.1.4**). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. 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 3*d* 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 4*p* 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.

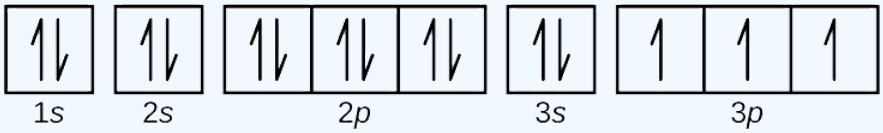
Example 2.1.1.1: Quantum Numbers and Electron Configurations

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 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2 2s^2 2p^6 3s^2 3p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 2.1.1.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer a

Mn

Answer b

Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure **2.1.1.3** or **2.1.1.4**. For instance, the electron configurations of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

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 their electron configurations are added to the table (Figure **2.1.1.6**), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because 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 Figure **2.1.1.6**, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure **2.1.1.6** 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, shown in blue and red in Figure **2.1.1.6**. This category includes all the nonmetallic elements, as well as many metals and the intermediate semimetallic elements. 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 [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). 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. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure **2.1.1.6**) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure **2.1.1.6**), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure **2.1.1.6**. 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: lanthanide (La) through lutetium (Lu)
    2. The actinide series: actinide (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

We have seen that 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 **2.1.1.2**: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram 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 Na^+: $1s^2 2s^2 2p^6 3s^1 = Na^+$: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so 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 dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
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 4*s* orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
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 trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

? Exercise 2.1.1.2

a. Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$?
b. Which ion with a +3 charge has this configuration?

Answer a

Tc^{2+}

Answer b

Ru^{3+}

Summary

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

Glossary

Aufbau principle
procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

core electron
electron in an atom that occupies the orbitals of the inner shells

electron configuration

electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Hund's rule

every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

orbital diagram

pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

valence electrons

electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

valence shell

outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level (*s* and *p* subshells) are in the valence shell, while for transition metals, the highest energy *s* and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d*, and *f* subshells are included

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2.1.2: Electron Configurations, Valence Electrons, and the Periodic Table

Learning Objectives

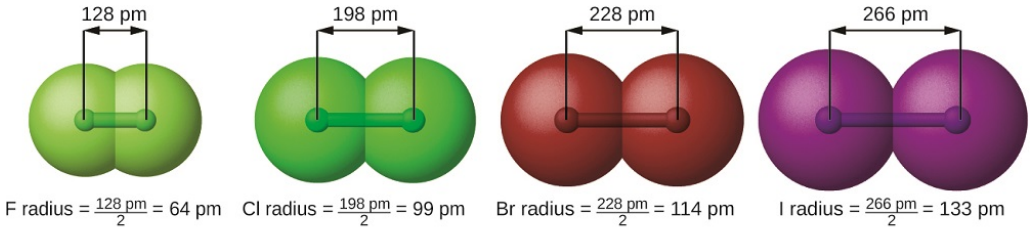
- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

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-grey solid that conducts electricity.

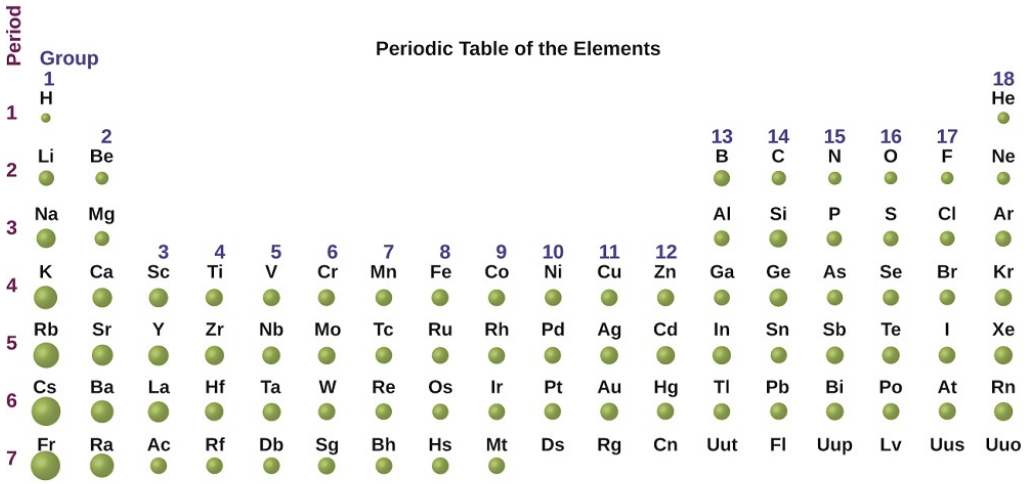
As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. 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 structure of the elements changes. 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 (Figure **2.1.2.1**), 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).



(a)



(b)

Figure **2.1.2.1**: (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.

This figure has two parts: a and b. In figure a, 4 diatomic molecules are shown to illustrate the method of determining the atomic radius of an atom. The first model, in light green, is used to find the F atom radius. Two spheres are pushed very tightly together. The distance between the centers of the two atoms is indicated above the diagram with a double headed arrow labeled, “128 p m.” The endpoints of this arrow connect to line segments that extend to the atomic radii below. Beneath the molecule is the label, “F radius equals 128 p m divided by 2 equals 64 p m.” The next three models are similarly used to show the atomic radii of additional atoms. The second diatomic molecule is in a darker shade of green. The distance between the radii is 198 p m. Beneath the molecule is the label, “C l radius equals 198 p m divided by 2 equals 99 pm.” The third diatomic molecule is in red. The distance between the radii is 228 p m. Beneath the molecule is the label, “B r radius equals 228 p m divided by 2 equals 114 pm.” The fourth diatomic molecule is in purple. The distance between the radii is 266 p m. Beneath the molecule is the label, “I radius equals 266 p m divided by 2 equals 133 p m.” In figure b, a periodic table layout is used to compare relative sizes of atoms using green spheres. No spheres are provided for the noble or inert gas, group 18 elements. General trends noted are increasing circle size moving from top to bottom in a group, with a general tendency toward increasing atomic radii toward the lower left corner of the periodic table.

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 Table **2.1.2.1** and Figure **2.1.2.1**. The trends for the entire periodic table can be seen in Figure **2.1.2.2**.

Table **2.1.2.1**: 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

As shown in Figure **2.1.2.2**, 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:

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

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.

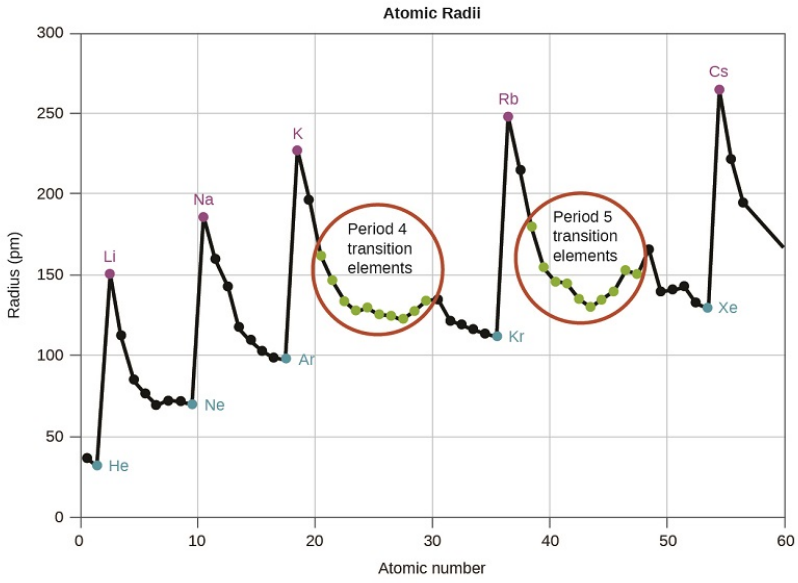


Figure **2.1.2.2**: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

This graph is labeled Atomic Number on the horizontal axis and Radius (p m) on the vertical axis. A black jagged line connects the radii values for elements with atomic numbers 1 through 60 on the graph. Peaks are evident at the locations of the alkali metals: L i, N a, K, R b, and C s. Similarly, minima exist at the locations of noble or inert gases: H e, N e, A r, K r, X e, and R n. The locations of period 4 and period 5 transition elements are provided with green dots.

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 2.1.2.1: Sorting Atomic Radii

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

Solution

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

Exercise 2.1.2.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

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 (Figure **2.1.2.3**). 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} (as discussed) and are drawn even closer to the nucleus.



Figure **2.1.2.3**: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

The figure includes spheres in green to represent the relative sizes of A l and S atoms. Beneath each of these spheres is a red sphere. The red sphere represents the ionic states of aluminum and sulfur respectively. While radius for the aluminum cation is smaller than aluminum, the sulfur anion has a greater radius than sulfur.

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 (Figure **2.1.2.3**). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

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 (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathrm{X}(g) \longrightarrow \mathrm{X}^{+}(g) + \mathrm{e}^{-} \quad \mathrm{IE}_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X}^{+}(g) \longrightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^{-} \quad \mathrm{IE}_2$$

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.

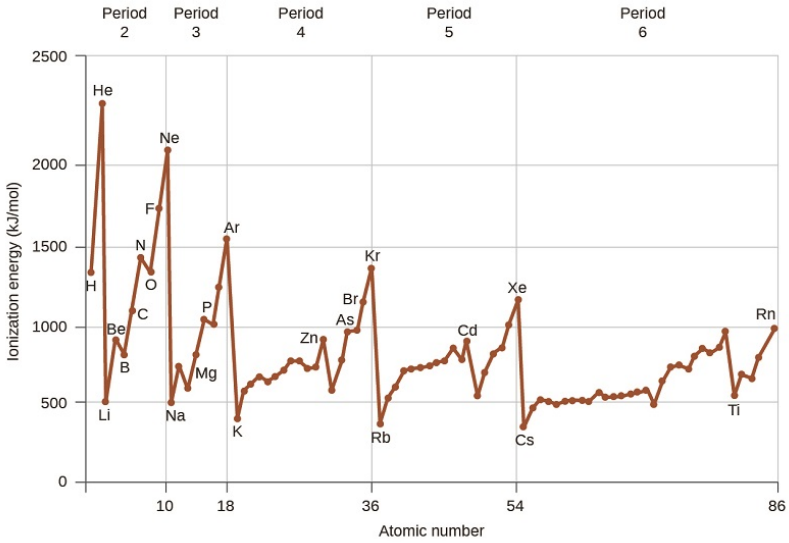


Figure **2.1.2.4**: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

This figure includes Atomic Number on the horizontal axis and, Ionization Energy (k J divided by mol) on the vertical axis. A red jagged line connects the ionization energies for elements with atomic numbers 1 through 86 on the graph. Peaks are evident at the locations of the noble or inert gases: H e, N e, A r, K r, X e, and R n. Similarly, minima exist at the locations of the alkali metals: L i, N a, K, R b, and C s.

Figure **2.1.2.4** graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing *Z*. Down a group, the IE_1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as *l* increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ($[He]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[He]2s^2 2p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

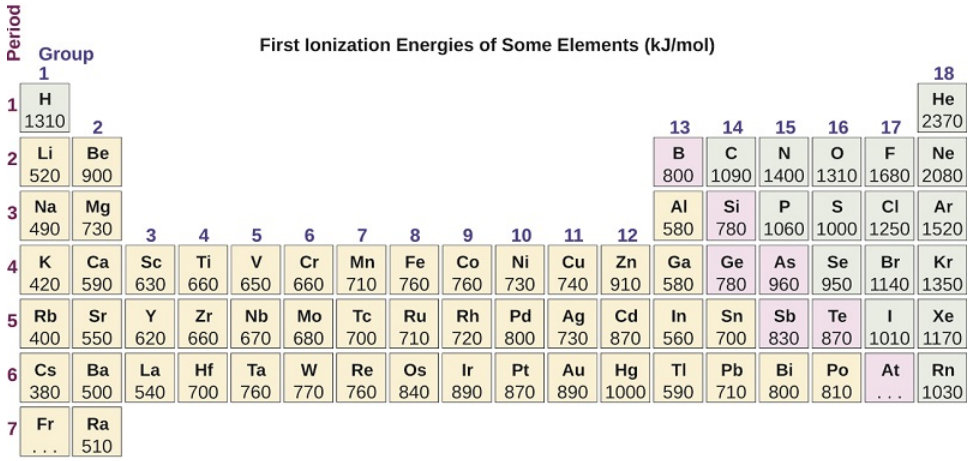
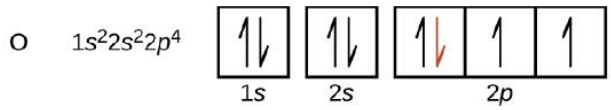


Figure **2.1.2.5**: This version of the periodic table shows the first ionization energy of (IE: $_1$), in kJ/mol, of selected elements. The trends for first ionization energies across periods and down groups are shown in this version of the periodic table.

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 IE_1 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 2*p* 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 **2.1.2.4**.



The electronic configuration for oxygen is 1s superscript 2, 2s superscript, 2p superscript 4. An orbital diagram shows 2 squares each filled with a pair of opposite pointing arrows to represent the 1s ans 2s orbitals. Each of the three connected square which represents the 2p orbitals are filled with one arrow respectively with the addition of 1 red arrow in the first of the three squares.

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 **2.1.2.2**, there is a large increase in the ionization energies (color change) for each element. 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.

Table 2.1.2.2: 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

Example 2.1.2.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher n orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from

$$\mathbf{Al} \quad (\mathbf{Al^{2+} \longrightarrow Al^{3+} + e^-})$$

requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. 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:

$$IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na).$$

Exercise 2.1.2.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer

Ba

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).

$$\mathbf{X}(g) + \mathbf{e^-} \longrightarrow \mathbf{X^-}(g) \quad \mathbf{EA_1}$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure **2.1.2.6**. 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. 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.

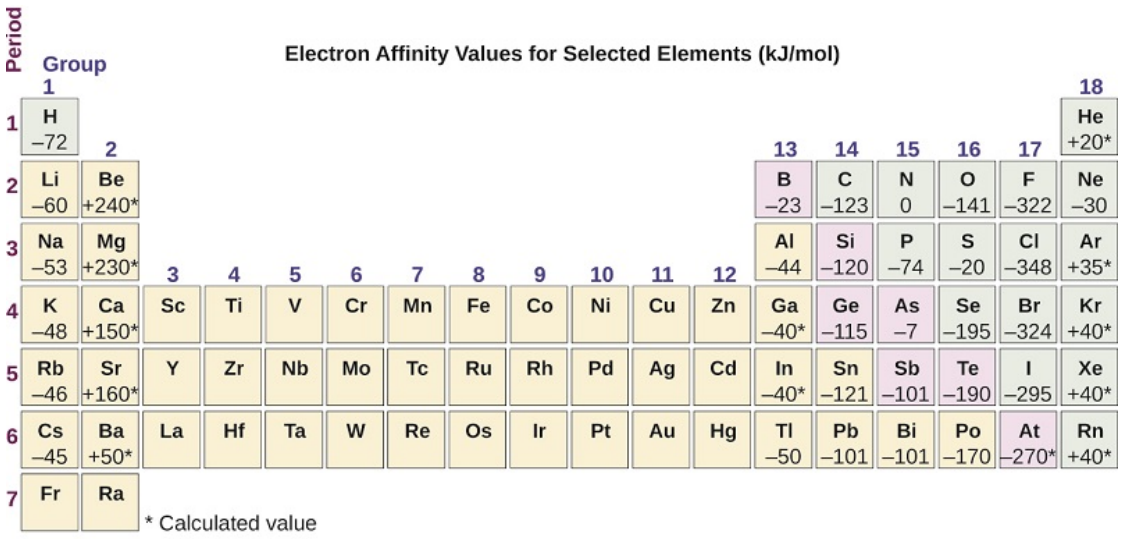


Figure 2.1.2.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:
The trend for electron affinity values across periods and down groups is shown in this version of the periodic table. Values are not shown for groups 3 to 12 as well as period 7.

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 largest 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 greatest EA. The reduction of the EA of the first member 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.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) 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.

Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger

than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Glossary

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity

energy required to add an electron to a gaseous atom to form an anion

ionization energy

energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic

group of ions or atoms that have identical electron configurations

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2.1.2: Electron Configurations, Valence Electrons, and the Periodic Table is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

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2.1.3: The Explanatory Power of the Quantum-Mechanical Model

The chemical properties of elements are largely determined by the number of valence electrons they contain

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2.1.4: Periodic Trends in the Size of Atoms and Effective Nuclear Charge

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes; however, some atoms are larger or smaller than others, and this influences their chemistry. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure **2.1.4.1** which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

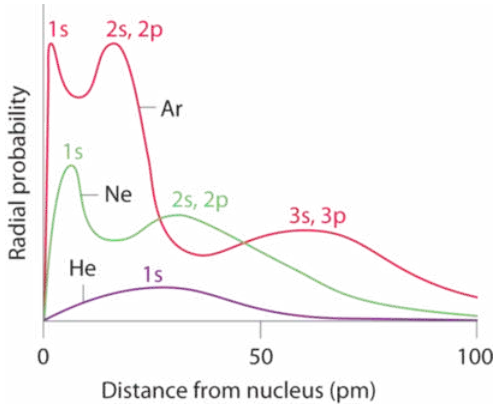


Figure **2.1.4.1**: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another maximum at ≈35 pm (the $n = 2$ shell). In Ar, the 1*s* electrons have a maximum at ≈2 pm, the 2*s* and 2*p* electrons combine to form a maximum at ≈18 pm, and the 3*s* and 3*p* electrons combine to form a maximum at ≈70 pm.

Figure **2.1.4.1** also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks. Argon, with filled $n = 1$, 2, and 3 principal shells, has three peaks. The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of *n*. Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the $n = 1$ shell also decreases tremendously (the filled 1*s* orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

Figure **2.1.4.1** illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a **covalent atomic radius** (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure **2.1.4.2***a*). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1\ Å = 1 \times 10^{-10}$ m = 100 pm.

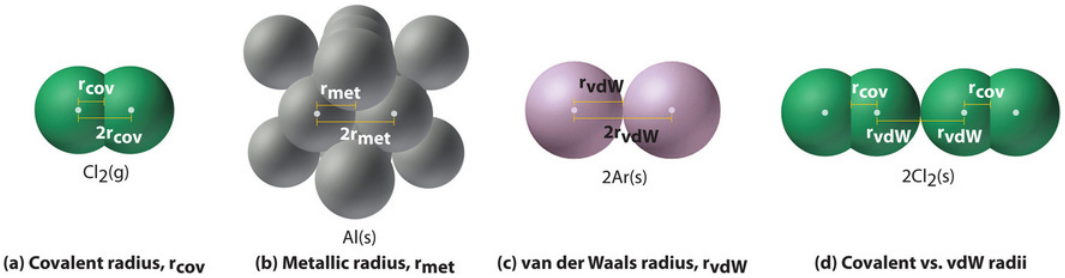


Figure **2.1.4.2**: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is half the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is half the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the **metallic atomic radius** (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure **2.1.4.2***b*). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the **van der Waals atomic radius** (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (Figure **2.1.4.2***c*). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_2(s)$ at low temperatures). These radii are generally not the same (Figure **2.1.4.2***d*).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure **2.1.4.3**).

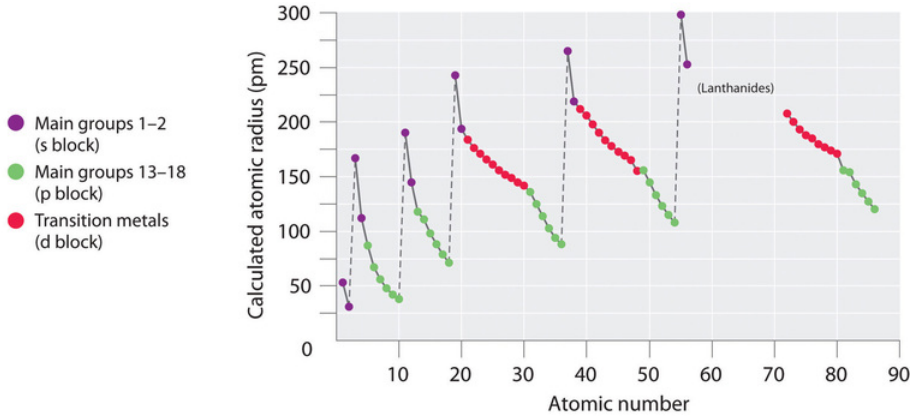


Figure **2.1.4.3**: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper

right corner (Figure 2.1.4.4).

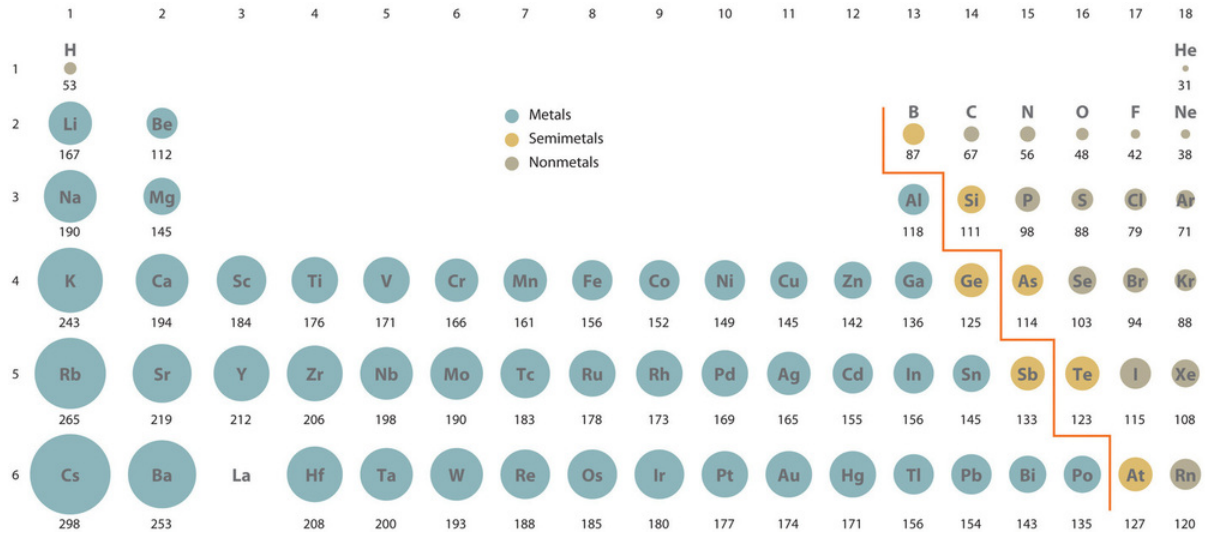


Figure 2.1.4.4 Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: Web elements [www.webelements.com]. Web Elements is an excellent online source for looking up atomic properties.

Trends in atomic size result from differences in the **effective nuclear charges** (Z_{eff}) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

> *Atomic radii decrease from left to right across a row and increase from top to bottom down a column.*

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure 2.1.4.5).

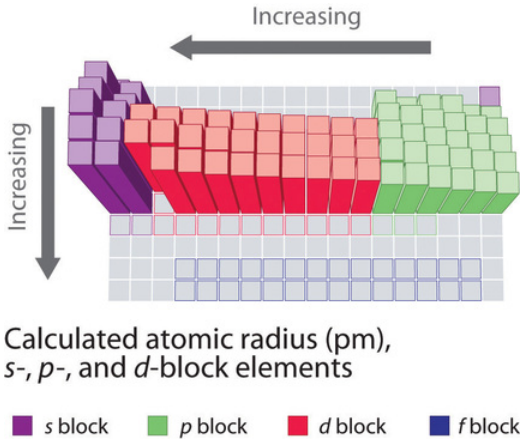


Figure **2.1.4.5**: The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Not all Electrons shield equally

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 2.1.4.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A. Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number *n*. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.

B. List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater.

B Combining the two inequalities gives the overall order: C < Si < Al.

? Exercise 2.1.4.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer

O < S < P < K



Atomic Radius: Atomic Radius, YouTube(opens in new window) [youtu.be]

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

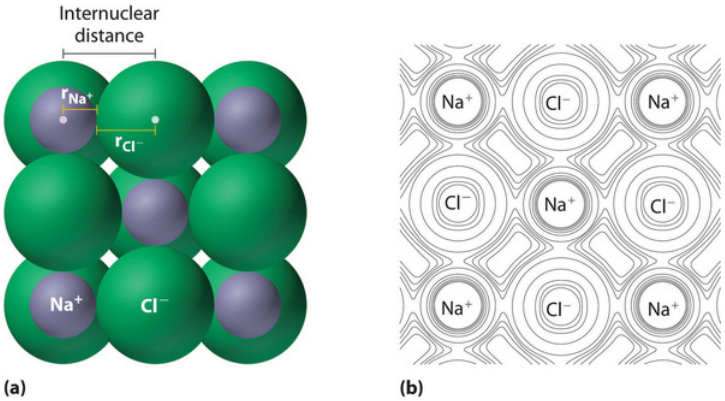


Figure **2.1.4.6**: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure **2.1.4.6**, the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

A comparison of ionic radii with atomic radii (Figure **2.1.4.7**) shows that *a cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases and the ion shrinks (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases and the ion expands (compare F at 42 pm with F^- at 133 pm).

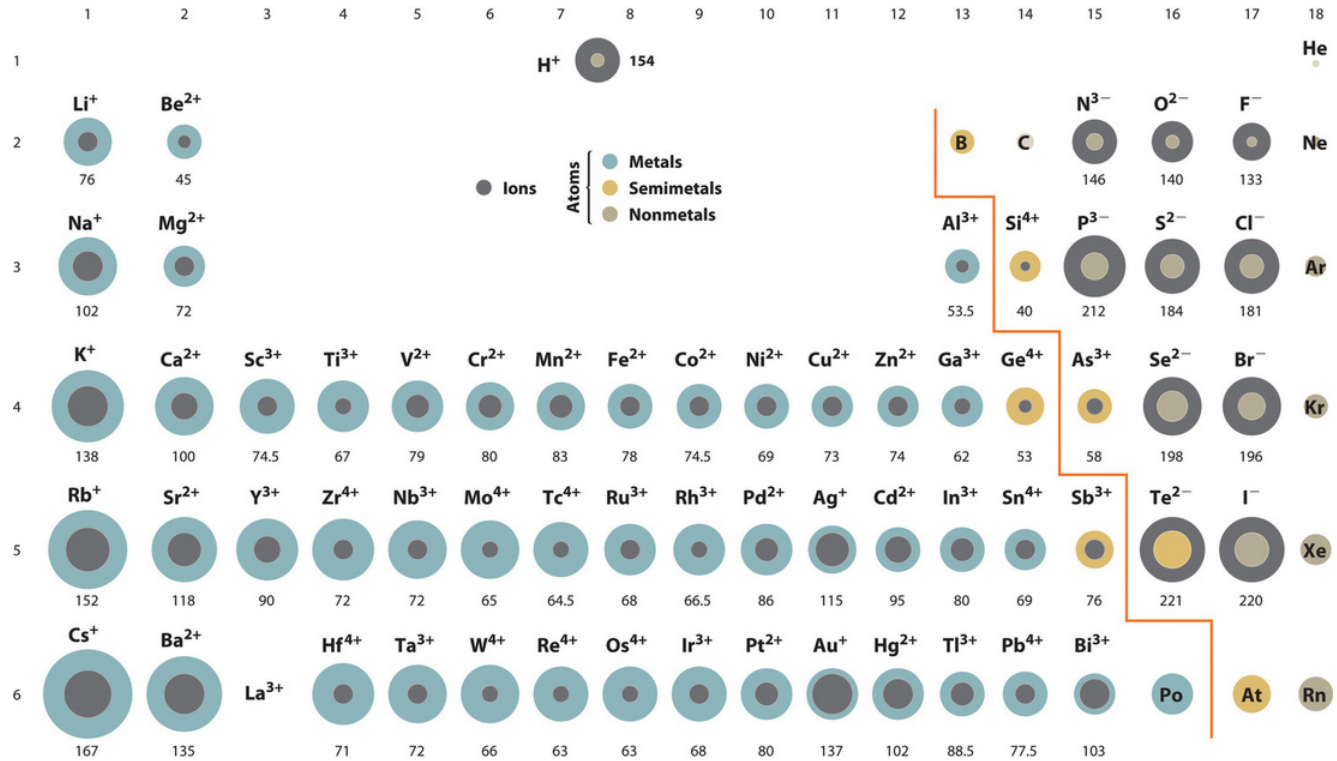


Figure **2.1.4.7**: Ionic Radii (in Picometers) of the Most Common Ionic States of the *s*-, *p*-, and *d*-Block Elements.Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

> *Cations are **always** smaller than the neutral atom and anions are **always** larger.*

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table **2.1.4.1**. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0),

and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

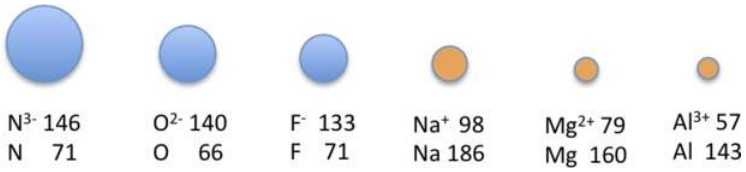
Table **2.1.4.1**: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 3s^2$
Radius (pm)	102	154*	202†

*The metallic radius measured for Na(s). †Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," Annual Review of Materials Science 23 (1993): 225–253.

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of n lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an **isoelectronic series**. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^2 2s^2 2p^6$) is shown in Table **2.1.4.3**.



The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table **2.1.4.3**, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table **2.1.4.3**: Radius of Ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^-	133	9
Na^+	98	11
Mg^{2+}	79	12
Al^{3+}	57	13

Example 2.1.4.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^-, K^+, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.

B. Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+, Cl^-, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge (Z = 19), its radius is smallest, and S^{2-} with Z = 16 has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}.

B The order must therefore be $K^+ < Cl^- < S^{2-} < Se^{2-}$.

Exercise 2.1.4.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer

$Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

Summary

Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges. A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Learning Objectives

- To understand the basics of electron shielding and penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at

a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies. These effects are the underlying basis for the periodic trends in elemental properties that we will explore in this chapter.

Electron Shielding and Effective Nuclear Charge

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Figure **2.1.4.1**). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z. This effect is called **electron shielding**.

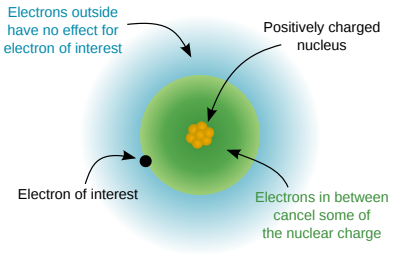


Figure **2.1.4.1**: This image shows how inner electrons can shield outer electrons from the nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z-1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z:

$$1 \leq Z_{eff} \leq Z.$$

Notice that $Z_{eff} = Z$ only for hydrogen (Figure **2.1.4.2**).

Definition: Shielding

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons insofar as it is shielded from them.

Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{eff} = Z - S \tag{2.1.4.1}$$

where Z is the atomic number (number of protons in nucleus) and S is the shielding constant and is approximated by number of electrons between the nucleus and the electron in question (*the number of nonvalence electrons*). The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

We can see from Equation 2.1.4.1 that the effective nuclear charge of an atom increases as the number of protons in an atom increases (Figure **2.1.4.2**). As we will discuss later on in the chapter, this phenomenon can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

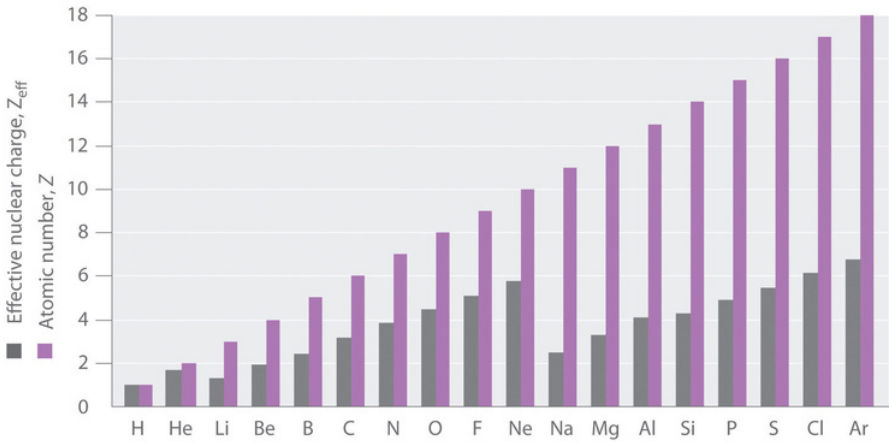


Figure **2.1.4.2**: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the (CC BY-SA-NC 3.0; anonynous)

The shielding constant can be estimated by totaling the screening by **all nonvalence electrons** (n) except the one in question.

$$S = \sum_{i}^{n-1} S_i \tag{2.1.4.2}$$

where S_i is the shielding of the ith electron.

> *Electrons that are shielded from the full charge of the nucleus experience an effective nuclear charge (Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ion.*

From Equations 2.1.4.1 and 2.1.4.2, Z_{eff} for a specific electron can be estimated is the shielding constants for that electron of all other electrons in species is known. A simple approximation is that all other non-valence electrons shield equally and fully:

$$S_i = 1 \tag{2.1.4.3}$$

This crude approximation is demonstrated in Example **2.1.4.1**.

✔ Example 2.1.4.1: Fluorine, Neon, and Sodium

What is the effective attraction Z_{eff} experienced by the valence electrons in the three isoelectronic species: the fluorine anion, the neutral neon atom, and sodium cation?

Solution

Each species has 10 electrons, and the number of nonvalence electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number A. This is an application of Equations 2.1.4.1 and 2.1.4.2. We use the simple assumption that all electrons shield equally and fully the valence electrons (Equation 2.1.4.3).

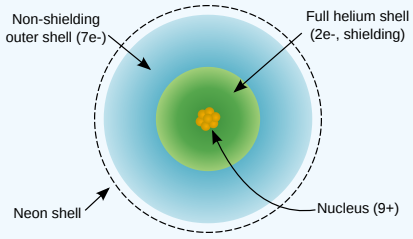


Diagram of a fluorine atom showing the extent of effective nuclear charge. (CC BY-SA 3.0; NikNaks via Wikipedia).

The charge Z of the nucleus of a fluorine atom is 9, but the valence electrons are screened appreciably by the core electrons (four electrons from the 1s and 2s orbitals) and partially by the 7 electrons in the 2p orbitals.

- $Z_{\text{eff}}(\text{F}^-) = 9 - 2 = 7+$

- $Z_{\text{eff}}(\text{Ne}) = 10 - 2 = 8+$
- $Z_{\text{eff}}(\text{Na}^+) = 11 - 2 = 9+$

So the sodium cation has the greatest effective nuclear charge. This also suggests that Na^+ has the smallest radius of these species and that is correct.

? Exercise 2.1.4.1: Magnesium Species

What is the effective attraction Z_{eff} experienced by the valence electrons in the magnesium anion, the neutral magnesium atom, and magnesium cation? Use the simple approximation for shielding constants. Compare your result for the magnesium atom to the more accurate value in Figure 2.1.4.2 and proposed an origin for the difference.

Answer

- $Z_{\text{eff}}(\text{Mg}^-) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}) = 12 - 10 = 2+$
- $Z_{\text{eff}}(\text{Mg}^+) = 12 - 10 = 2+$

Remember that the simple approximations in Equations 2.1.4.2 and 2.1.4.3 suggest that valence electrons **do not shield** other valence electrons. Therefore, each of these species has the same number of non-valence electrons and Equation 2.1.4.1 suggests the effective charge on each valence electron is identical for each of the three species.

This is not correct and a more complex model is needed to predict the experimental observed Z_{eff} value. The ability of valence electrons to shield other valence electrons or in partial amounts (e.g., $S_i \neq 1$) is in violation of Equations 2.1.4.2 and 2.1.4.3. That fact that these approximations are poor is suggested by the experimental Z_{eff} value shown in Figure 2.1.4.2 for **Mg** of 3.2+. This is appreciably larger than the +2 estimated above, which means these simple approximations overestimate the total shielding constant S. A more sophisticated model is needed.

Electron Penetration

The approximation in Equation 2.1.4.3 is a good first order description of electron shielding, but the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.1.4.2 for the elements of the first three rows of the periodic table.

Penetration describes the proximity to which an electron can approach to the nucleus. In a multi-electron system, electron penetration is defined by an electron's relative electron density (probability density) near the nucleus of an atom (Figure 2.1.4.3). Electrons in different orbitals have different electron densities around the nucleus. In other words, penetration depends on the shell (n) and subshell (l).

For example, a 1s electron (Figure 2.1.4.3; purple curve) has greater electron density near the nucleus than a 2p electron (Figure 2.1.4.3; red curve) and has a greater penetration. This related to the shielding constants since the 1s electrons are closer to the nucleus than a 2p electron, hence the 1s screens a 2p electron almost perfectly ($S = 1$. However, the 2s electron has a lower shielding constant ($S < 1$ because it can penetrate close to the nucleus in the small area of electron density within the first spherical node (Figure 2.1.4.3; green curve). In this way the 2s electron can "avoid" some of the shielding effect of the inner 1s electron.

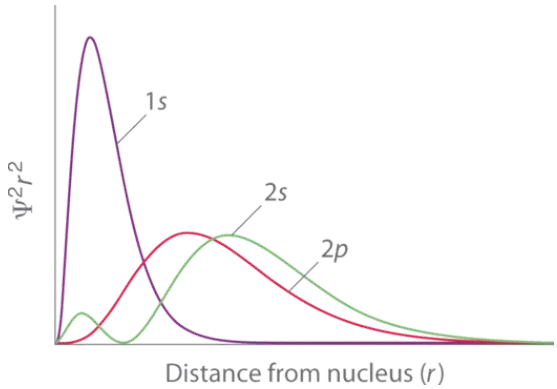


Figure **2.1.4.3**: Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital. (CC BY-NC-SA 3.0; Anonymous)

For the same shell value (n) the penetrating power of an electron follows this trend in subshells (Figure **2.1.4.3**):

$$s > p > d \approx f. \tag{2.1.4.4}$$

for different values of shell (n) and subshell (l), penetrating power of an electron follows this trend:

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f \ \ldots \tag{2.1.4.5}$$

Definition: Penetration

Penetration describes the proximity of electrons in an orbital to the nucleus. Electrons that have greater penetration can get closer to the nucleus and effectively block out the charge from electrons that have less proximity.

Table **2.1.4.1**: Effective Nuclear Charges for Selected Atoms

Atom	Sublevel	Z	Z_{eff}
H	1s	1	1
He	1s	2	1.69
Li	1s, 2s	3	2.69, 1.28
Be	1s, 2s	4	3.68, 1.91
B	1s, 2s, 2p	5	4.68, 2.58, 2.42
F	1s, 2s, 2p	9	8.65, 5.13, 5.10
Na	1s, 2s, 2p, 3s	11	10.63, 6.57, 6.80, 2.51

Data from E. Clementi and D. L. Raimondi; The Journal of Chemical Physics 38, 2686 (1963).

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

A Better Estimation of Shielding: Slater Rules

The concepts of electron shielding, orbital penetration and effective nuclear charge were introduced above, but we did so in a qualitative manner (e.g., Equations 2.1.4.4 and 2.1.4.5). A more accurate model for estimating electron shielding and

corresponding effective nuclear charge experienced is Slater's Rules. However, the application of these rules is outside the scope of this text.



Zeff and Electron Shielding: Zeff and Electron Shielding(opens in new window) [youtu.be]

Summary

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of *l* and the same value of *n* overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

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2.1.5: Ions- Configurations, Magnetic Properties, Radii, and Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. Why is this so? In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^+_{(g)} + e^- \qquad \text{energy required=I} \tag{2.1.5.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 2.1.5.1. Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

$$\mathrm{E(g)} \rightarrow \mathrm{E^+(g) + e^-} \qquad I_1 = \text{1st ionization energy} \tag{2.1.5.2}$$

$$\mathrm{E^+(g)} \rightarrow \mathrm{E^{2+}(g) + e^-} \qquad I_2 = \text{2nd ionization energy} \tag{2.1.5.3}$$

$$\mathrm{E^{2+}(g)} \rightarrow \mathrm{E^{3+}(g) + e^-} \qquad I_3 = \text{3rd ionization energy} \tag{2.1.5.4}$$

Values for the ionization energies of *Li* and *Be* listed in Table 2.1.5.1 show that successive ionization energies for an element increase as they go; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

> *Successive ionization energies for an element* ***increase****.*

Table 2.1.5.1: Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Reaction	Electronic Transition	I	Reaction	Electronic Transition	I
$\mathrm{Li\,(g) \rightarrow Li^+(g) + e^-}$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2	$\mathrm{Be\,(g) \rightarrow Be^+(g) + e^-}$	$1s^2 2s^2 \rightarrow 1s^2 2s^1$	I_1 = 899.5
$\mathrm{Li^+(g) \rightarrow Li^{2+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$\mathrm{Be^+(g) \rightarrow Be^{2+}(g) + e^-}$	$1s^2 2s^1 \rightarrow 1s^2$	I_2 = 1757.1
$\mathrm{Li^{2+}(g) \rightarrow Li^{3+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$\mathrm{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^-}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$\mathrm{Be^{3+}(g) \rightarrow Be^{4+}(g) + e^-}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The increase in successive ionization energies, however, is not linear, but increases drastically when removing electrons in lower n orbitals closer to the nucleus. The most important consequence of the values listed in Table 2.1.5.1 is that the chemistry of Li is

dominated by the $\mathbf{Li^+}$ ion, while the chemistry of **Be** is dominated by the +2 oxidation state. The energy required to remove the *second* electron from **Li**:

$$\mathbf{Li^+(g) \rightarrow Li^{2+}(g) + e^-} \tag{2.1.5.5}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from **Be**:

$$\mathbf{Be^{2+}(g) \rightarrow Be^{3+}(g) + e^-} \tag{2.1.5.6}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both $\mathbf{Li^+}$ and $\mathbf{Be^{2+}}$ have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

> *The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.*



Ionization Energy: Ionization Energy, YouTube(opens in new window) [youtu.be] (opens in new window)

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of ***Li*** and ***Be*** (Table **2.1.5.2**): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table **2.1.5.2**. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from ***Al***, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table **2.1.5.2**: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	577.4.4	1816.7	2744.8	**11,577.4.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.4.4	2914.1	4963.6	6274.0	**21,267.4.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3

*Inner-shell electron

Example 2.1.5.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.

b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^-$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise 2.1.5.1: Lowest Second Ionization Energy

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer

Sr

The first column of data in Table **2.1.5.2** shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

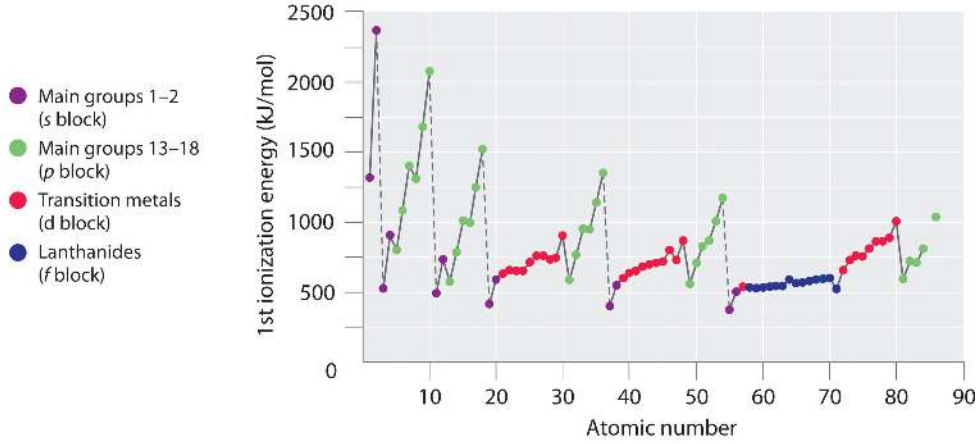


Figure **2.1.5.1**: A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

the main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electron configurations of these "exceptions" provide the answer why. The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does and the *p* electron is more easily removed. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

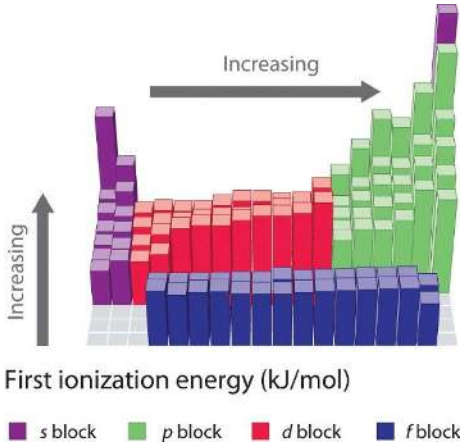


Figure **2.1.5.2**: First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements

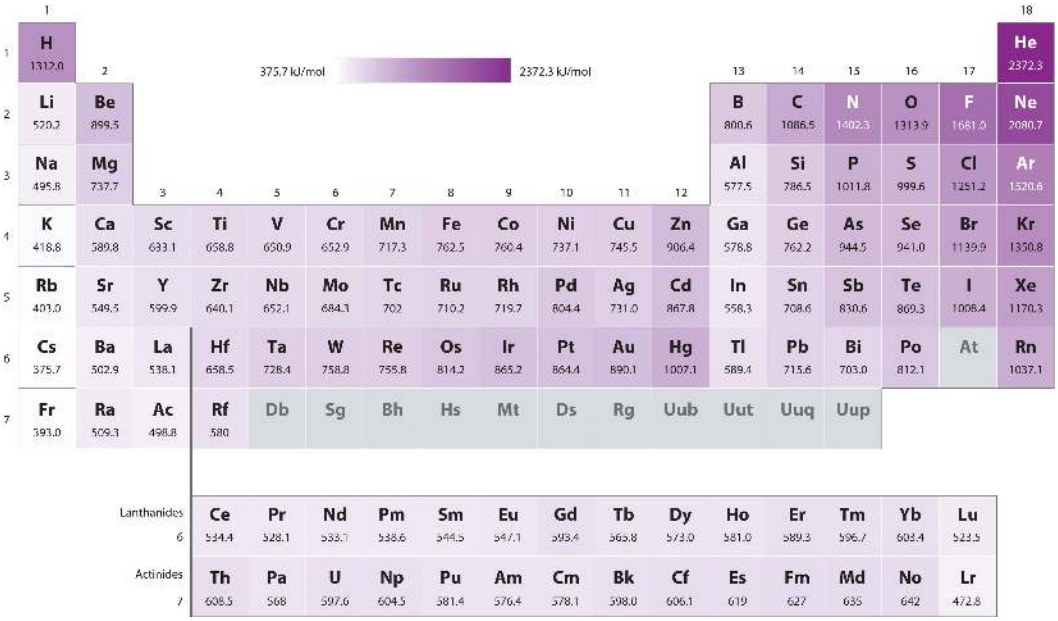
The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. First ionization energy increase from left to right and from bottom to top.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure **2.1.5.1** and are presented numerically and graphically in Figure **2.1.5.2**. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the

transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12).

2. First ionization energies generally decrease down a column. Although the principal quantum number n increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius typically corresponds to a lower ionization energy*.
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).



The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

> *Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.*

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[Ar]4s^23d^{10}4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the $4p$ subshell, shielding the single $4p$ electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[Ar]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier p-block elements. They are sometimes referred to as *pseudo noble gas configurations*. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the $(n-1)d^{10}$ filled subshell*.

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the s- and p-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the ns electrons before the $(n-1)d$ or $(n-2)f$ electrons, respectively. This means that transition metal cations have $(n-1)d^n$ valence electron configurations, and lanthanide cations have $(n-2)f^n$ valence electron configurations. Because the $(n-1)d$ and $(n-2)f$ shells are closer to the nucleus than the ns shell, the $(n-1)d$ and $(n-2)f$ electrons screen the ns electrons quite effectively, reducing the

effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the *ns* electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the *ns*, the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

✔ Example 2.1.5.2: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

? Exercise 2.1.5.2: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer

As

Summary

The tendency of an element to lose electrons is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

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2.1.6: Electron Affinities and Metallic Character

Learning Objectives

- To master the concept of electron affinity as a measure of the energy required to add an electron to an atom or ion.
- To recognize the inverse relationship of ionization energies and electron affinities

The electron affinity (***EA***) of an element ***E*** is defined as the energy change that occurs when an electron is added to a gaseous atom or ion:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA \tag{2.1.6.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released (Figure **2.1.6.1**).

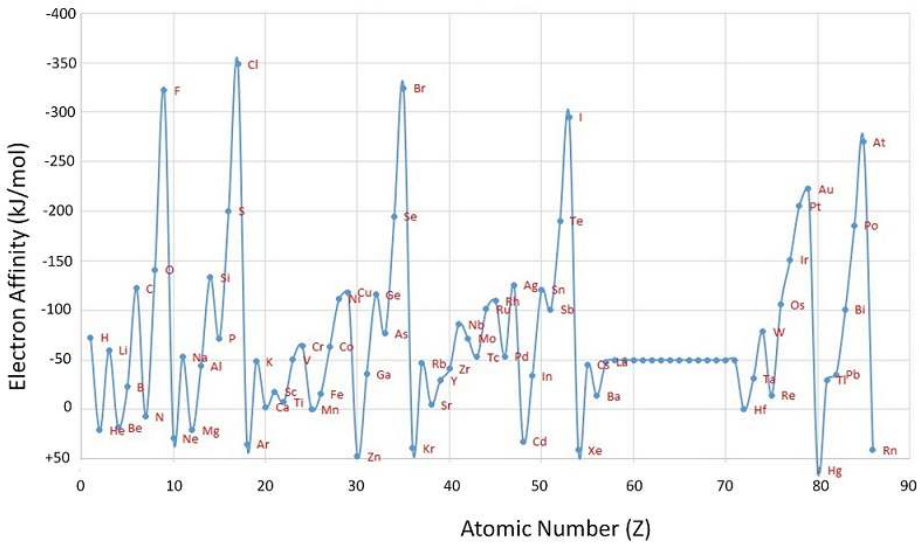


Figure **2.1.6.1**: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies).

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

\[\ce{ Cl(g) + e^- \rightarrow Cl^- (g)} \;\;\;\;\;\; EA=-346\; kJ/mol \label{7.5.2} \]

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$\mathrm{Be\,(g) + e^-} \rightarrow \mathrm{Be^-\,(g)} \qquad EA \geq 0 \tag{2.1.6.2}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$\mathrm{N\,(g) + e^-} \rightarrow \mathrm{N^-\,(g)} \qquad EA \approx 0 \tag{2.1.6.3}$$

> *Generally, electron affinities become more negative across a row of the periodic table.*

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus.

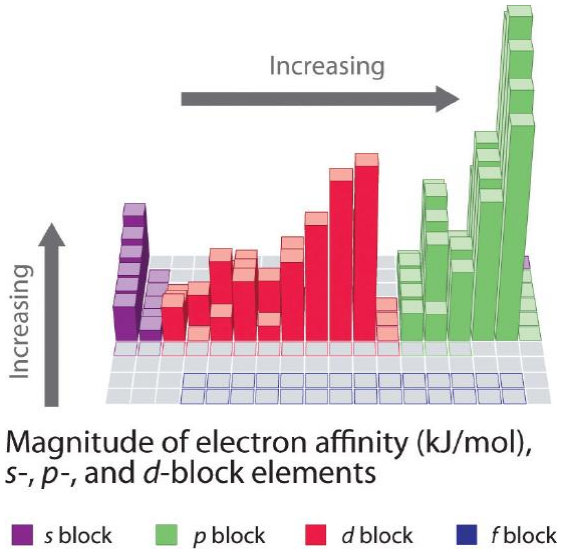


Figure **2.1.6.2**: Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electron affinity increases from left to right and bottom to top.

Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing *n*, so that formation of an anion from the heavier elements becomes energetically more favorable.

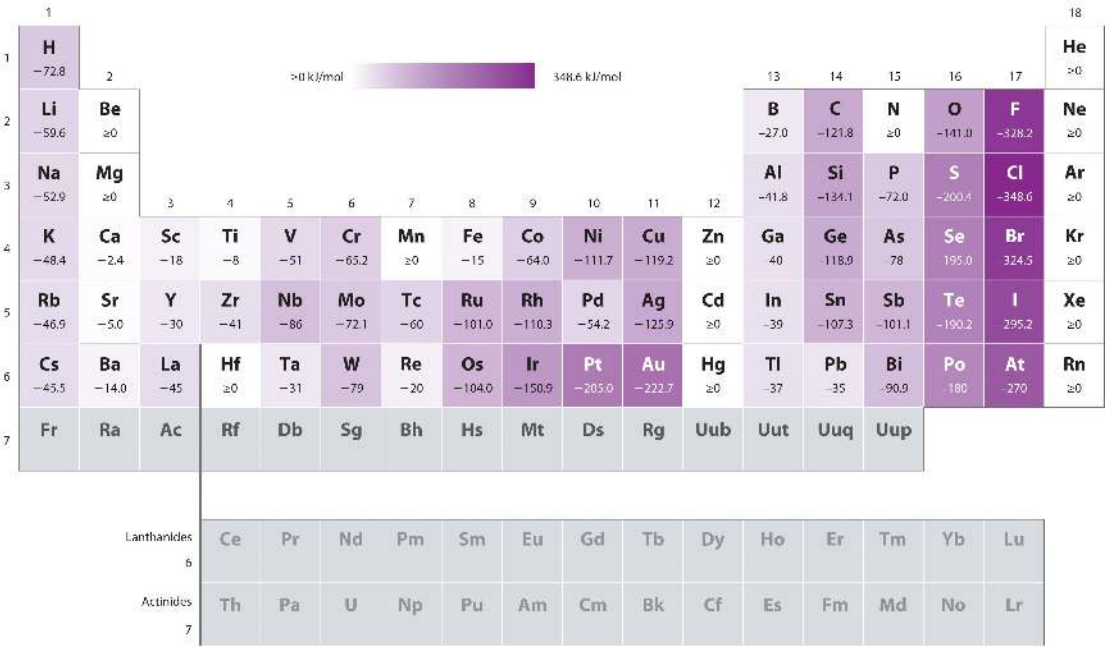


Figure **2.1.6.3**: There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from *Journal of Physical and Chemical Reference Data* 28, no. 6 (1999).

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{2.1.6.4}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{2.1.6.5}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{2.1.6.6}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{2.1.6.7}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{2.1.6.8}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

> *While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.*



Electron Affinity: Electron Affinity, YouTube(opens in new window) [youtu.be] (opens in new window)

If energy is required to form both positively charged cations and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt.*

Example 2.1.6.1: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.

B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 2.1.6.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer

Rb

Summary

The **electron affinity** (*EA*) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

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SECTION OVERVIEW

2.2: STRUCTURE

STRUCTURE

2.2.1: Representing Valance Electrons with Dots

2.2.2: Ionic Bonding

2.2.3: Covalent Bonding- Lewis Structure

2.2.4: Electronegativity and Bond Polarity

2.2.5: Lewis Structures

2.2.6: Resonance and Formal Charge

2.2.7: Exceptions to the Octet Rule

2.2.8: Bond Energies and Bond Lengths

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2.2.1: Representing Valance Electrons with Dots

Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

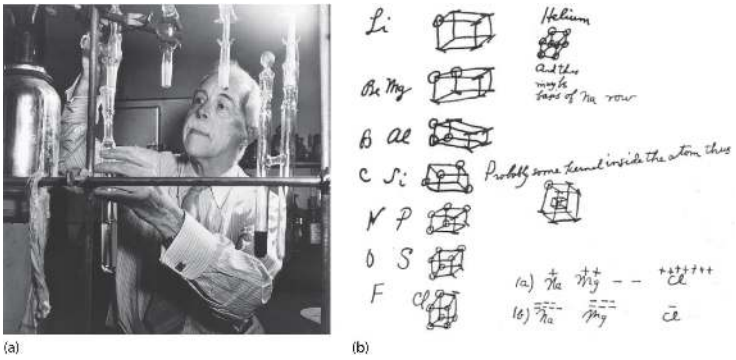


Figure **2.2.1.1**: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]3s^{2}3p^4, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

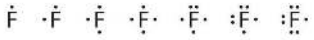


Figure 8.1.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.1.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	[He]$2s^1$	Li•
Be	[He]$2s^2$	•Be•
B	[He]$2s^2 2p^1$	•B•
C	[He]$2s^2 2p^2$	•C•
N	[He]$2s^2 2p^3$	•N:
O	[He]$2s^2 2p^4$	:O:
F	[He]$2s^2 2p^5$	:F:
Ne	[He]$2s^2 2p^6$	:Ne:

Figure **2.2.1.2**: Lewis Dot Symbols for the Elements in Period 2

L i has one dot on the right, B e has one dot on the left and right, B has one dot on the left, right, and above. C has one dot above, below, on the left and on the right. N has one dot above, below, on the left and two dots on the right. O has two dots on the left and right and one dot above and below. F has two dots above, on the left, on the right and on dot below. N e has two dots above, below, on the right, and on the left.



The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory. The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability

have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Definition: Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., $\mathbf{H_2}$
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., $\mathbf{CH_4}$

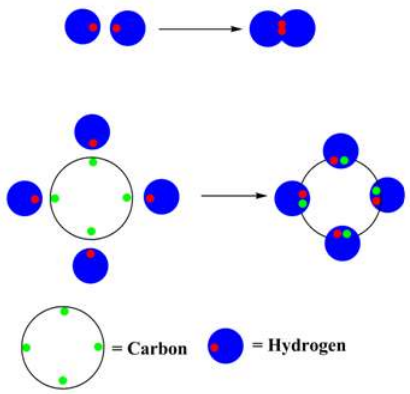


Figure 1: Bonding in $\boldsymbol{H_2}$ and methane ($\boldsymbol{CH_4}$)

A hydrogen bonds with each of the four valence electrons of a carbon meaning that four hydrogens can bond with one carbon.

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 2.2.1.1: Salt

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be

much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

> *Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.*

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

Summary

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

Contributors and Attributions

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2.2.2: Ionic Bonding

Learning Objectives

- To describe the characteristics of ionic bonding.
- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. **Ionic bonding** is the attraction between positively- and negatively-charged ions. These oppositely charged ions attract each other to form ionic networks (or **lattices**). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

Generating Ionic Bonds

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

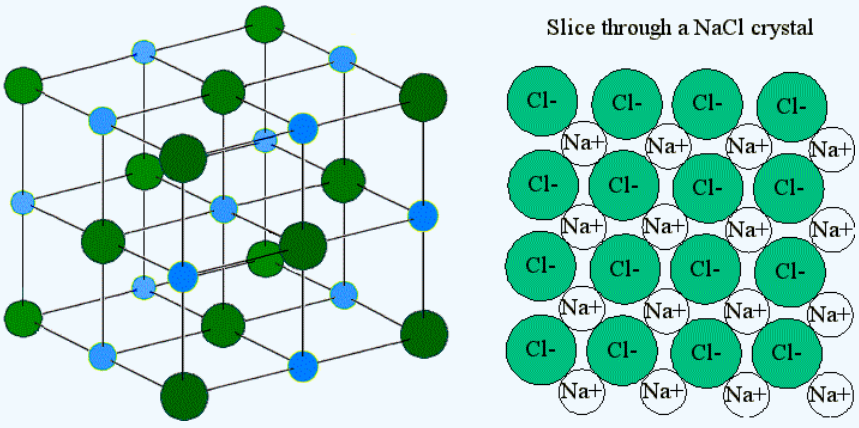
In the overall ionic compound, positive and negative charges must be balanced, because electrons cannot be created or destroyed, only transferred. Thus, the total number of electrons lost by the cationic species must equal the total number of electrons gained by the anionic species.

Example 2.2.2.1: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is NaCl.

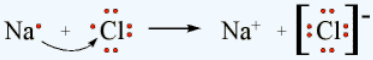
$$2\,Na\,(s) + Cl\,2\,(g) \rightarrow 2\,NaCl\,(s)$$

These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):



NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattes. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization energy. Thus the chlorine gains an electron from the sodium atom. This can be represented using ewis dot symbols (here we will consider one chlorine atom, rather than Cl_2):



Chlorine becomes more negative when it takes the one valence electron from sodium when it makes an octet.

The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its valence shell:

- $Na^{+:}$ $2s^2 2p^6$
- Cl^-: $3s^2 3p^6$

Energetics of Ionic Bond Formation

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. Consider a single pair of ions, one cation and one anion. How strong will the force of their attraction be? According to **Coulomb's Law**, the energy of the electrostatic attraction (E) between two charged particles is proportional to the magnitude of the charges and inversely proportional to the internuclear distance between the particles (r):

$$E \propto \frac{Q_1 Q_2}{r} \tag{2.2.2.1}$$

$$E = k\frac{Q_1 Q_2}{r} \tag{2.2.2.2}$$

where each ion's charge is represented by the symbol Q. The proportionality constant k is equal to 2.31×10^{-28} J·m. This value of k includes the charge of a single electron (1.6022×10^{-19} C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, k, equals 8.999 × 109 J·m/C^2. In the example given, $Q_1 = +1(1.6022 \times 10^{-19}$ C) and $Q_2 = -1(1.6022 \times 10^{-19}$ C). If Q_1 and Q_2 have opposite signs (as in NaCl, for example, where Q_1 is +1 for Na^+ and Q_2 is −1 for Cl^-), then E is negative, which means that energy is *released* when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

> *Energy is always released when a bond is formed and correspondingly, it always requires energy to break a bond.*

As shown by the green curve in the lower half of Figure **2.2.2.1**, the maximum energy would be released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure **2.2.2.1**. The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure **2.2.2.1** shows that the total energy of the system reaches a minimum at r_0, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured **bond distance**.

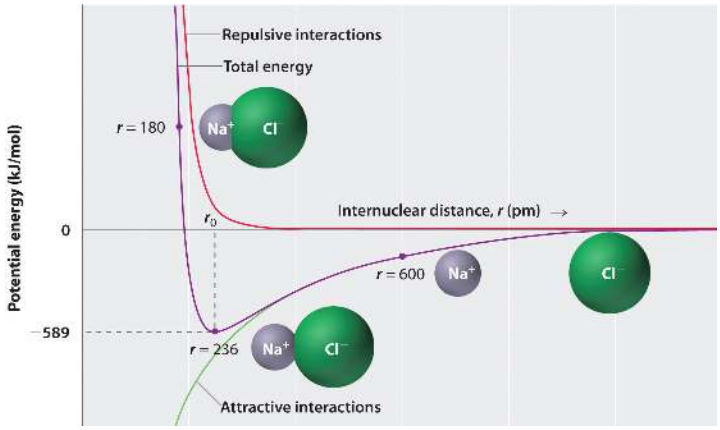


Figure 2.2.2.1: A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na^+ Ion and a Gaseous Cl^- Ion. The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

Consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $Na^+_{(g)}$ ion and a $Cl^-_{(g)}$ ion is as follows:

$$\begin{aligned} E &= k\frac{Q_1Q_2}{r_0} \\ &= (2.31 \times 10^{-28}\,\mathrm{J \cdot \cancel{m}})\left(\frac{(+1)(-1)}{236\ \cancel{\mathrm{pm}} \times 10^{-12}\ \cancel{\mathrm{m/pm}}}\right) \\ &= -9.79 \times 10^{-19}\ J/ion\ pair \end{aligned}$$

The negative value indicates that energy is released. Our convention is that if a chemical process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

$$E = \left(-9.79 \times 10^{-19}\ J/\cancel{ionpair}\right)\left(6.022 \times 10^{23}\ \cancel{ion\ pair}/mol\right) = -589\ kJ/mol \tag{2.2.2.3}$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the **lattice energy** of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

- At r_0, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at r_0, energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

✔ Example 2.2.2.2: LiF

Calculate the amount of energy released when 1 mol of gaseous Li^+F^- ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 2.2.2.2 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

Solution:

Inserting the values for Li^+F^- into Equation 2.2.2.2 (where Q_1 = +1, Q_2 = −1, and r = 156 pm), we find that the energy associated with the formation of a single pair of Li^+F^- ions is

$$\begin{aligned} E &= k\frac{Q_1Q_2}{r_0} \\ &= \left(2.31 \times 10^{-28}\, J \cdot \cancel{m}\right)\left(\frac{(+1)(-1)}{156\ pm \times 10^{-12}\ \cancel{m}/pm}\right) \\ &= -1.48 \times 10^{-18} \end{aligned}$$

Then the energy released per mole of Li^+F^- ion pairs is

$$\begin{aligned} E &= \left(-1.48 \times 10^{-18} J/\cancel{\text{ion pair}}\right)\left(6.022 \times 10^{23}\ \cancel{\text{ion pair}}/mol\right) \\ &- 891\ kJ/mol \end{aligned}$$

Because Li^+ and F^- are smaller than Na^+ and Cl^- (see Section 7.3), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation 2.2.2.2, much more energy is released when 1 mol of gaseous Li^+F^- ion pairs is formed (−891 kJ/mol) than when 1 mol of gaseous Na^+Cl^- ion pairs is formed (−589 kJ/mol).

? Exercise 2.2.2.2: Magnesium oxide

Calculate the amount of energy released when 1 mol of gaseous **MgO** ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

Answer

−3180 kJ/mol = -3.18×10^3 kJ/mol

Electron Configuration of Ions

How does the energy released in lattice formation compare to the energy required to strip away a second electron from the Na^+ ion? Since the Na^+ ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would require more energy than what is released during lattice formation (Sodium I_2 = 4,560 kJ/mol). Thus, sodium is present in ionic compounds as Na^+ and not Na^{2+}. Likewise, adding an electron to fill a valence shell (and achieve noble gas electron configuration) is exothermic or only slightly endothermic. To add an additional electron into a ***new*** subshell requires tremendous energy - more than the lattice energy. Thus, we find Cl^- in ionic compounds, but not Cl^{2-}.

Table **2.2.2.1**: Lattice energies range from around 700 kJ/mol to 4000 kJ/mol:

Compound	Lattice Energy (kJ/mol)
LiF	1024
LiI	744
NaF	911
NaCl	788
NaI	693
KF	815
KBr	682
KI	641
MgF_2	2910
$SrCl_2$	2130
MgO	3938

This amount of energy can compensate for values as large as I_3 for valence electrons (i.e. can strip away up to 3 valence electrons). Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core. A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell. (The remaining electrons in the unfilled d subshell are the reason for the bright colors observed in many transition metal compounds!) For example, iron ions will **not** form a noble gas core:

- Fe: $[Ar]4s^2 3d^6$
- Fe^{2+}: $[Ar]\ 3d^6$
- Fe^{3+}: $[Ar]\ 3d^5$

Some metal ions can form a pseudo noble gas core (and be colorless), for example:

- Ag: $[Kr]5s^1 4d^{10}$ Ag^+ $[Kr]4d^{10}$ Compound: AgCl
- Cd: $[Kr]5s^2 4d^{10}$ Cd^{2+} $[Kr]4d^{10}$ Compound: CdS

The valence electrons do not adhere to the "octet rule" in this case (a limitation of the usefulness of this rule). Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state.

> *When a positive ion is formed from an atom, electrons are **always** lost first from the subshell with the largest principle quantum number*

Polyatomic Ions

Not all ionic compounds are formed from only two elements. Many **polyatomic ions** exist, in which two or more atoms are bound together by covalent bonds. They form a stable grouping which carries a charge (positive or negative). The group of atoms as a whole acts as a charged species in forming an ionic compound with an oppositely charged ion. Polyatomic ions may be either positive or negative, for example:

- NH_4^+ (ammonium) = cation
- SO_4^{2-} (sulfate) = anion

The principles of ionic bonding with polyatomic ions are the same as those with monatomic ions. Oppositely charged ions come together to form a crystalline lattice, releasing a lattice energy. Based on the shapes and charges of the polyatomic ions, these compounds may form crystalline lattices with interesting and complex structures.

Summary

The amount of energy needed to separate a gaseous ion pair is its bond energy. The formation of ionic compounds are usually ***extremely exothermic***. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Contributors and Attributions

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2.2.3: Covalent Bonding- Lewis Structure

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure **2.2.3.1**):

- The electrons in the two atoms repel each other because they have the same charge (
- *The electrons in the two atoms repel each other because they have the same charge (E > 0).*
- *Similarly, the protons in adjacent atoms repel each other (E > 0).*
- *The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa (E < 0). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

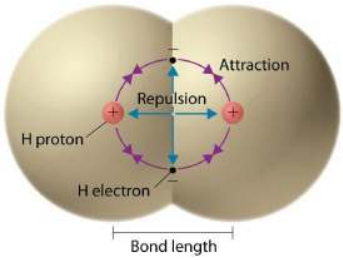


Figure **2.2.3.1**: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure **2.2.3.2**) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures **2.2.3.1** and **2.2.3.2**, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

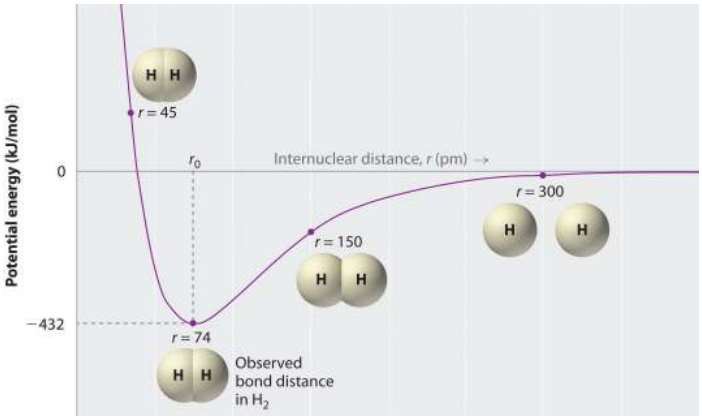


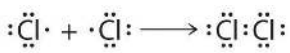
Figure **2.2.3.2**: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the

internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

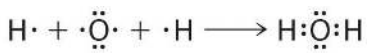
Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:

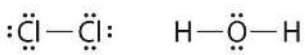


Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.

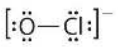
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

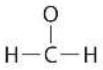
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



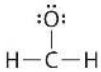
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

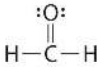
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 2.2.3.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

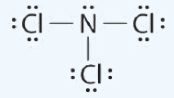
Asked for: Lewis electron structures

Strategy:

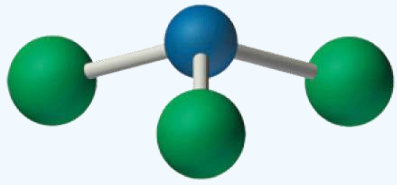
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

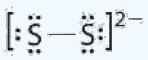


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

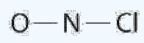


Nitrogen trichloride

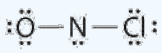
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



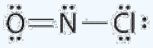
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



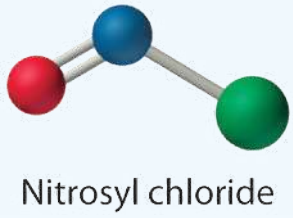
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



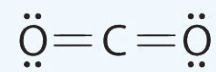
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



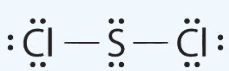
? Exercise 2.2.3.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

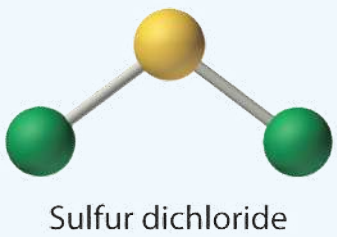
Answer

1. 



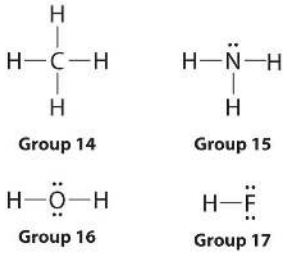
2. 

Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.

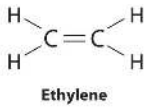


Using Lewis Electron Structures to Explain Stoichiometry

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure **2.2.3.3**). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

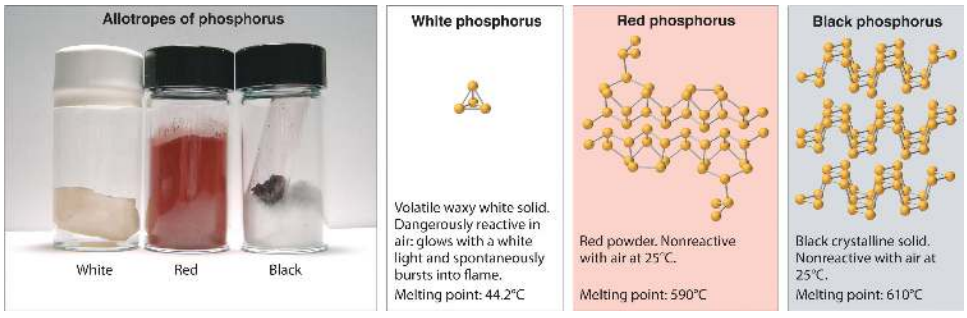


Figure **2.2.3.3**: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure

by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

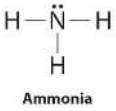
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$\textit{formal charge} = \underset{(\textit{free atom})}{\textit{valence } e^-} - \underset{(\textit{atom in Lewis structure})}{\left(\textit{non} - \textit{bonding } e^- + \frac{\textit{bonding } e^-}{2}\right)} \text{ (atom in Lewis structure)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^-/2)]. Substituting into Equation 2.2.3.1, we obtain

$$\textit{formal charge}\,(N) = 5\ \textit{valence } e^- - \left(2\ \textit{non} - \textit{bonding } e^- + \frac{6\ \textit{bonding } e^-}{2}\right) = 0 \qquad (2.2.3.1)$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 2.2.3.1 to calculate the formal charge on hydrogen, we obtain

$$\textit{formal charge}\,(H) = 1\ \textit{valence } e^- - \left(0\ \textit{non} - \textit{bonding } e^- + \frac{2\ \textit{bonding } e^-}{2}\right) = 0 \qquad (2.2.3.2)$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.



Example 2.2.3.2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

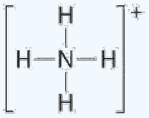
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 2.2.3.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

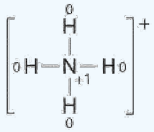
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



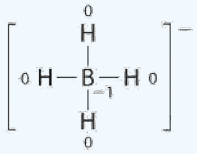
In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 2.2.3.2

Write the formal charges on all atoms in BH_4^-.

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

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2.2.4: Electronegativity and Bond Polarity

Learning Objectives

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the bonding electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. As demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The greater the value, the greater the attractiveness for electrons.*

Electronegativity is a function of:

1. the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and
2. the atom's ***electron affinity*** (how strongly the atom attracts other electrons).

Both of these are properties of the *isolated* atom. An element will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

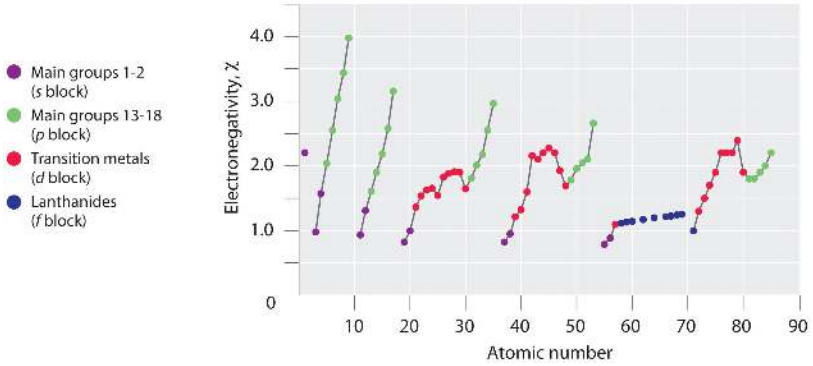
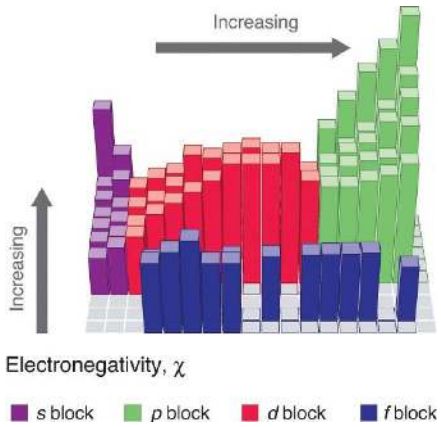


Figure **2.2.4.1**: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table
The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations in Pauling's electronegativity values are illustrated in Figures **2.2.4.1** and **2.2.4.2**. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

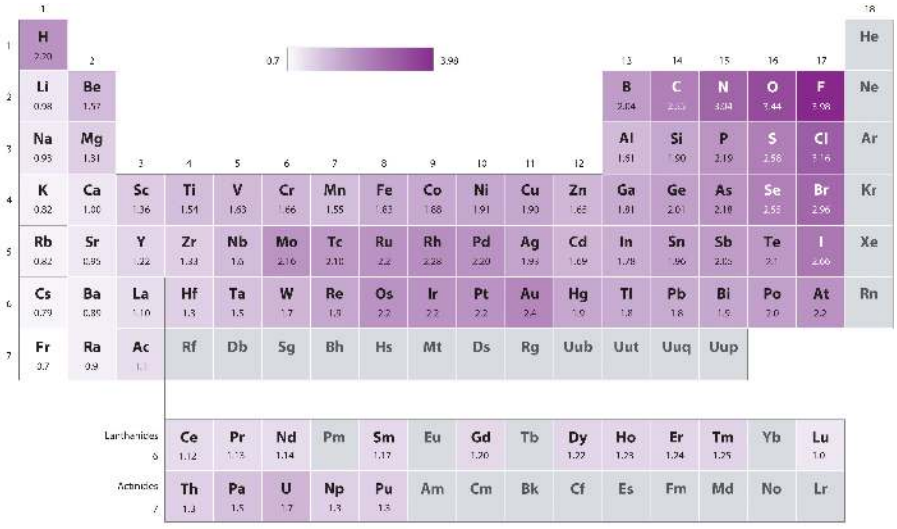


The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

***Figure* 2.2.4.2:** *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school, but was later denied a high school degree, and had to work several jobs to put himself through college. Pauling would go on to become one of the most influential chemists of the century if not all time. He won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962.



Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem, e.g., the Mulliken, Allred-Rochow, and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.



Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure **2.2.4.2**) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **metalloids** (or semimetals), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure **2.2.4.3** shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

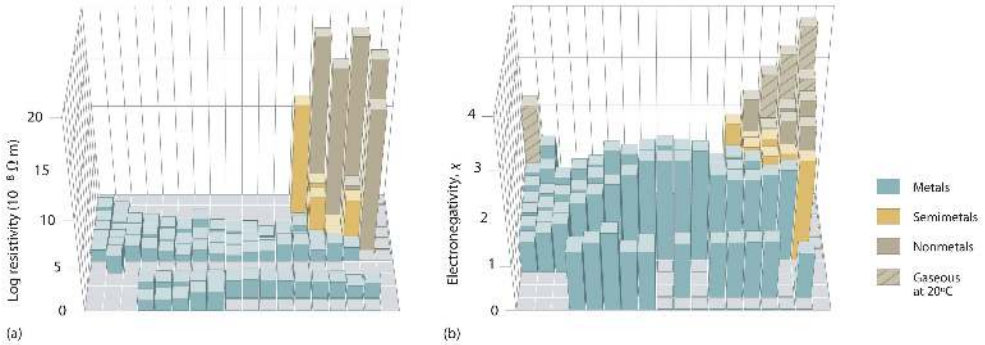


Figure **2.2.4.3**: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Metals are blue, semimetals are yellow, nonmetals are gray, gaseous at 20 degrees C are gray with dashed lines.

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states(opens in new window) are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

✔ Example 2.2.4.1: Increasing Electronegativity

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a metalloid according to its location about the diagonal belt of metalloids running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a metalloid, and Se and Cl are nonmetals.

? Exercise 2.2.4.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a metalloid.

Answer

Rb < Zr < Ge < N < O; metals (Rb, Zr); metalloid (Ge); nonmetal (N, O)

Percent Ionic Character of a Covalent polar bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure **2.2.4.4** compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

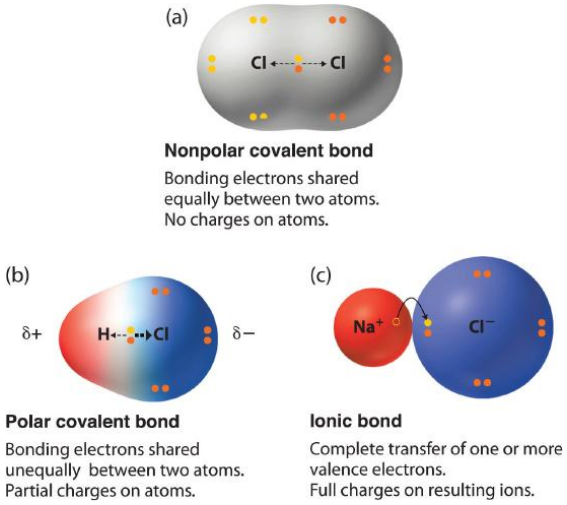


Figure **2.2.4.4**: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\underset{\textit{less electronegative}}{A}} - \underset{\delta^-}{\underset{\textit{more electronegative}}{B}} \qquad (2.2.4.1)$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: χ_{Cl} = 3.16, χ_H = 2.20, and χ_{Na} = 0.93. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{2.2.4.2}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{2.2.4.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure **2.2.4.4**).

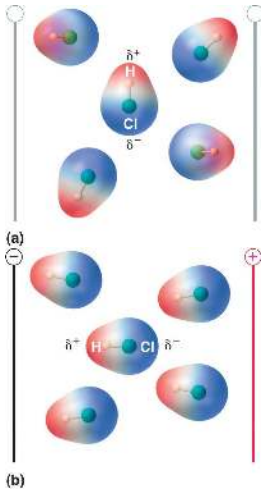


Figure **2.2.4.5**: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 2.2.4.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) = 2.901 \times 10^{-20}\ C \tag{2.2.4.4}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} = 0.1811\ e^- \tag{2.2.4.5}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta+}{H} - \overset{0.18\delta-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure **2.2.4.6** shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure **2.2.4.6** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example **2.2.4.2**.

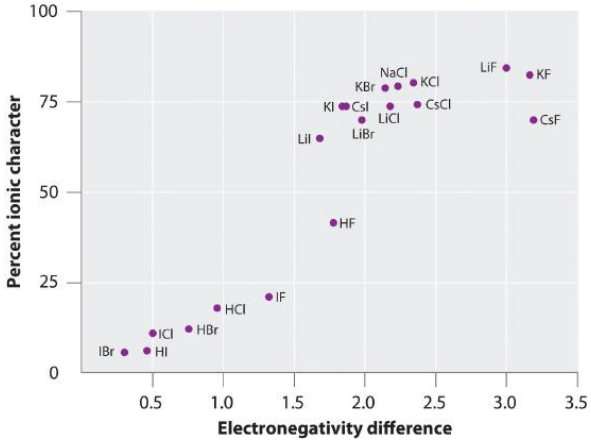


Figure **2.2.4.6**: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 2.2.4.2

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

https://chem.libretexts.org/@go/page/544105

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 2.2.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r}$$

$$= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1 \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\%$$

? Exercise 2.2.4.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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2.2.5: Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure **2.2.5.1**):

- The electrons in the two atoms repel each other because they have the same charge (
- *The electrons in the two atoms repel each other because they have the same charge (E > 0).*
- *Similarly, the protons in adjacent atoms repel each other (E > 0).*
- *The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa (E < 0). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

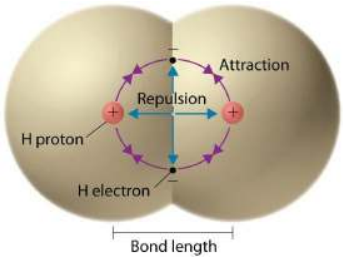


Figure **2.2.5.1**: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure **2.2.5.2**) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures **2.2.5.1** and **2.2.5.2**, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

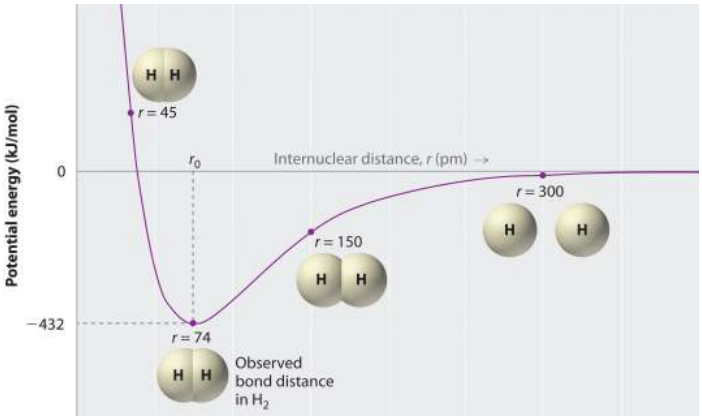


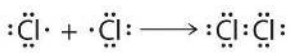
Figure **2.2.5.2**: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the

internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

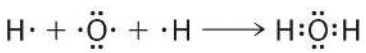
Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:

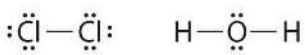


Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

> The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.

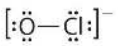
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

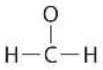
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



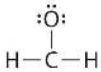
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

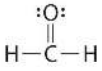
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 2.2.5.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

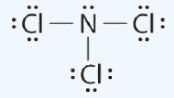
Asked for: Lewis electron structures

Strategy:

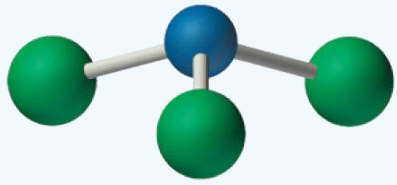
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

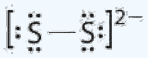


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

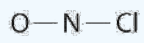


Nitrogen trichloride

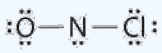
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



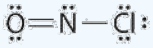
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



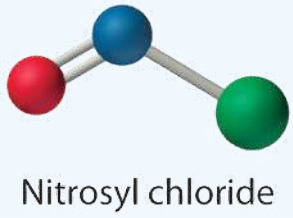
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



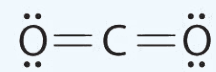
All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



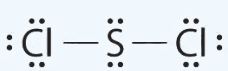
? Exercise 2.2.5.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

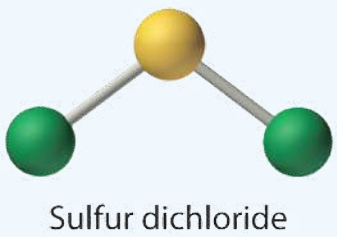
Answer

1. 



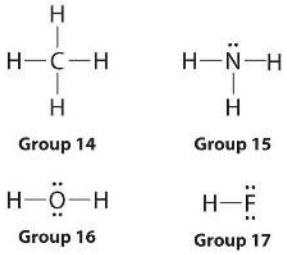
2. 

Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.

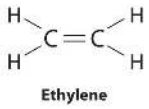


Using Lewis Electron Structures to Explain Stoichiometry

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group 17 (the halogens), this number is one; for the elements of Group 16 (the chalcogens), it is two; for Group 15 elements, three; and for Group 14 elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

> Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure **2.2.5.3**). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

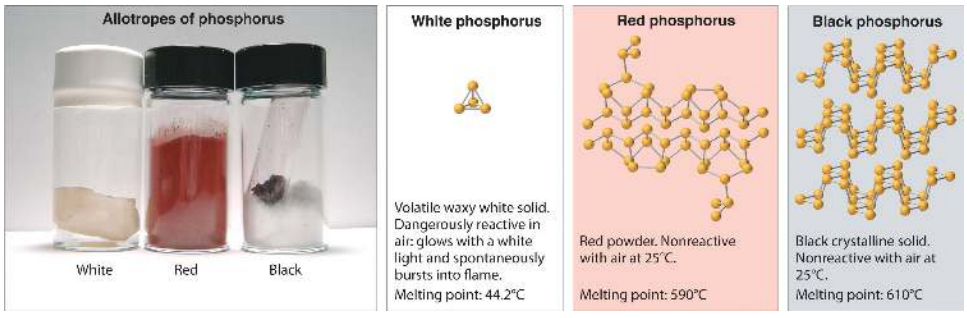


Figure **2.2.5.3**: The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure

by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

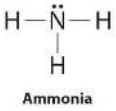
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$\textit{formal charge} = \underset{(\textit{free atom})}{\textit{valence } e^-} - \underset{(\textit{atom in Lewis structure})}{\left(\textit{non} - \textit{bonding } e^- + \frac{\textit{bonding } e^-}{2}\right)} \text{ (atom in Lewis structure)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^-/2)]. Substituting into Equation 2.2.5.1, we obtain

$$\textit{formal charge}\,(N) = 5\ \textit{valence } e^- - \left(2\ \textit{non} - \textit{bonding } e^- + \frac{6\ \textit{bonding } e^-}{2}\right) = 0 \qquad (2.2.5.1)$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^-/2)]. Using Equation 2.2.5.1 to calculate the formal charge on hydrogen, we obtain

$$\textit{formal charge}\,(H) = 1\ \textit{valence } e^- - \left(0\ \textit{non} - \textit{bonding } e^- + \frac{2\ \textit{bonding } e^-}{2}\right) = 0 \qquad (2.2.5.2)$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

> An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.



Example 2.2.5.2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

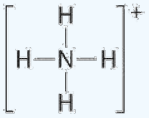
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 2.2.5.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

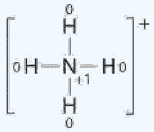
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ???, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



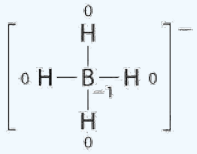
In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise 2.2.5.2

Write the formal charges on all atoms in BH_4^-.

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

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2.2.6: Resonance and Formal Charge

Learning Objectives

- To understand the concept of resonance.

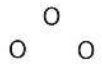
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

Sometimes one Lewis Structure is not Enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone ($\mathbf{O_3}$), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

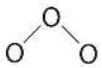
Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:



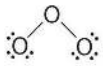
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



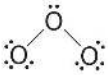
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

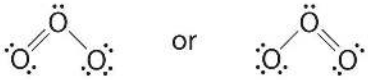


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

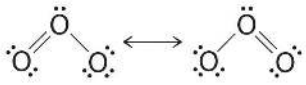


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



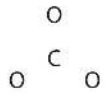
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:



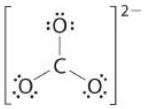
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:



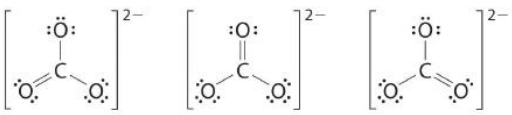
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



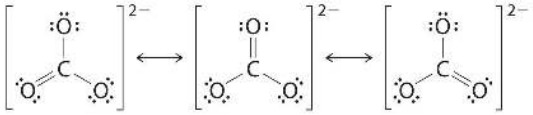
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



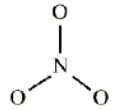
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

The Nitrate (NO_3^-) ion

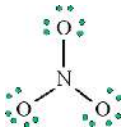
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

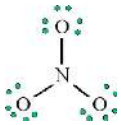


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

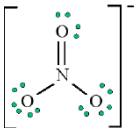


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

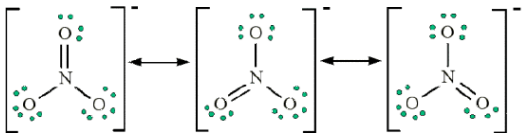
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the $\mathbf{NO_3^-}$ ion to be somewhat shorter than a single bond.



Example 2.2.6.1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

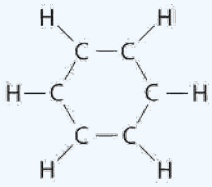
Asked for: resonance structures

Strategy:

A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
C. Draw the resonance structures for benzene.

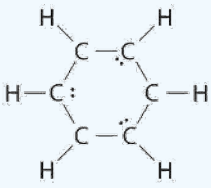
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

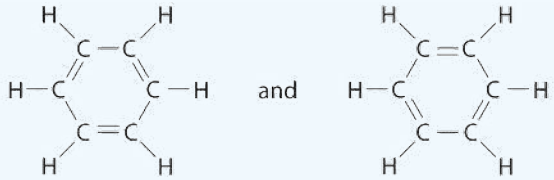
B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:



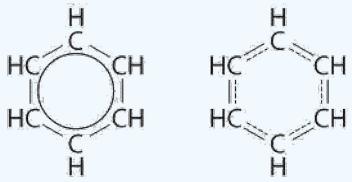
Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of

electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

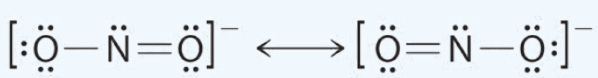


Benzene

Exercise 2.2.6.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example **2.2.6.1**. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance

structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

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2.2.7: Exceptions to the Octet Rule

Learning Objectives

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide also called nitric oxide (**NO**. Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest* formal charge possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in.*

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitric oxide. nitric oxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitric oxide had ten valence electrons we would come up with the Lewis Structure (Figure **2.2.7.1**):

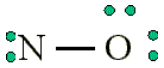


Figure **2.2.7.1**: This is if nitric oxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure **2.2.7.2** based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure **2.2.7.1**, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure **2.2.7.1**, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitric oxide (Figure **2.2.7.2**):

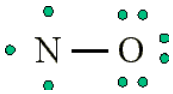


Figure **2.2.7.2**: The proper Lewis structure for NO molecule

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may by familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, an odd Number of Valence Electrons will result in the molecule being paramagnetic.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one were to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure **2.2.7.2**):

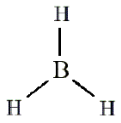


Figure **2.2.7.3**: The structure of $\boldsymbol{BH_3}$ is square planer.

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3, the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure **2.2.7.4**).

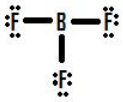


Figure **2.2.7.4**

If you look Figure **2.2.7.4**, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure **2.2.7.5**):

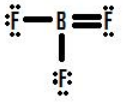


Figure **2.2.7.5**

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group Seven elements have seven valence electrons), so it has a formal charge of +1. The two flourines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see Bond Order and Lengths). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure **2.2.7.5**, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\chi = 4.0$). Boron on the other hand, with

the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3, signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure **2.2.7.6**:

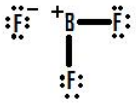


Figure **2.2.7.6**

A bond is broken between one of the fluorine's and the boron making the free fluorine negatively charged and the boron positively charged.

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a resonance of all three structures: the one with the incomplete octet (Figure **2.2.7.4**), the one with the double bond (Figure **2.2.7.5**), and the one with the ionic bond (Figure **2.2.7.6**). The most contributing structure is probably the incomplete octet structure (due to Figure **2.2.7.5** being basically impossible and Figure **2.2.7.6** not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3. This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

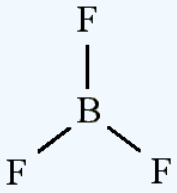
Example **2.2.7.1**: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

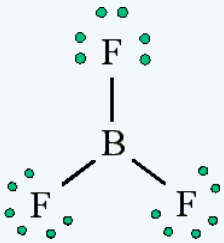
Solution

1. Add electrons (3*7) + 3 = **24**

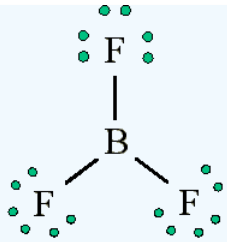
2. Draw connectivities:



3. Add octets to outer atoms:

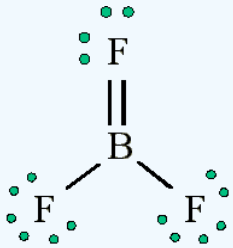


4. Add extra electrons (24-24=0) to central atom:



5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

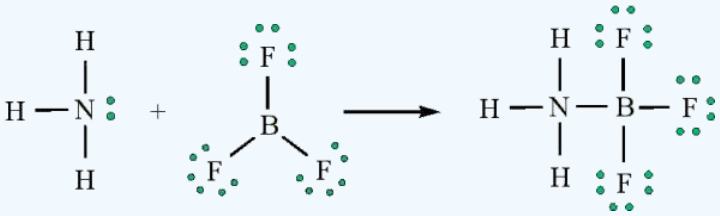


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

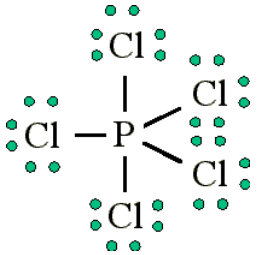
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF_3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



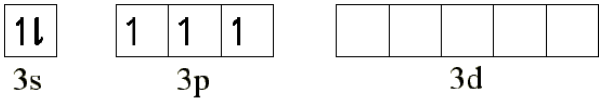
Exception 3: Expanded Valence Shells

More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below*, which those terminal atoms bond to. For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



Expanded valence shells are observed **only** for elements in period 3 (i.e. n=3) and beyond

The 'octet' rule is based upon available n*s* and n*p* orbitals for valence electrons (2 electrons in the *s* orbitals, and 6 in the *p* orbitals). Beginning with the n=3 principle quantum number, the d orbitals become available (*l*=2). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the 3p and 3d orbitals, and as such it is plausible for extra electrons to easily fill the 3d orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.



Example **2.2.7.2**: The SO_4^{-2} ion

Such is the case for the sulfate ion, SO_4^{-2}. A strict adherence to the octet rule forms the following Lewis structure:

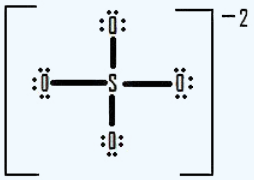


Figure **2.2.7.12**

Four oxygens are bonded to a central sulfur. Each oxygen has 3 lone pairs. The molecule has a minus 2 charge.

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has

four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

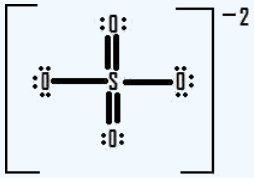


Figure **2.2.7.13**

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero. The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal charges (or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure **2.2.7.12**, as opposed to +2 and -1 (difference of 3) in Figure **2.2.7.12**) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

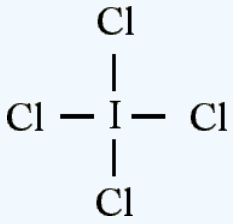
Example **2.2.7.3**: The ICl_4^- Ion

Draw the Lewis structure for ICl_4^- ion.

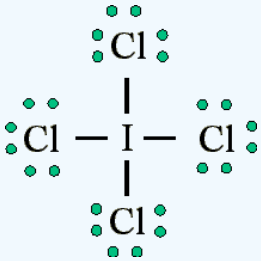
Solution

1. Count up the valence electrons: 7+(4*7)+1 = **36** electrons

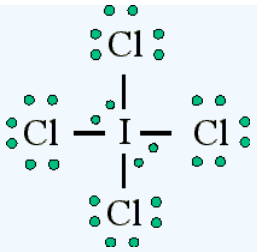
2. Draw the connectivities:



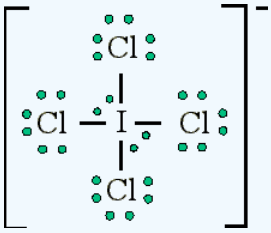
3. Add octet of electrons to outer atoms:



4. Add extra electrons (36-32=**4**) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the 5*d* orbitals)



Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

Summary

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

References

1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.
2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry; The Molecular Science. 2nd Ed. 2004.

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2.2.8: Bond Energies and Bond Lengths

Learning Objectives

- The define Bond-dissociation energy (bond energy)
- To correlate bond strength with bond length
- To define and used *average bond energies*

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The stability of a molecule is a function of the strength of the covalent bonds holding the atoms together.

The Relationship between Bond Order and Bond Energy

Triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table **2.2.8.1** lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table **2.2.8.1**: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942
H–Cl	428	C–I	213			S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222					I–I	149	O=O	494
H–I	295	Si–O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.11).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.11. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of

electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

$$\mathbf{Cl{-}Cl > Br{-}Br > F{-}F > I{-}I}$$

Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

> Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

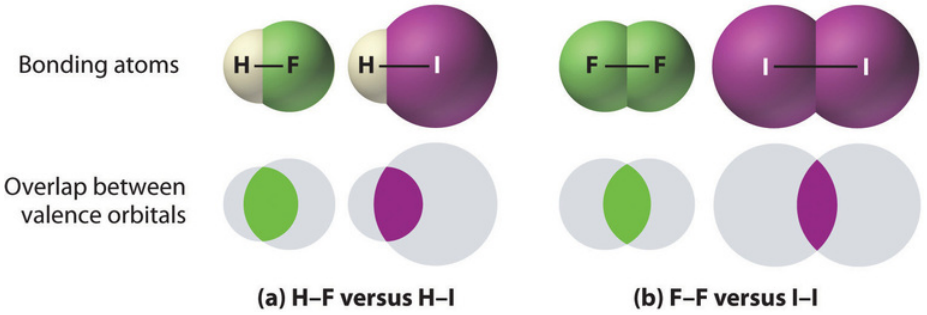


Figure **2.2.8.1**: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 8.6. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

> *Bond strengths increase as bond order **increases**, while bond distances **decrease**.*

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table **2.2.8.2**); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table **2.2.8.1** are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table **2.2.8.2**: Energies for the Dissociation of Successive C–H Bonds in Methane. Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Reaction	D (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{rxn} < 0$):

$$\Delta H_{rxn} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \tag{2.2.8.1}$$

The ≈ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn}.

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:

$$CH_3(CH_2)_5CH_3\,(l) + 11\,O_2\,(g) \rightarrow 7\,CO_2\,(g) + 8\,H_2O\,(g) \tag{2.2.8.2}$$

In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Binds Broken (kJ/mol) and Bonds Formed (kJ/mol)

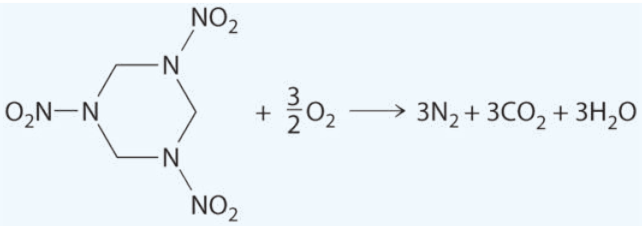
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344
11 O=O	494 × 11 = 5434		**Total** = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately −4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f° values ($\Delta H_{rxn} = -481\ 7 kJ/mol$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f° values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

Example 2.2.8.1: Explosives

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 2.2.8.1 to estimate the ΔH_{rxn} per mole of RDX.



RDX

Given: chemical reaction, structure of reactant, and Table **2.2.8.1**.

Asked for: ΔH_{rxn} per mole

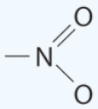
Strategy:

A. List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.

B. Use Equation **2.2.8.1** to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($–NO_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	411 × 6 = 2466	6 C=O	799 × 6 = 4794
3 N–N	167 × 3 = 501	6 O–H	459 × 6 = 2754
3 N–O	201 × 3 = 603		**Total** = 10,374
3 N=O	607 × 3 = 1821		
1.5 O=O	494 × 1.5 = 741		
	Total = 7962		

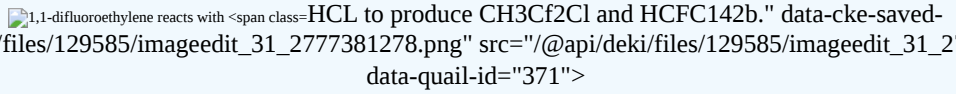
B From Equation **2.2.8.1**, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed}) \\ &= 7962\ kJ/mol - 10,374\ kJ/mol \\ &= -2412\ kJ/mol\end{aligned}$$

Thus this reaction is also highly exothermic

Exercise 2.2.8.1: Freon

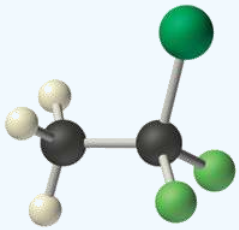
The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:



Use tabulated bond energies to calculate ΔH_{rxn}.

Answer

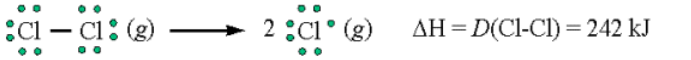
−54 kJ/mol



HCFC-142b

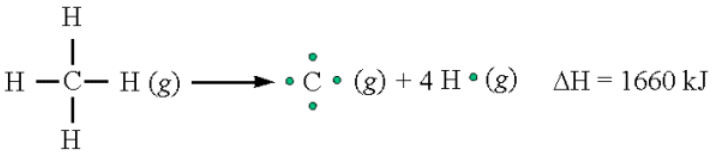
Bond Dissociation Energy

Bond Dissociation Energy (also referred to as Bond energy) is the enthalpy change (ΔH, heat input) required to break a bond (in 1 mole of a gaseous substance)



where "D(Cl-Cl)" represents the bond dissociation energy for the Cl-Cl bonc

What about when we have a compound which is not a diatomic molecule? Consider the dissociation of ***methane***:



There are four equivalent C-H bonds, thus we can that the dissociation energy for a single C-H bond would be:

$$D(C-H) = (1660/4)\ kJ/mol$$
$$= 415\ kJ/mol$$

The bond energy for a given bond is influenced by the rest of the molecule. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms). Thus, the bond energy for most bonds varies little from the average bonding energy for that type of bond

Bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation)

Table 2.2.8.4: Average bond energies:

Bond	(kJ/mol)
C-F	485
C-Cl	328
C-Br	276
C-I	240
C-C	348
C-N	293
C-O	358
C-F	485
C-C	348
C=C	614
C≡C	839

The more stable a molecule (i.e. the stronger the bonds) the less likely the molecule is to undergo a chemical reaction.



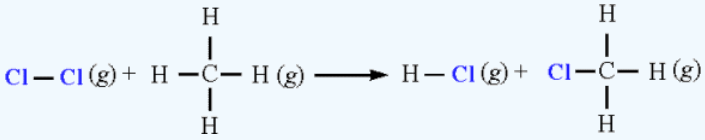
Bond Energies and the Enthalpy of Reactions

If we know which bonds are broken and which bonds are made during a chemical reaction, we can estimate the enthalpy change of the reaction (ΔH_{rxn}) even if we do not know the enthalpies of formation ((ΔH_f°)for the reactants and products:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \tag{2.2.8.3}$$

Example 2.2.8.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 2.2.8.3, which requires tabulating bonds broken and formed.

- **Bonds broken**: 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
- **Bonds formed**: 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

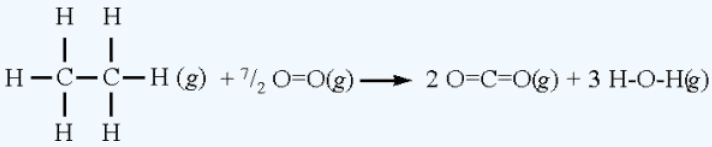
$$\begin{aligned}\Delta H &= [D(Cl-Cl)+D(C-H)]-[D(H-Cl)+D(C-Cl)]\\ &= [242kJ+413kJ]-[431kJ+328kJ]\\ &= -104\,kJ\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 2.2.8.3: Combustion of Ethane

What is the enthalpy of reaction for the combustion of 1 mol of ethane?

$$C_2H_6(g) + {}^7/_2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$



Solution

We use Equation 2.2.8.3, which requires tabulating bonds broken and formed.

- **bonds broken**: 6 moles C-H bonds, 1 mol C-C bonds, $^7/_2$ moles of O=O bonds
- **bonds formed**: 4 moles C=O bonds, 6 moles O-H bonds

$$\begin{aligned}\Delta H &= [(6\times 413)+(348)+(\frac{7}{2}\times 495)]-[(4\times 799)+(6\times 463)]\\ &= 4558-5974\\ &= -1416\,kJ\end{aligned}$$

Therefor the reaction is exothermic.

Table 2.2.8.5: Bond strength and bond length

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C-C	348	1.54
C=C	614	1.34
C≡C	839	1.

As the number of bonds between two atoms increases, the bond grows shorter and stronger

Summary

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

The breakage and formation of bonds is similar to a relationship: you can either get married or divorced and it is more favorable to be married.

- Energy is always **released** to make bonds, which is why the enthalpy change for breaking bonds is always **positive**.
- Energy is always **required** to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is always **negative** because the system is releasing energy when forming bond.

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SECTION OVERVIEW

2.3: SHAPE

SHAPE

2.3.1: Covalent Bonding

2.3.2: Molecular Shape

2.3.3: VSEPR Theory - The Five Basic Shapes

2.3.4: VSPER Theory - Predicting Molecular Geometries

2.3.5: VSPER Theory - Predicting Molecular Geometries

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2.3.3: VSEPR Theory - The Five Basic Shapes

Learning Objectives

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced "vesper"), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

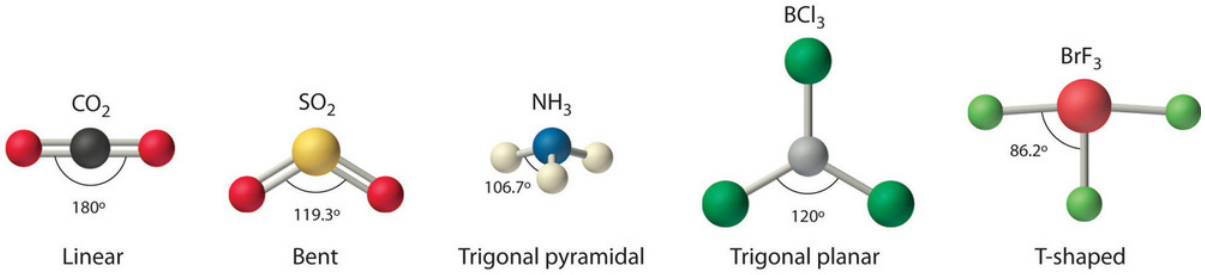


Figure **2.3.3.1**: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures **2.3.3.1** and **2.3.3.2**.

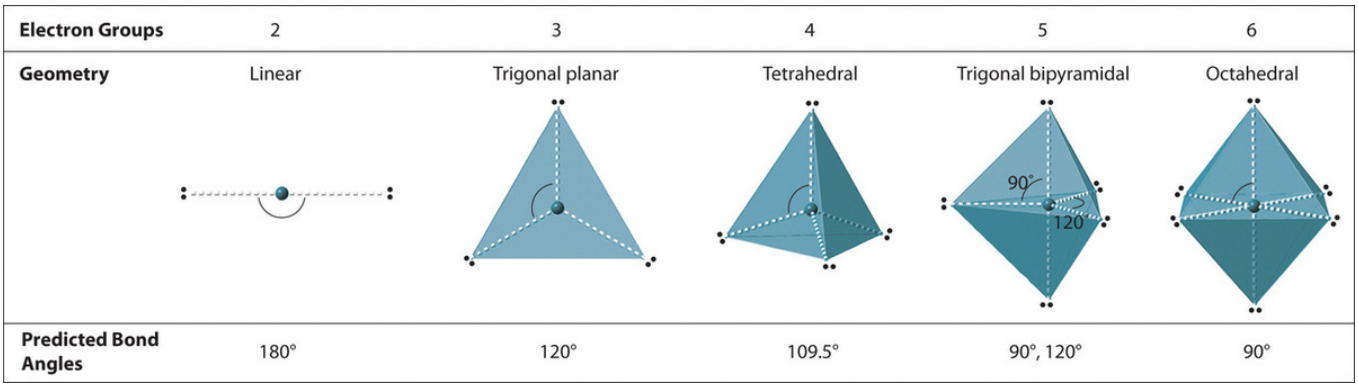


Figure **2.3.3.2**: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

VESPR Produce to predict Molecular geometry

This VESPR procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure **2.3.3.2** and Figure **2.3.3.3**, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

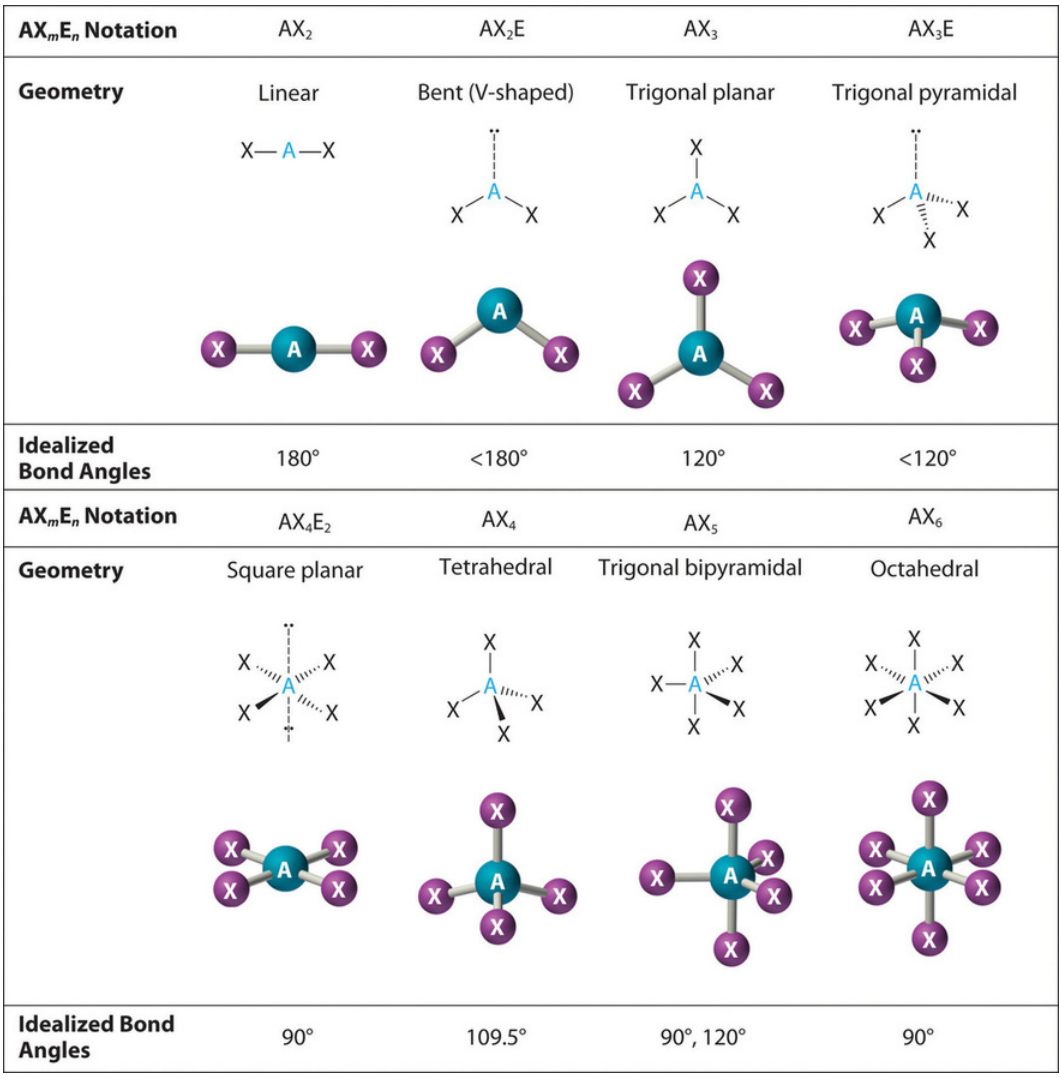


Figure **2.3.3.3**: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

Linear, bent, trigonal planar, trigonal pyramidal, square planar, tetrahedral, trigonal bipyramidal, octahedral.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, $\boldsymbol{BeH_2}$.

AX_2 Molecules: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

H:Be:H or H—Be—H

Lewis structure

Figure **2.3.3.2** that the arrangement that minimizes repulsions places the groups 180° apart. (CC BY-NC-SA; anonymous)

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure **2.3.3.3** we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 Molecules: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

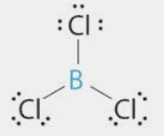
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure **2.3.3.3**). The structure of $\mathbf{CO_2}$ is shown in Figure **2.3.3.1**.

Three Electron Groups

AX_3 Molecules: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

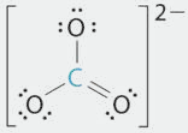
Figure **2.3.3.2**): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure **2.3.3.3** we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure **2.3.3.2**.

AX_3 Molecules: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



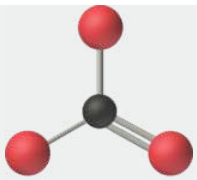
Lewis structure

Figure **2.3.3.2**).

The three oxygens are arranged in a triangular shape with carbon at the center. Two of the oxygens have three lone pairs. One ocht oxygens has 2 lone pairs and is double bonded to the carbon. The molecule has a minus 2 charge.

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure **2.3.3.3** that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E Molecules: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.

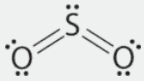


Figure **2.3.3.2**): (CC BY-NC-SA; anonymous)

The two oxygens are double bonded to the sulfur. The oxygens have 2 lone pairs while sulfur had one lone pair.

3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure **2.3.3.4**). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures **2.3.3.2** and **2.3.3.3**). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

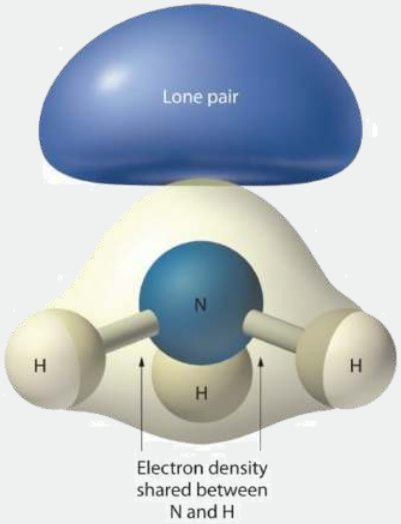
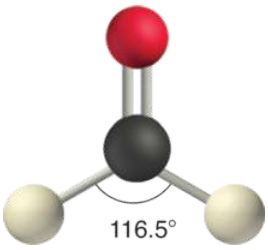


Figure **2.3.3.4**: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose

structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

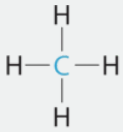


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4 Molecules: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

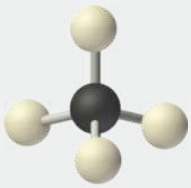


Lewis structure

2. There are four electron groups around the central atom. As shown in Figure **2.3.3.2**, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

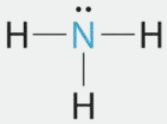
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure **2.3.3.3**).



Molecular geometry
(tetrahedral)

AX_3E Molecules: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure **2.3.3.3**). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure **2.3.3.3** and Figure **2.3.3.4**).

AX_2E_2 Molecules: H_2O

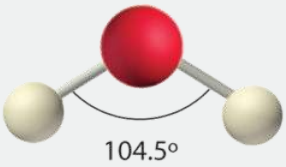
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



Figure **2.3.3.2**: (CC BY-NC-SA; anonymous)

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.



Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5 Molecules: PCl_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is

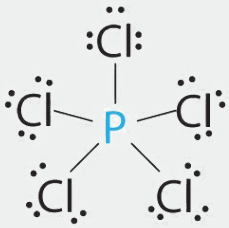
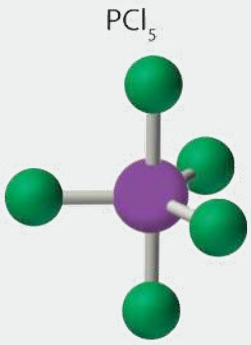


Figure **2.3.3.2**): (CC BY-NC-SA; anonymous)

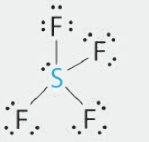
3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure **2.3.3.3**. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E Molecules: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Four fluorenes are bonded to a central sulfur. Each fluorine has three lone pairs. Sulfur has one lone pair.

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure **2.3.3.2**.

3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP–BP repulsions at 90°. If we place it in the equatorial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position is more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

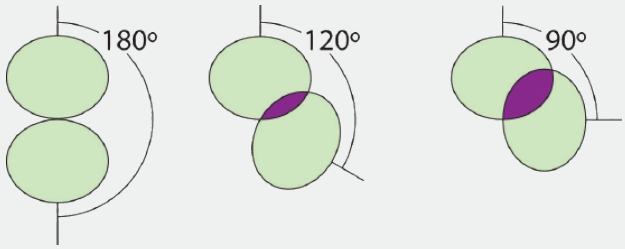
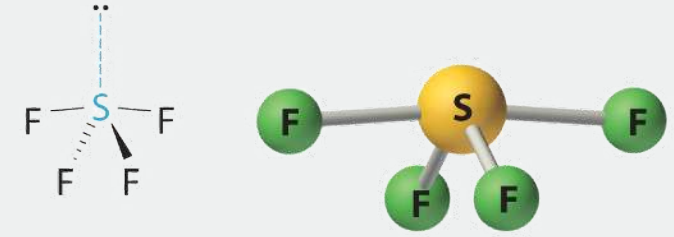


Figure **2.3.3.5**: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

180 degree angle has no shared space between teo electron pair, 120 degree angle has some shared area between two electron pairs. 90 degree angle has more shared space than 120.

At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

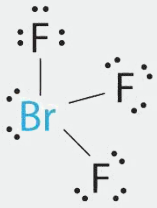
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 Molecules: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Three fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has two lone pairs.

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

If the lone pairs are axiam, the 90 degree LP-LP interactions are o and the 90 degree LP-BP interaction is zero. If the Lone pares are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP intereactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP

repulsions (Figure 2.3.3.2.1).

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

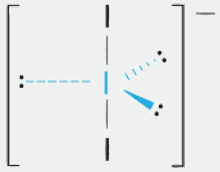
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



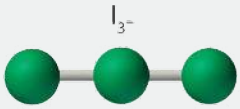
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.



Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 2.3.3.2.)

AX_6 Molecules: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



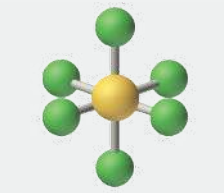
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 2.3.3.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

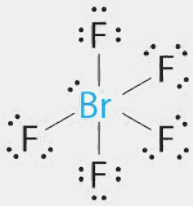
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E Molecules: BrF_5

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is

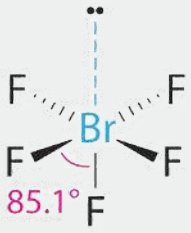


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

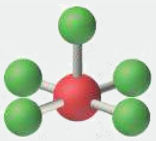
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

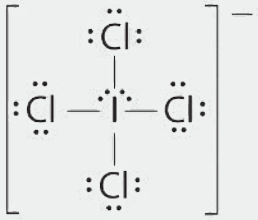
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



Molecular geometry
(square pyramidal)

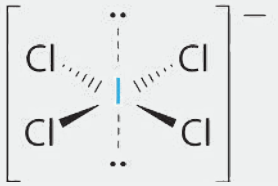
AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



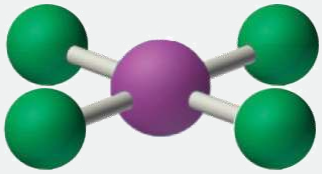
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl4− ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure **2.3.3.6**.

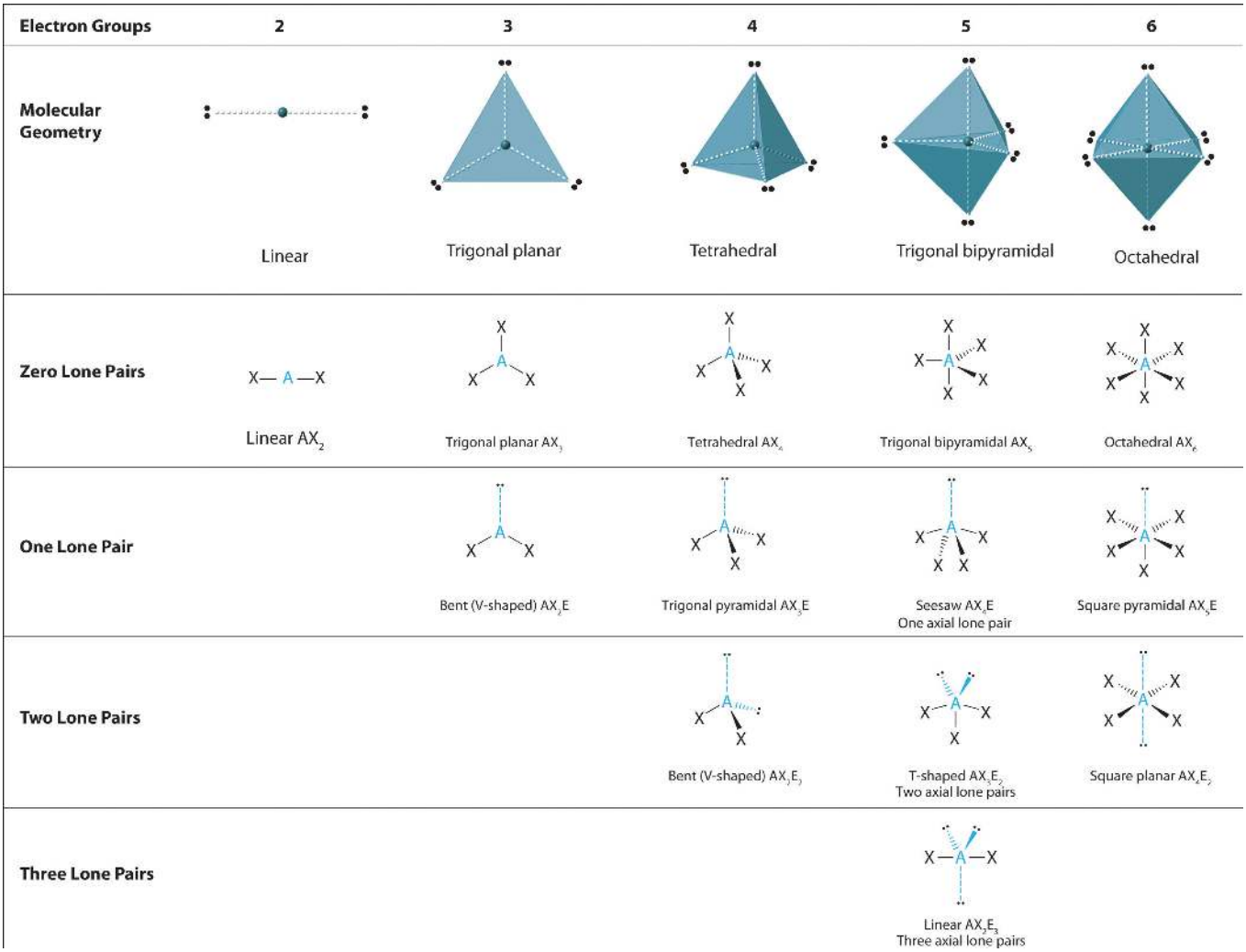


***Figure* 2.3.3.6:** *Overview of Molecular Geometries*



Example 2.3.3.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.

B. Determine the electron group arrangement around the central atom that minimizes repulsions.

C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is

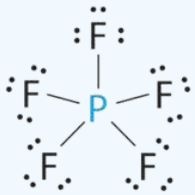


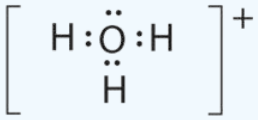
Figure **2.3.3.6**): (CC BY-NC-SA; anonymous)

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is

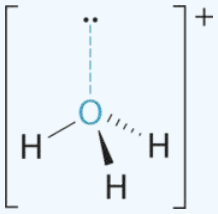


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise 2.3.3.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 2.3.3.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example **2.3.3.1**.

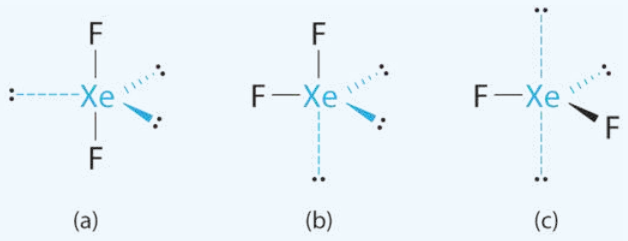
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



Interactions			
90 LP–LP	0	2	2

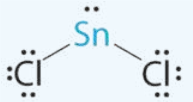
If the two F atoms are axial ther are zero 90 LP-LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90 LP-LP interactions.

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around

the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



Two chlorines are bonded to a central tin. Each chlorine has three lone pairs. Tin has one lone pair.

B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

? Exercise 2.3.3.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

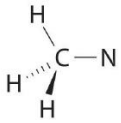


Molecules with No Single Central Atom

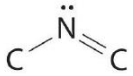
The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India,

when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:

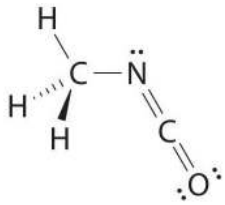


Figure **2.3.3.7**).

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

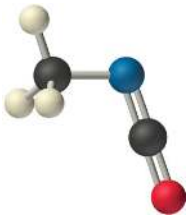


Figure **2.3.3.7**: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Example 2.3.3.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C{\equiv}CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure **2.3.3.3** to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

? Exercise 2.3.3.3

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Molecular Dipole Moments

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (Figure **2.3.3.8*a***). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure **2.3.3.8*b***); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

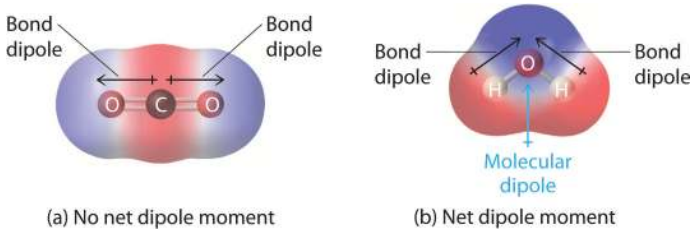


Figure **2.3.3.8**: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure **2.3.3.9**. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment. Molecules with asymmetrical charge distributions have a net dipole moment.

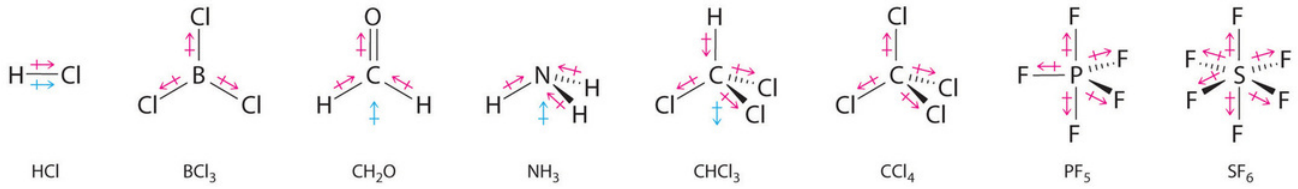


Figure **2.3.3.9**: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).



Example 2.3.3.4

Which molecule(s) has a net dipole moment?

a. **H_2S**
b. **NHF_2**
c. **BF_3**

Given: three chemical compounds

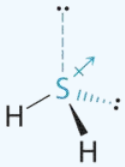
Asked for: net dipole moment

Strategy:

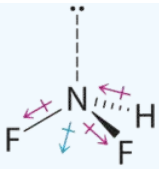
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

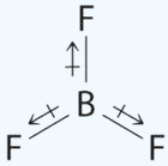
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of **H_2S** is bent (Figure **2.3.3.6**). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



3. The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



? Exercise 2.3.3.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer

CH_3Cl and XeO_3

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

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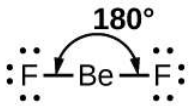
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2.3.4: VSPER Theory - Predicting Molecular Geometries

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure **2.3.4.2**) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure **2.3.4.2**).



A Lewis structure is shown. A fluorine atom with three lone pairs of electrons is single bonded to a beryllium atom which is single bonded to a fluorine atom with three lone pairs of electrons. The angle of the bonds between the two fluorine atoms and the beryllium atom is labeled, “180 degrees.”

Figure **2.3.4.2**: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure **2.3.4.3** illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

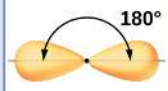
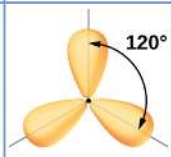
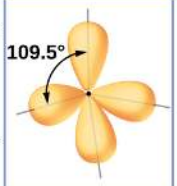
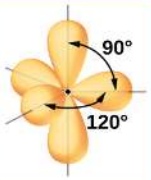
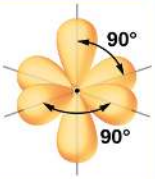
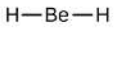
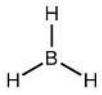
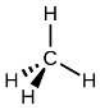
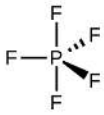
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure **2.3.4.3**: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

In this table summarizing the geometries proposed by VSPER Theory, the number of regions along with spatial arrangement, line-dash-wedge notation, and electron pair geometry are shown.

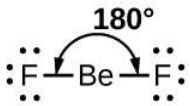
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2.3.5: VSPER Theory - Predicting Molecular Geometries

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure **2.3.5.2**) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure **2.3.5.2**).



A Lewis structure is shown. A fluorine atom with three lone pairs of electrons is single bonded to a beryllium atom which is single bonded to a fluorine atom with three lone pairs of electrons. The angle of the bonds between the two fluorine atoms and the beryllium atom is labeled, “180 degrees.”

Figure **2.3.5.2**: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure **2.3.5.3** illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

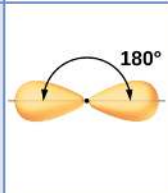
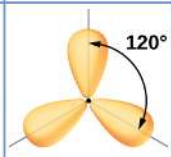
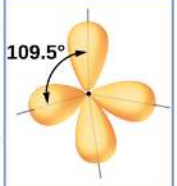
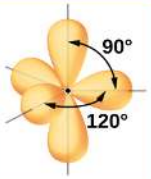
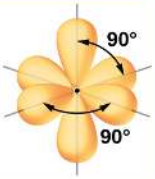
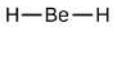
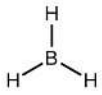
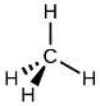
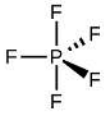
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure **2.3.5.3**: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

In this table summarizing the geometries proposed by VSPER Theory, the number of regions along with spatial arrangement, line-dash-wedge notation, and electron pair geometry are shown.

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SECTION OVERVIEW

2.4: MOLECULAR ORBITALS

MOLECULAR ORBITALS

2.4.1: Molecular Shape and Polarity

2.4.2: Valence Bond Theory- Orbital Overlap as a Chemical Bond

2.4.3: Valence Bond Theory- Hybridization of Atomic Orbitals

2.4.4: MO Theory

2.4.5: Molecular Orbital Theory- Electron Delocalization

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2.4.1: Molecular Shape and Polarity

Learning Objectives

- To calculate the percent ionic character of a covalent polar bond

Previously, we described the two idealized extremes of chemical bonding:

- **ionic bonding**—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
- **covalent bonding**, in which electrons are shared *equally* between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure **2.4.1.1** compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a *polar bond*.

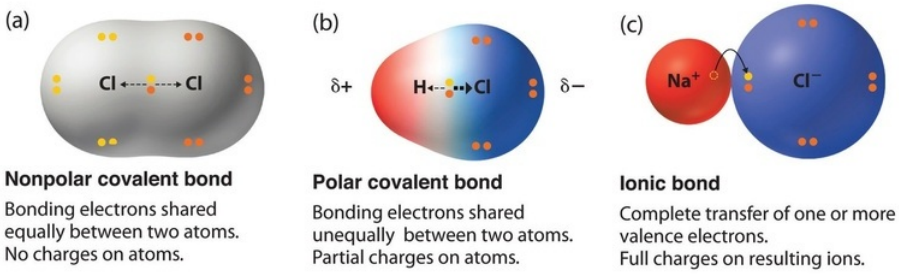


Figure **2.4.1.1**: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. *Electronegativity* (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\textit{less electronegative}}{A}} - \underset{\delta^-}{\overset{\textit{more electronegative}}{B}} \qquad (2.4.1.1)$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms:

$$\Delta\chi = \chi_B - \chi_A.$$

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms (Table A2): $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq\approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and

Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

> Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in **NaCl**, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as **HCl** produces a dipole moment where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{2.4.1.2}$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{2.4.1.3}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure **2.4.1.2**).

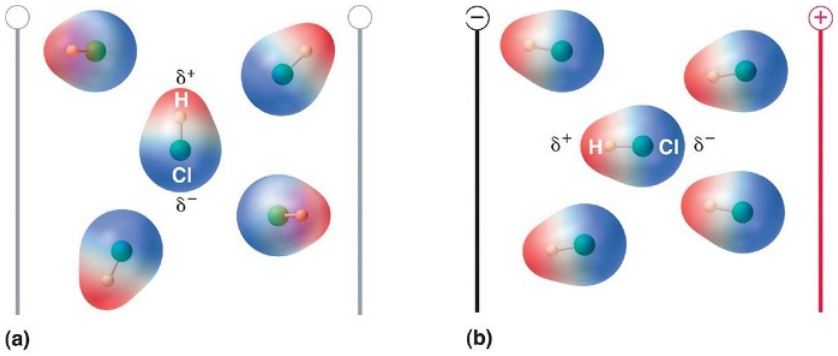


Figure **2.4.1.2**: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the**HCl**molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as **HCl** using Equation 2.4.1.2. If the bonding in **HCl** were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of **HCl** is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) \\ &= 2.901 \times 10^{-20}\ C \end{aligned}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in**HCl** is asymmetric and that effectively it appears that there is a net negative charge on the **Cl** of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the **Cl** atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} = 0.1811\ e^- \tag{2.4.1.4}$$

To form a neutral compound, the charge on the **H** atom must be equal but opposite. Thus the measured dipole moment of **HCl** indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing **HCl** as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta+}{H} - \overset{0.18\delta-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_H = 2.20$ and $\chi_{Cl} = 3.16$) so

$$\chi_{Cl} - \chi_H = 0.96$$

This is a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.



A warning about Dipole Moment arrows

As the figure above shows, we represent dipole moments by an arrow with a length proportional to μ and pointing from the positive charge to the negative charge. However, the **opposite** convention is still widely used especially among physicists.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure **2.4.1.2** shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as $NaCl_{(g)}$ and $CsF_{(g)}$ is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure **2.4.1.2** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example **2.4.1.1**.

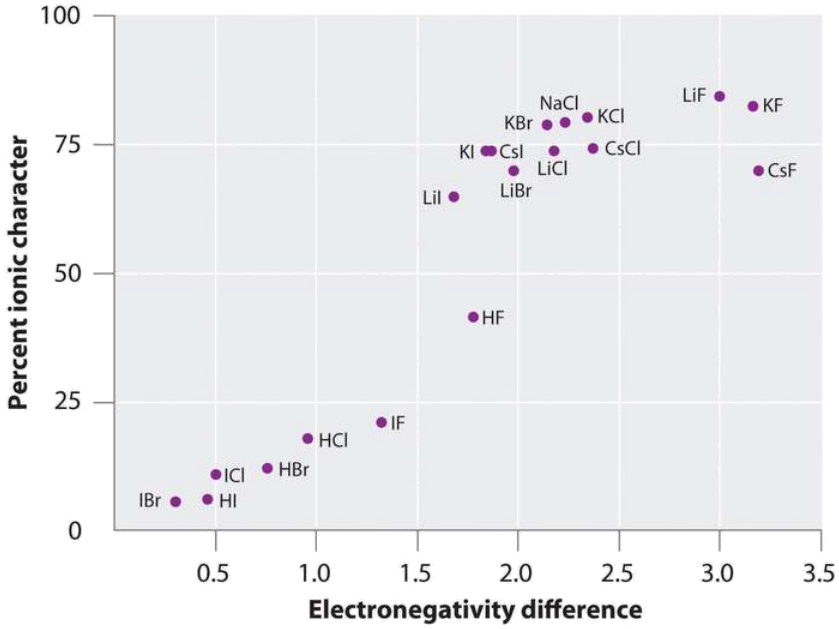


Figure 2.4.1.2: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 2.4.1.1: percent ionic character

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A. Compute the charge on each atom using the information given and Equation 2.4.1.2

B. Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) \\ &= 1.272 \times 10^{-19}\ C \end{aligned}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\begin{aligned} \text{ionic character} &= \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) \\ &= 79.39\% \simeq 79\% \end{aligned}$$

Exercise 2.4.1.1

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer

55.5%

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity.

$$\mu = Qr$$

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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2.4.2: Valence Bond Theory- Orbital Overlap as a Chemical Bond

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of $\mathbf{H_2O}$ and $\mathbf{NH_3}$, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in $\mathbf{H_2O}$ and $\mathbf{NH_3}$. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including $\mathbf{SrF_2}$ and $\mathbf{BaF_2}$, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

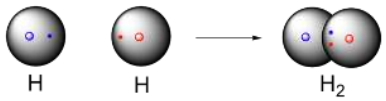
Introduction

As we have talked about using Lewis structures to depict the bonding in covalent compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF, our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

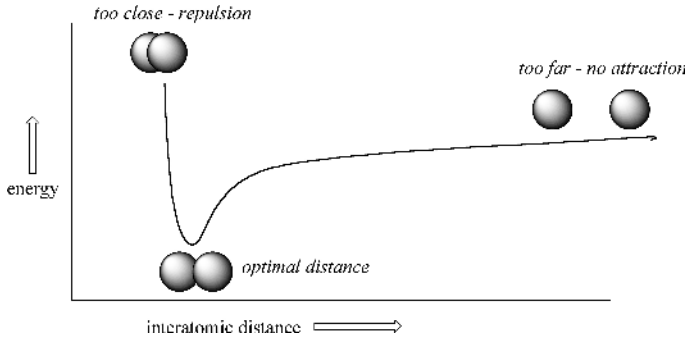
Example: The H_2 molecule

The simplest case to consider is the hydrogen molecule, H_2. When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1*s* orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of 'chemical glue' holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1*s* orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



Graph of increasing energy against increasting interatomic distance. If the two are too close there is repulsion, if the two are too far there is no attraction. There is an optimal distance.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74 x 10^{-12} meters, or 0.74 Å (Å means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol.

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about 1.5 Å long (Å means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about 1.3 Å, carbon-oxygen double bonds are about 1.2 Å, and carbon-hydrogen bonds are in the range of 1.0 – 1.1 Å. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole. You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

Balls and Springs

Although we tend to talk about "bond length" as a specific distance, it is not accurate to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

Valence Bond Theory: A Localized Bonding Approach

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure **2.4.2.1**). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure **2.4.2.1**).

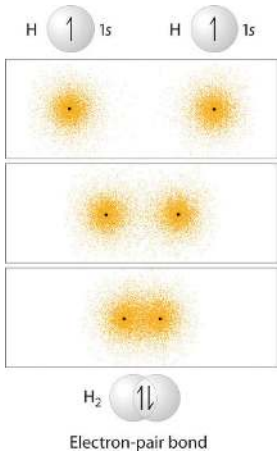


Figure **2.4.2.1**: Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2. The formation of H_2 from two hydrogen atoms, each with a single electron in a 1*s* orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure **2.4.2.2** shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where $n = 2$. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other) and are *in phase* (represented by colors in Figure **2.4.2.2**).

> Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

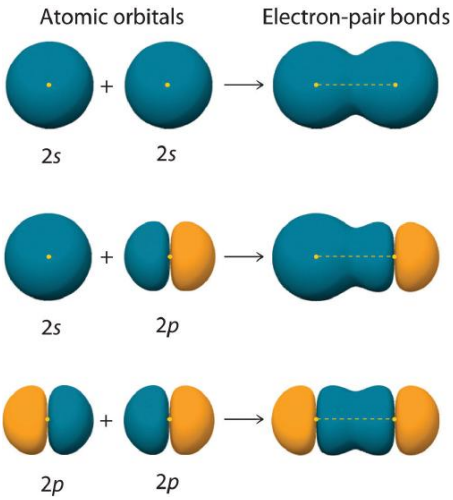
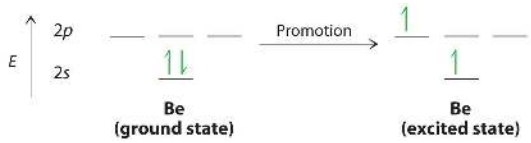


Figure **2.4.2.2** : Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two *ns* atomic orbitals (a), an *ns* and an *np* atomic orbital (b), and two *np* atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the

maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion:



The ground state of beryllium has one electron pair in the 2s orbital. The excited state of beryllium takes one of the electrons from the 2s orbital and moves it to the 2p orbital.

In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce $\mathbf{BeH_2}$, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as $\mathbf{BeH_2}$ form, scientists developed the concept of hybridization.

Contributors and Attributions

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2.4.3: Valence Bond Theory- Hybridization of Atomic Orbitals

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure **2.4.3.1**.

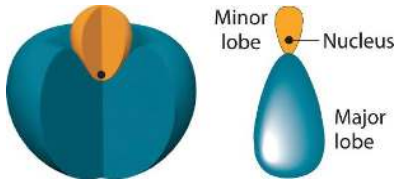


Figure **2.4.3.1:** The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference A − B can also be written as A + (−B), in Figure **2.4.3.2** and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by −1 and adding. This gives us Equation **2.4.3.2**, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \tag{2.4.3.1}$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \tag{2.4.3.2}$$

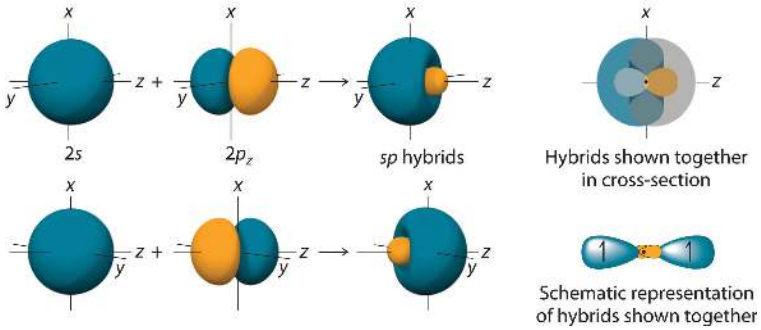


Figure **2.4.3.2**: The Formation of *sp* Hybrid Orbitals. Taking the sum and difference of an *ns* and an *np* atomic orbital where *n* = 2 gives two equivalent *sp* hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

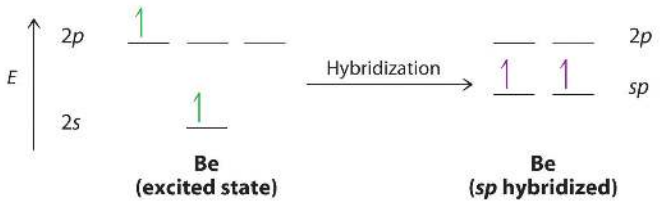


Figure **2.4.3.3**. each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear $\boldsymbol{BeH_2}$ molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in $\boldsymbol{BeH_2}$ are equivalent in energy and why $\boldsymbol{BeH_2}$ has a linear geometry.

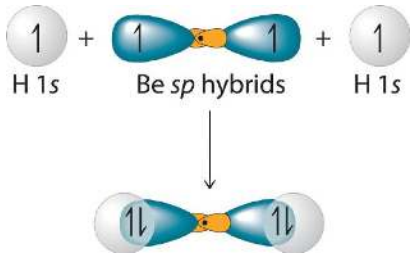


Figure **2.4.3.3**: Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals. Each singly occupied *sp* hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1*s* orbital of a hydrogen atom. Because the two *sp* hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure **2.4.3.4**). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

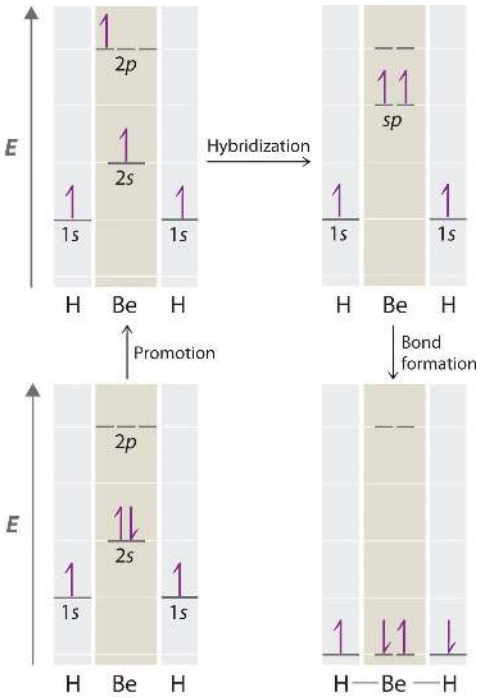


Figure **2.4.3.4**: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2*s* orbital of beryllium to one of the 2*p* orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.



The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

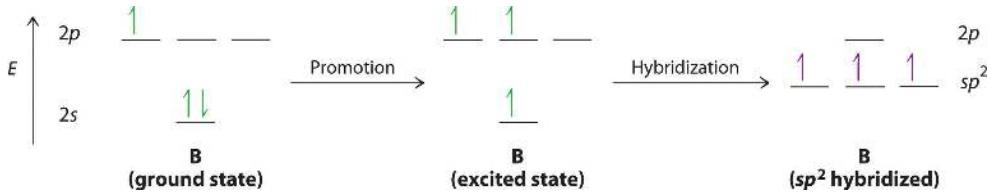


Figure 2.4.3.5). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced "s-p-two" or "s-p-squared"). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

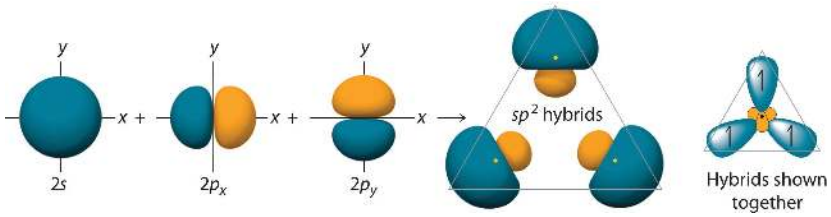


Figure 2.4.3.5: Formation of sp^2 Hybrid Orbitals. Combining one *ns* and two *np* atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.



Looking at the $2s^2 2p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent

bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:

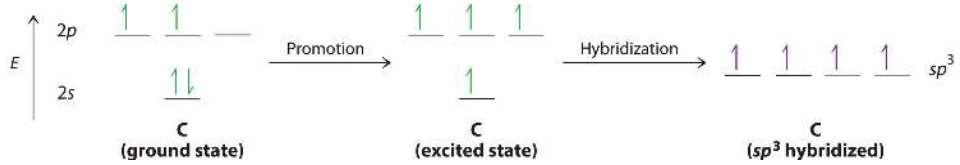


Figure **2.4.3.6**). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

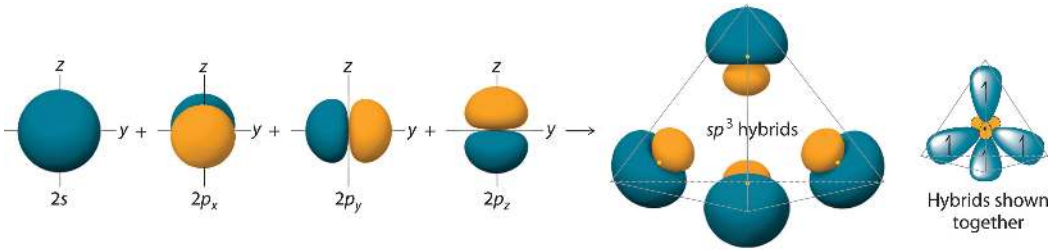
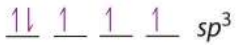


Figure **2.4.3.6**: Formation of sp^3 Hybrid Orbitals. Combining one *ns* and three *np* atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that only form in certain chemical reactions.

> *Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.*

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in NH_3 and H_2O, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.



Example 2.4.3.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A. Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 2.4.3.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion

b. hydrazine ($H_2N–NH_2$)

Answer a

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

Answer b

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Hybridization Using d Orbitals

Hybridization is not restricted to the *ns* and *np* atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its *ns* and *np* orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the *ns* orbital, all three *np* orbitals, and one $(n - 1)d$ orbital gives a set of five sp^3d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure **2.4.3.7**). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 9.5.6). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

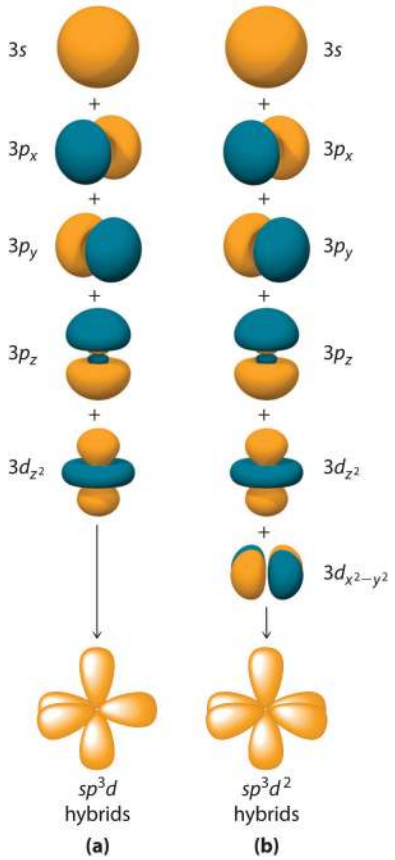


Figure **2.4.3.7**: Hybrid Orbitals Involving *d* Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from *ns*, *np*, and *nd* atomic orbitals where $n = 4$.

Example 2.4.3.2

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. XeF_4
b. SO_4^{2-}
c. SF_4

Given: three chemical species

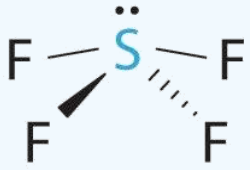
Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example **2.4.3.1**. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.
B. Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.
b. **A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.
c. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise 2.4.3.2

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl_4^+
b. BrF_3
c. SiF_6^{2-}

Answer a

sp^3 with four P–Cl bonds

Answer a

sp^3d with three Br–F bonds and two lone pairs

Answer a

sp^3d^2 with six Si–F bonds

Hybridization using *d* orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-}. Because there are no 2*d* atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.



Example 2.4.3.3: OF_4

What is the hybridization of the oxygen atom in OF_4? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A. Predict the geometry of OF_4 using the VSEPR model.
B. From the number of electron pairs around O in OF_4, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only *d* orbital available for forming a set of sp^3d hybrid orbitals is a 3*d* orbital, which is *much* higher in energy than the 2*s* and 2*p* valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise 2.4.3.3

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer a

sp^3d^2 hybridization; no

Summary

Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty *np* or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an *ns* and an *np* orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an *ns* and two or three *np* orbitals produces three equivalent $\boldsymbol{sp^2}$ **hybrids** or four equivalent $\boldsymbol{sp^3}$ **hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six $\boldsymbol{sp^3d^2}$ **hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

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2.4.4: MO Theory

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2.4.5: Molecular Orbital Theory- Electron Delocalization

Learning Objectives

- To use molecular orbital theory to predict bond order

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 9, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) &= AO(atom\ A) + AO(atom B) \\ MO(1) &= AO(atom\ A) - AO(atom B) \end{aligned} \tag{2.4.5.1}$$

The molecular orbitals created from Equation 2.4.5.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

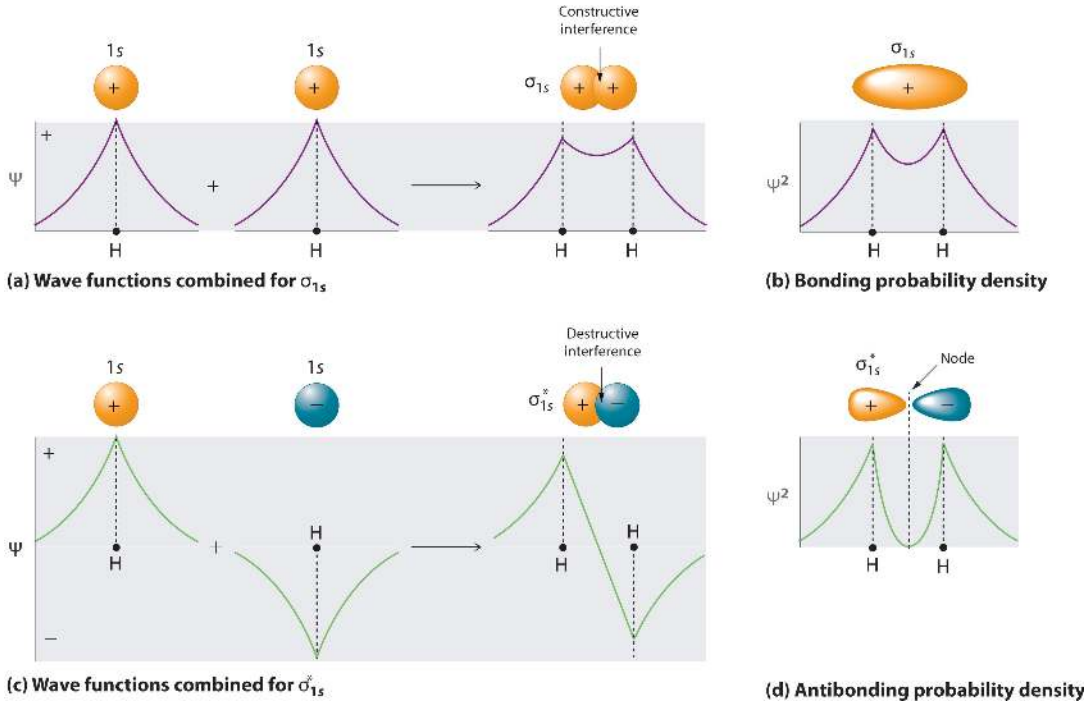


Figure **2.4.5.1**: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1*s* atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the *square* of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1*s* atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced "sigma one ess") (part (a) and part (b) in Figure **2.4.5.1**). In a sigma (σ) orbital, (i.e., a bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry), the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{2.4.5.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure **2.4.5.1**). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} ("sigma one ess star"). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B) \tag{2.4.5.3}$$

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{1s}

orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the σ^*_{1s} orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the σ^*_{1s} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ^*_{1s} (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure **2.4.5.2**

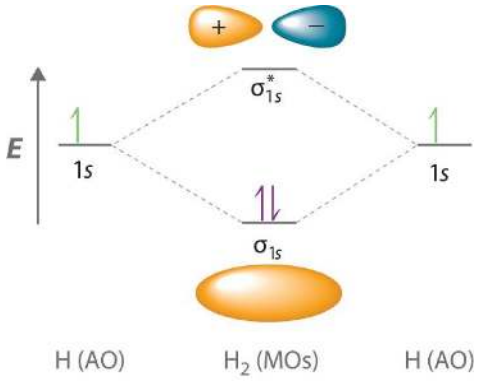


Figure **2.4.5.2**: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure **2.4.5.2**). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{2.4.5.4}$$

To calculate the bond order of H_2, we see from Figure **2.4.5.2** that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2}=1 \tag{2.4.5.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3. We can use energy-level diagrams such as the one in Figure **2.4.5.2** to describe the bonding in other pairs of atoms and ions where n = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

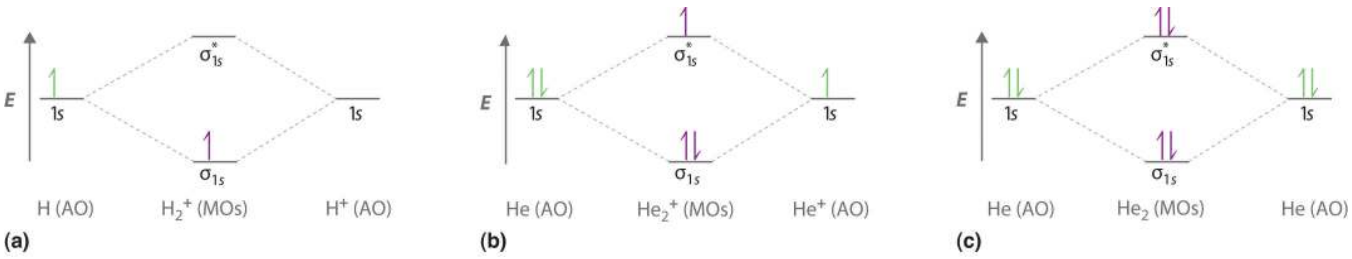


Figure **2.4.5.3**: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

for the H2+ ion the H has one unpaired electron in the 1s orbital so the H2+ has one unpaired electron in the sigmas 1 s orbital. for He2+ ion, He has a full 1 s orbital and He+ has one upaired electron in the 1 s orbital. This means that the sigmal 1s orbital is full and the sigmal*1s orbital has one upaired electron. For the He2 molecule, each He has a full 1 s orbital. This means that sigma 1s and sigma * 1s orbital are full.

Figure **2.4.5.3***a* shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is

$$\frac{1-0}{2}=1/2$$

Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table **2.4.5.1**, these predictions agree with the experimental data.

Figure **2.4.5.3***b* is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ^*_{1s} antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration. This electron configuration gives a bond order of

$$\frac{2-1}{2}=1/2$$

As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table **2.4.5.1**).

Table **2.4.5.1**: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure **2.4.5.3c** is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ^*_{1s} antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^*_{1s})^2$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

> *In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.*



Example 2.4.5.1

Use a molecular orbital energy-level diagram, such as those in Figure **2.4.5.2**, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbital

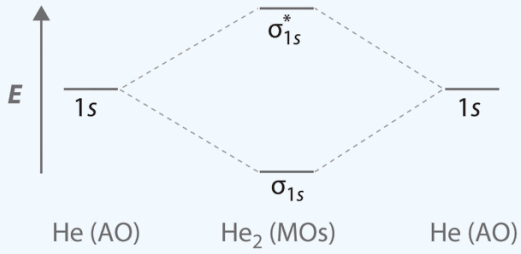
B. s. Draw the molecular orbital energy-level diagram for the system.

C. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

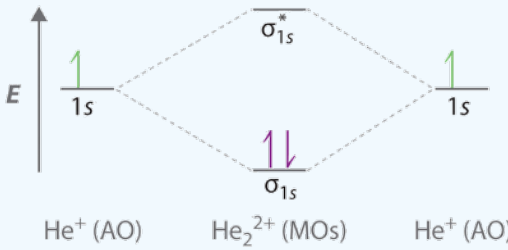
D. Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ^*_{1s} antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



Each He+ has one unpaired electron in the 1 s orbital. This means that He2 2+ has a full sigma 1 s orbital.

The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

? Exercise 2.4.5.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure **2.4.5.4**, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure **2.4.5.4**. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

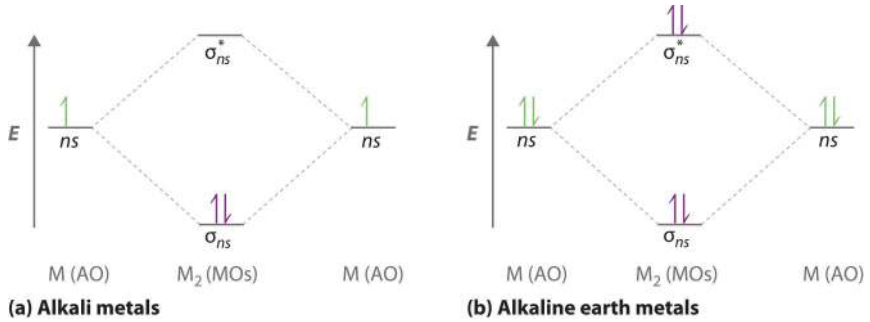


Figure **2.4.5.4** : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure **2.4.5.2**. As shown in part (b) in Figure **2.4.5.4**, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 2.4.5.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

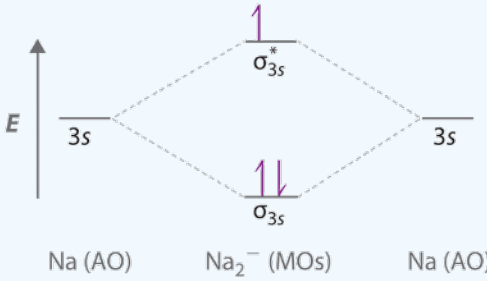
A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^*_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

? Exercise 2.4.5.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma_{4s}^*)^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{2.4.5.6}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure **2.4.5.5**, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{2.4.5.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{2.4.5.8}$$

In this combination, shown in part (b) in Figure **2.4.5.5**, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

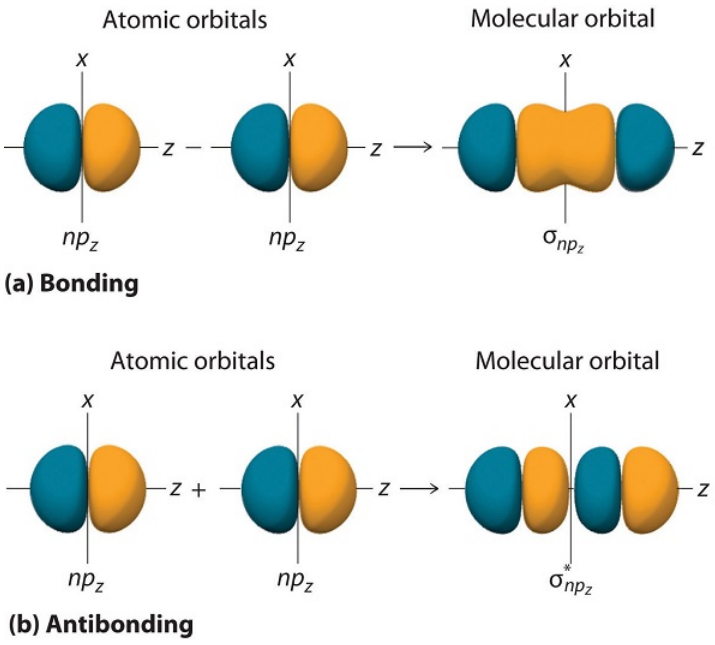


Figure **2.4.5.5** Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure **2.4.5.6**, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{2.4.5.9}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{2.4.5.10}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

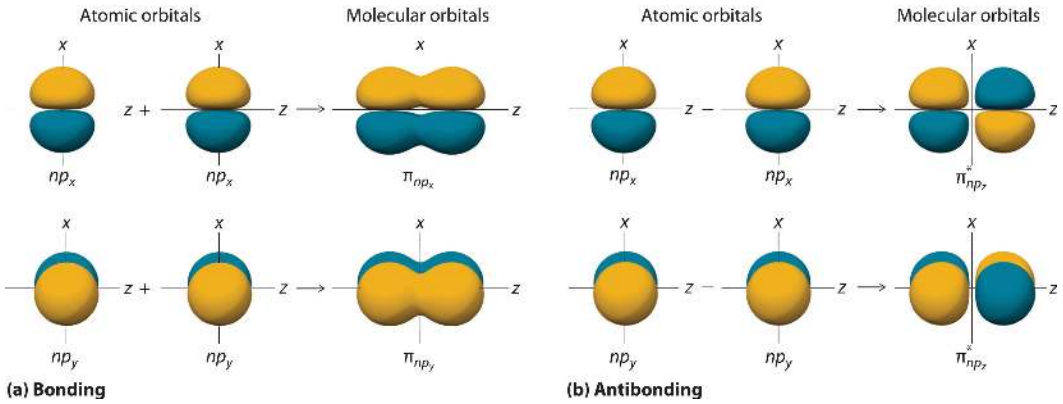


Figure 2.4.5.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 2.4.5.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

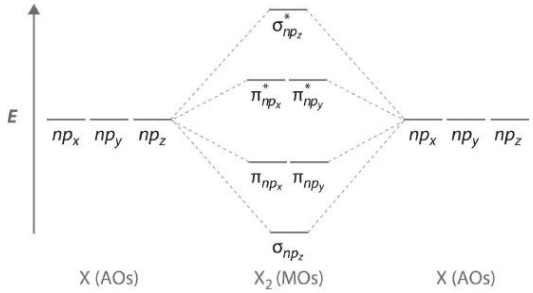


Figure 2.4.5.7 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 2.4.5.8, the sum of the two atomic wave functions (*ns* + np_z) produces a σ bonding molecular orbital. Their difference (*ns* − np_z) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

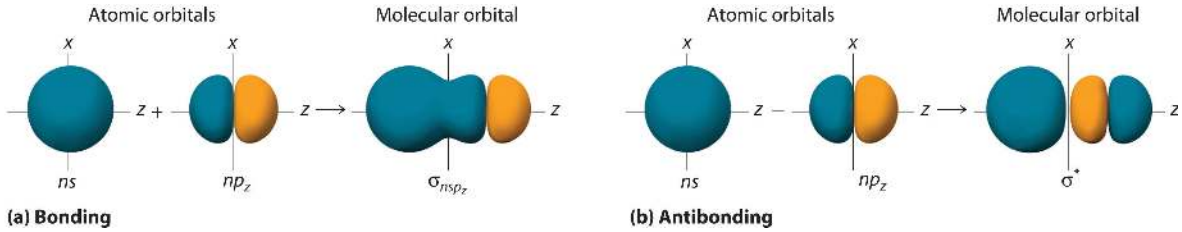


Figure 2.4.5.8 : Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Summary

Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach. A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

Learning Objectives

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character. We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2.

four key points to remember when drawing molecular orbital diagrams:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the *"law of conservation of orbitals"*).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure **2.4.5.1**; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of (8 − 6) ÷ 2 = 1. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

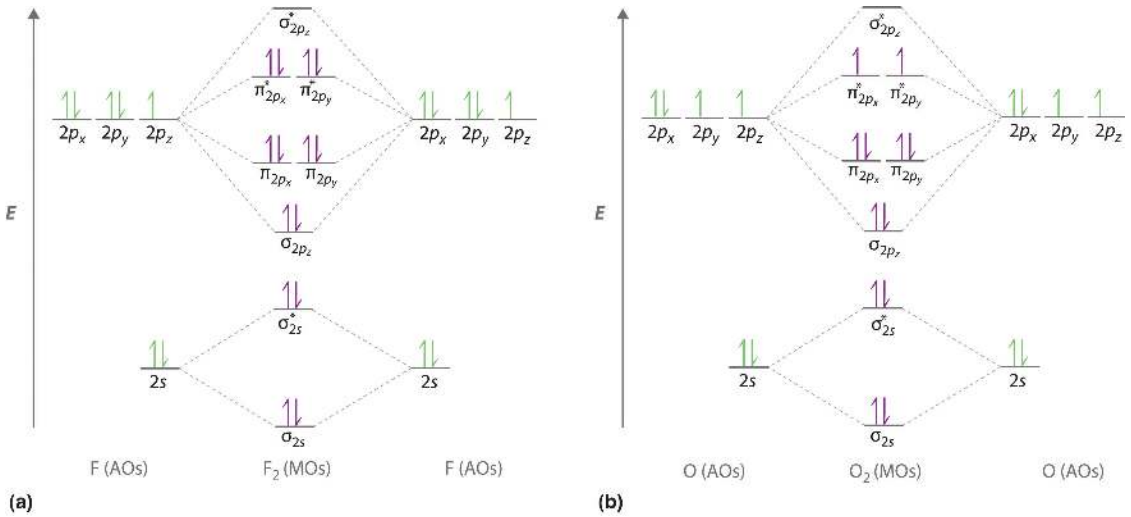


Figure **2.4.5.1**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $(\pi^*_{np_x}, \pi^*_{np_y})$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure **2.4.5.1**. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π*

orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of (8 − 4) ÷ 2 = 2, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure **2.4.5.2**, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



Figure **2.4.5.2**: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure **2.4.5.3** Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **2.4.5.3**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

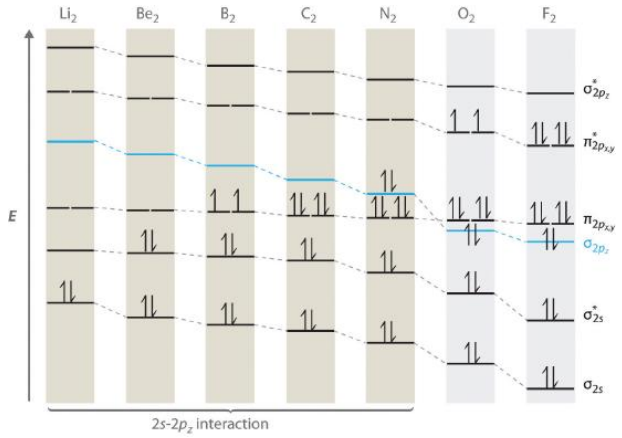


Figure **2.4.5.3**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

✔ Example **2.4.5.3**: Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

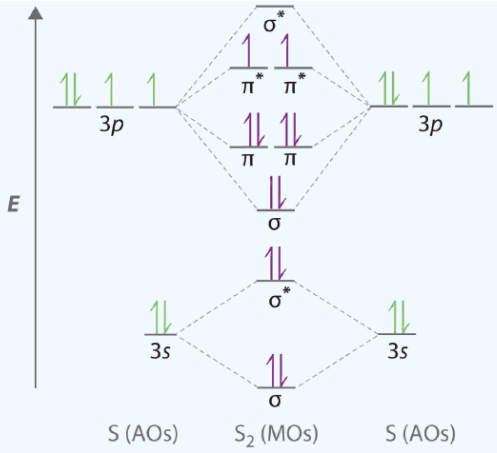
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure **2.4.5.1** and Figure **2.4.5.3**, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure **2.4.5.3**), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Two filled sigma orbitals, one filled sigma * orbital, two filled pi orbitals, and two pi * orbitals with one unpaired electron.

Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_x}$ and $\pi^*_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi^*_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 2.4.5.3: The Peroxide Ion

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi^*_{2p_{x,y}})^4$ bond order of 1; no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure **2.4.5.4**. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

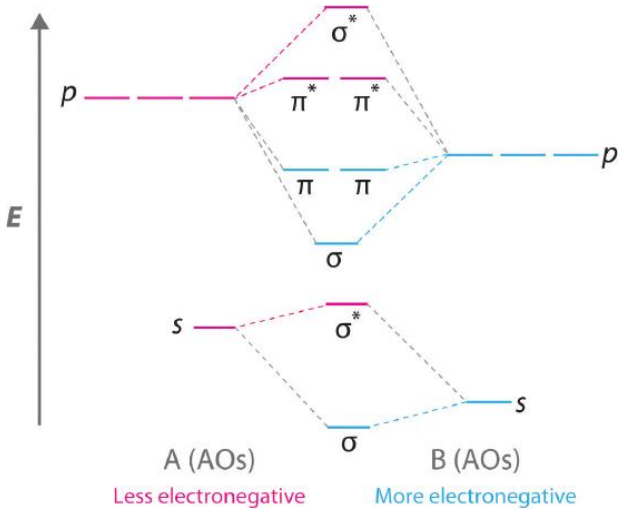


Figure **2.4.5.4**: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure **2.4.5.13**) shows that the general pattern is similar to that for the O_2 molecule (Figure **2.4.5.11**). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

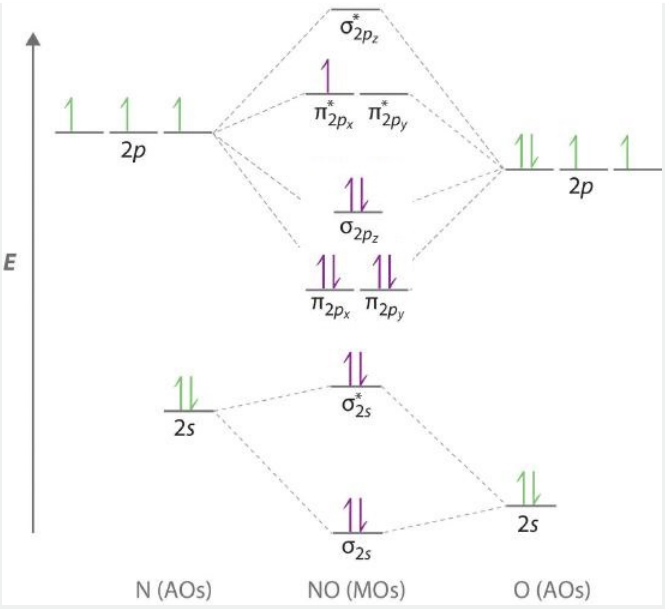


Figure **2.4.5.13**: Molecular Orbital Energy-Level Diagram for **NO**. Because **NO** has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_z}, \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of **NO** to be $(\sigma_{2s})^2(\sigma^{\star}_{2s})^2\left(\pi_{2p_{z,y}}\right)^4(\sigma_{2p_z})^2\left(\pi^{\star}_{2p_{z,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{z,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the **NO** molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure **2.4.5.11**).

Molecular orbital theory can also tell us something about the *chemistry* of ***NO***. As indicated in the energy-level diagram in Figure **2.4.5.13**, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, ***NO*** is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure **2.4.5.6** that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}--Cl^{\delta-}$.

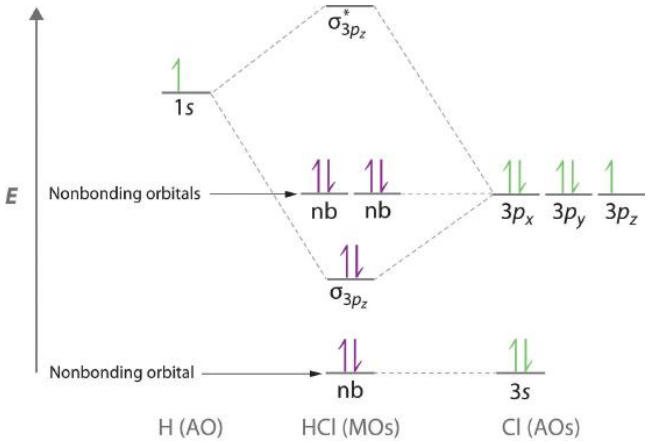


Figure **2.4.5.6**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have no effect on bond order.*

Example **2.4.5.4**: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **2.4.5.4** to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

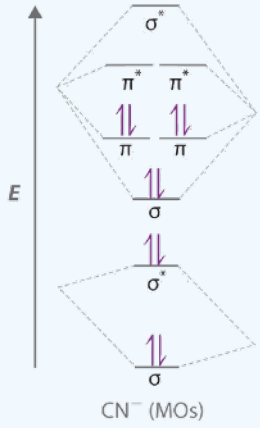
Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **2.4.5.4** in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure **2.4.5.4** fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 2.4.5.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.



Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

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SECTION OVERVIEW

3.1: KMT vs IMF

KMT vs IMF

3.1.1: Solids, Liquids, and Gases- A Molecular Comparison

3.1.2: Rearrangements of the Ideal Gas Law

3.1.3: The Kinetic-Molecular Theory - A Model for Gas Behavior

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3.1.1: Solids, Liquids, and Gases- A Molecular Comparison

Learning Objectives

- To be familiar with the kinetic molecular description of liquids.

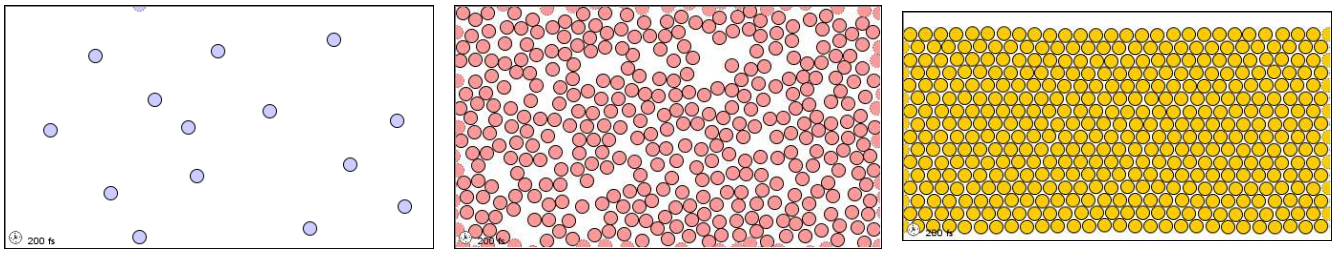
The *physical* properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same *chemical* properties, but their *physical* properties are considerably different. In general *covalent bonds* determine: molecular shape, bond energies, *chemical* properties, while *intermolecular forces* (non-covalent bonds) influence the *physical* properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.



Figure **3.1.1.1**: The three common states of matter. From the left, they are solid, liquid, and gas, represented by an ice sculpture, a drop of water, and the air around clouds, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces are attractive forces that try to draw the particles together (Figure **3.1.1.2**). A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.

Molecular level picture of gases, liquids and solids.



(a) in the gaseous state	*(b) as a liquid*	(c) *in solid form*

Figure **3.1.1.2**: Molecular level picture of gases, liquids and solids.

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of any significant attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit non-ideal behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gasses
- Liquids have a definite volume, independent of the size and shape of their container
- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

> *Thus, liquids can be poured and assume the shape of their containers.*

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in position
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

> *Due to the strong intermolecular forces between neighboring molecules, solids are rigid.*

- Cooling a gas may change the state to a liquid
- Cooling a liquid may change the state to a solid
- Increasing the pressure on a gas may change the state to a liquid
- Increasing the pressure on a liquid may change the state to a solid



Video **3.1.1.1**: Video highlighting the properties for the three states of matter. Source found at www.youtube.com/watch?v=s-KvoVzukHo.

Physical Properties of Liquids

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described previously. This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers. A kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces. Solids and liquids have particles that are fairly close to one another, and are thus called "**condensed phases**" to distinguish them from gases

- **Density**: The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore

more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.

- **Molecular Order:** Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids, the molecules in liquids are not arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.
- **Compressibility**: Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.
- **Thermal Expansion**: The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table S1 (with a shorten version in Table **3.1.1.1**) that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

Table **3.1.1.1**: The Density of Water at Various Temperatures

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

- **Diffusion**: Molecules in liquids diffuse because they are in constant motion. A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.
- **Fluidity**: Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure **3.1.1.3**).

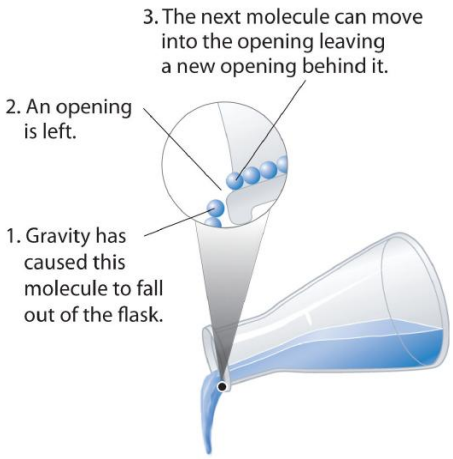


Figure **3.1.1.3**: Why Liquids Flow. Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container. (CC BY-SA-NC; Anonymous vy request).

Contributors and Attributions

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3.1.2: Rearrangements of the Ideal Gas Law

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3.1.3: The Kinetic-Molecular Theory - A Model for Gas Behavior

Learning Objectives

- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gases explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

five postulates of Kinetic Molecular Theory

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.

Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of gases we have been discussing. In the following sections, we explain how this theory must be modified to account for the behavior of real gases.

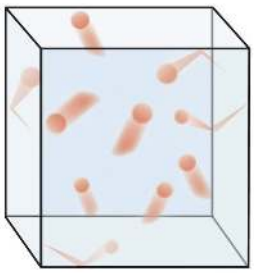


Figure **3.1.3.1**: Visualizing molecular motion. Molecules of a gas are in constant motion and collide with one another and with the container wall.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure **3.1.3.2**).

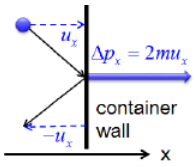


Figure **3.1.3.2**: Momentum transfer (impulse) from a molecule to the container wall as it bounces off the wall. u_x and Δp_x are the x component of the molecular velocity and the momentum transferred to the wall, respectively. The wall is perpendicular to x axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity u_x in x direction hits is expressed as:

$$\Delta p_x = 2mu_x \tag{3.1.3.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{3.1.3.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{3.1.3.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2, which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{3.1.3.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}.$$

Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed (u^2) over all molecules. Since

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

for each molecule, then

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}.$$

By substituting $\frac{1}{3}\overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{3.1.3.5}$$

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. Postulate 5 refers to the *average translational* kinetic energy of the molecules of a gas ($\overline{e_K}$), which can be represented as *and states that at a given Kelvin temperature* (T), *all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A} T \tag{3.1.3.6}$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A:

$$N_A\overline{e_K} = \frac{1}{2}M\overline{u^2} = \frac{3}{2}RT \tag{3.1.3.7}$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$. By rearranging the equation, we can get the relationship between the root-mean square speed (u_{rms}) and the temperature. The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{3.1.3.8}$$

where N is the number of particles and u_i is the speed of particle i.

The relationship between u_{rms} and the temperature is given by:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{3.1.3.9}$$

In Equation 3.1.3.9, u_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K•mol). Equation 3.1.3.9 shows that u_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (vp) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 3.1.3.8 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and vp increases.

> *At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.*

Example 3.1.3.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_{m}).

Given: particle speeds

Asked for: average speed (v_{av}), root mean square speed (v_{rms}), and most probable speed (v_{m})

Strategy:

Use Equation 3.1.3.6 to calculate the average speed and Equation 3.1.3.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{\text{av}} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \mathrm{m^2/s^2}}{8}} = 6.2\ \mathrm{m/s}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence $v_m = 6.0$ m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature. Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure **3.1.3.3**. Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Although the mathematics behind curves such as those in Figure **3.1.3.3** were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributions, after one of the other major figures responsible for the kinetic molecular theory of gases.

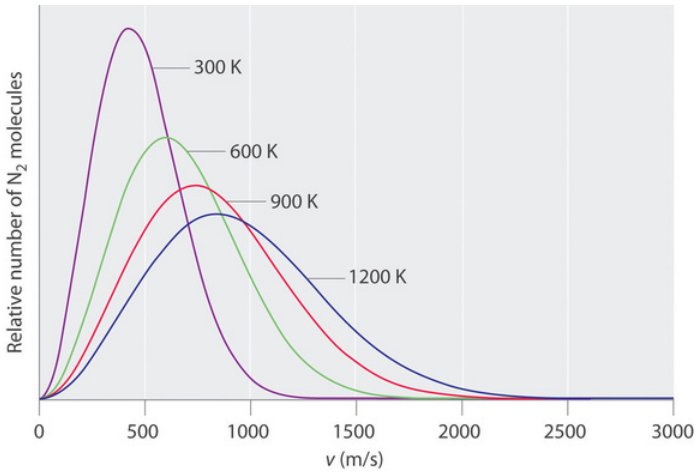


Figure **3.1.3.3**: The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperatures. Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

- **Pressure versus Volume**: At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.
- **Volume versus Temperature**: Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the

pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.

- **Pressure of Gas Mixtures**: Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

Example 3.1.3.2

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

a. average kinetic energy of the N_2 molecules?
b. rms speed of the N_2 molecules?
c. average speed of the N_2 molecules?
d. impact of each N_2 molecule on the wall of the container during a collision with the wall?
e. total number of collisions per second of N_2 molecules with the walls of the entire container?
f. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
g. pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

a. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
b. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
c. If the rms speed of the N_2 molecules increases, the average speed also increases.
d. If, on average, the particles are moving faster, then they strike the container walls with more energy.
e. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
f. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.
g. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

Exercise 3.1.3.2

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

a. average kinetic energy of the He atoms?
b. rms speed of the He atoms?
c. average speed of the He atoms?
d. impact of each He atom on the wall of the container during a collision with the wall?
e. total number of collisions per second of He atoms with the walls of the entire container?
f. number of collisions per second of He atoms with each square centimeter of the container wall?
g. pressure of the He gas?

Answer a

no change

Answer b

no change

Answer c

no change

Answer d

no change

Answer e

decreases

Answer f

decreases

Answer g

decreases



Summary

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.
- **Average kinetic energy:**

$$\overline{e_K} = \frac{1}{2} m {u_{\text{rms}}}^2 = \frac{3}{2} \frac{R}{N_A} T n$$

- **Root mean square speed:**

$$u_{\text{rms}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}}$$

- **Kinetic molecular theory of gases:**

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same

root mean square (rms) speed (v_{rms}). The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average.

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3.1.4: Real Gases - Deviations from Ideal Behavior

Learning Objectives

- To recognize the differences between the behavior of an ideal gas and a real gas
- To understand how molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of PV/nRT versus P gives a horizontal line with an intercept of 1 on the PV/nRT axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (Figure **3.1.4.1***a*). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (Figure **3.1.4.1***b*).

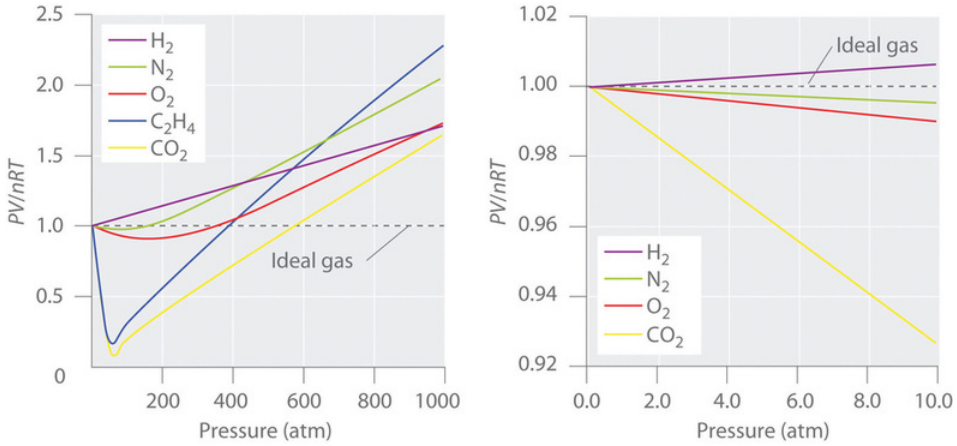


Figure **3.1.4.1**: Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures. (a) In these plots of PV/nRT versus P at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.

Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure **3.1.4.2** for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

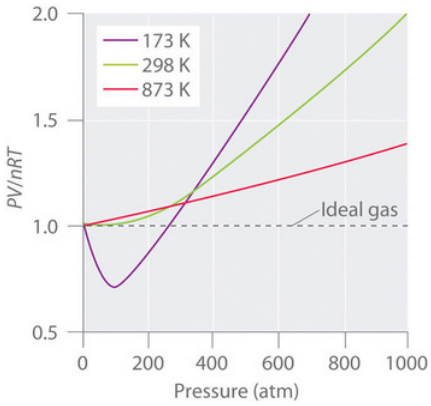


Figure **3.1.4.2**: The Effect of Temperature on the Behavior of Real Gases. A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure **3.1.4.3**). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of *PV*/*nRT* is greater than the value predicted by the ideal gas law.

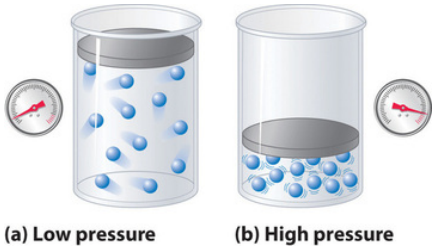


Figure **3.1.4.3**: The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures. (a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure **3.1.4.4**). Thus as shown in Figure **3.1.4.2**, at low temperatures, the ratio of \(PV/nRT\) is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

> *Nonzero molecular volume makes the actual volume greater than predicted at high pressures; intermolecular attractions make the pressure less than predicted.*

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas

behavior, the so-called *van der Waals* equation,

$$\underbrace{\left(P+\frac{an^2}{V^2}\right)}_{\text{Pressure Term}}\overbrace{(V-nb)}^{\text{Pressure Term}}=nRT \tag{3.1.4.1}$$

a and *b* are empirical constants that are different for each gas. The values of a and b are listed in Table **3.1.4.1** for several common gases.

Table **3.1.4.1**:: van der Waals Constants for Some Common Gases (see Table A8 for more complete list)

Gas	a (L^2·atm)/mol^2)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

The pressure term in Equation 3.1.4.1 corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure **3.1.4.4**. The volume term corrects for the volume occupied by the gaseous molecules.

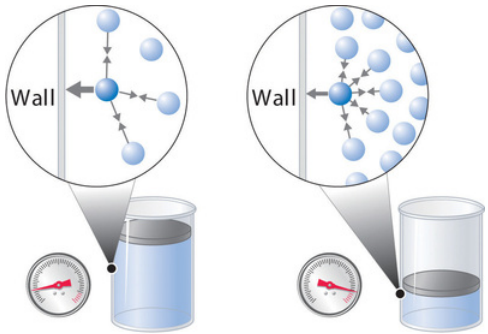


Figure **3.1.4.4**: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls. (a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on *V* and *P*, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

Example 3.1.4.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.00 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table **3.1.4.1**. Use the van der Waals equation (3.1.4.1) to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$n = \frac{m}{M} \tag{3.1.4.2}$$

$$= \frac{500\ \text{g}}{70.906\ \text{g/mol}} \tag{3.1.4.3}$$

$$= 7.052\ mol$$

Using the ideal gas law and the temperature in kelvin (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} \tag{3.1.4.4}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L}} \tag{3.1.4.5}$$

$$= 43.1\ atm \tag{3.1.4.6}$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table **3.1.4.1**. Solving for P gives

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{3.1.4.7}$$

$$= \frac{7.052\ \text{mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}}{4.00\ \text{L} - 7.052\ \text{mol} \times 0.0542 \frac{\text{L}}{\text{mol}}} - \frac{6.260 \frac{\text{L}^2\text{atm}}{\text{mol}^2} \times (7.052\ \text{mol})^2}{(4.00\ \text{L})^2} \tag{3.1.4.8}$$

$$= 28.2\ \text{atm} \tag{3.1.4.9}$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise 3.1.4.1

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

a. ideal gas law.
b. van der Waals equation.

Answer a

77 atm

Answer b

67 atm

Liquefaction of Gases

Liquefaction of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals a coefficients are relatively easy to liquefy because large a coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small a coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2, N_2, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points.

> *A large value of a in the van der Waals equation indicates the presence of relatively strong intermolecular attractive interactions.*

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids, from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing.” They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



Figure **3.1.4.5**: A Liquid Natural Gas Transport Ship.

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels (Figure **3.1.4.5**). Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of PV/nRT versus P at a given temperature; for an ideal gas, PV/nRT versus P = 1 under all

conditions. At high pressures, most real gases exhibit larger *PV*/*nRT* values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit *PV*/*nRT* values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

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3.1.5: Intermolecular Forces- The Forces that Hold Condensed Phases Together

Learning Objectives

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids, but are more similar to solids.*

Intermolecular forces determine bulk properties, such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

In this section, we explicitly consider three kinds of intermolecular interactions. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding, and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure **3.1.5.1***a*.

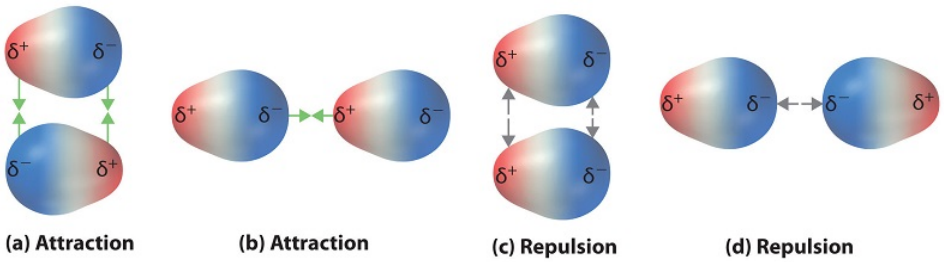


Figure **3.1.5.1**: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions. (CC BY-SA-NC; anonymous)

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure **3.1.5.1*c***). Hence dipole–dipole interactions, such as those in Figure **3.1.5.1*b***, are *attractive intermolecular interactions*, whereas those in Figure **3.1.5.1*d*** are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure **3.1.5.2**. On average, however, the attractive interactions dominate.

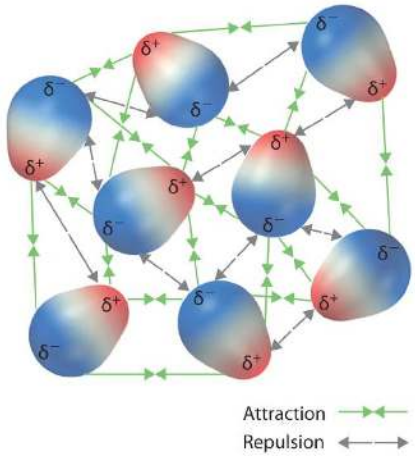


Figure **3.1.5.2**: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

The green arrows pointing towards each other represent attraction. The gray arrows pointing away from each other represent repulsion

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as **HCl**, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure. Conversely, **NaCl**, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table **3.1.5.1**.

Table **3.1.5.1**: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

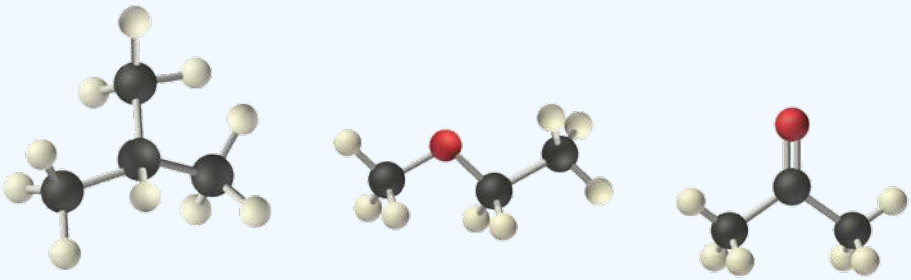
> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*



Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 3.1.5.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



2-Methylpropane Ethyl methyl ether Acetone

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

2-methylpropane < ethyl methyl ether < acetone

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 3.1.5.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far, we have considered only interactions between polar molecules. Other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature; why others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table **3.1.5.2**).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table **3.1.5.2**: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure **3.1.5.3**, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

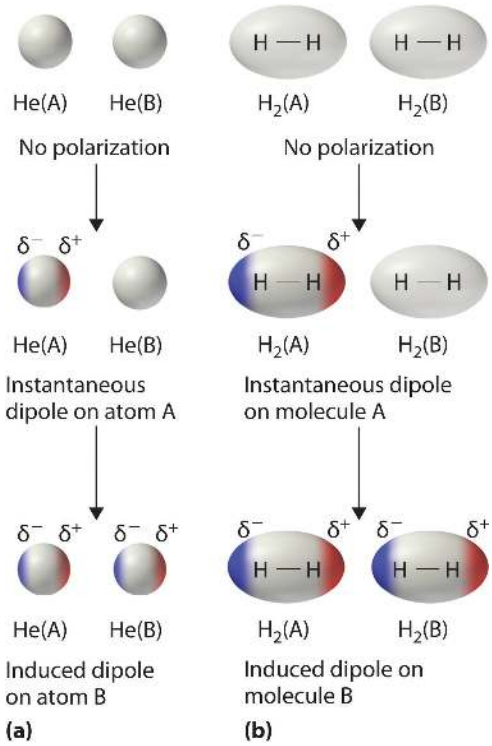


Figure **3.1.5.3**: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure **3.1.5.3**, tends to become more pronounced as atomic and molecular masses increase (Table **3.1.5.2**). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus, London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure **3.1.5.4**). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure **3.1.5.4** shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

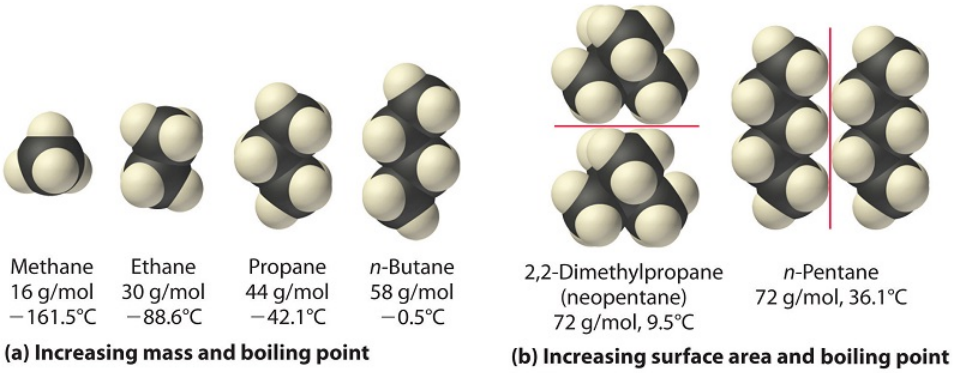


Figure **3.1.5.4**: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.



Video Discussing London/Dispersion Intermolecular Forces. Source: Dispersion Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 3.1.5.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds, and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane

to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? Exercise 3.1.5.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent, Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure **3.1.5.5**. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

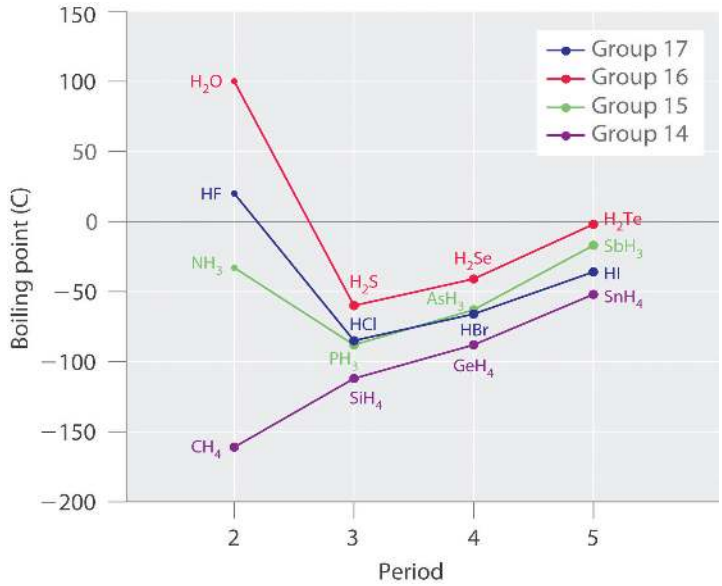


Figure **3.1.5.5**: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Group 14 is in purple, group 15 is in green, group 16 is red, and group 17 is blue. Graph of boiling point against period.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure **3.1.5.6**. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms

and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water, rather than sinks.

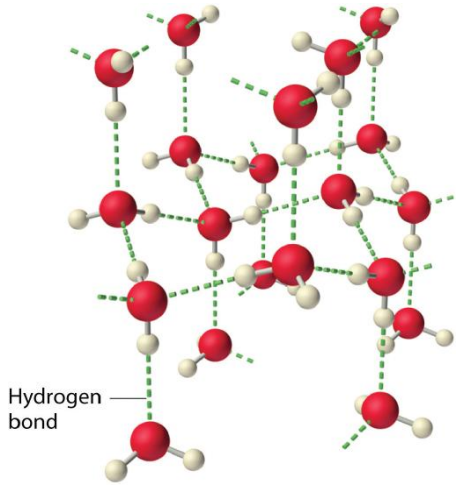


Figure **3.1.5.6**: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.



Video Discussing Hydrogen Bonding Intermolecular Forces. Source: Hydrogen Bonding Intermolecular Force, YouTube(opens in new window) [youtu.be]

Example 3.1.5.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

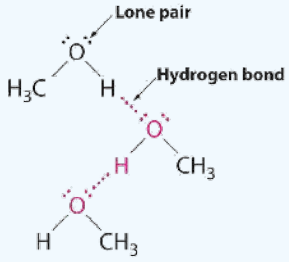
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A. Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B. The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



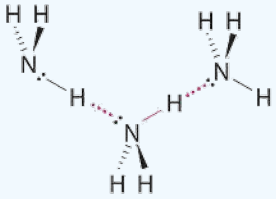
Hydrogen bonding in methanol

Exercise 3.1.5.3

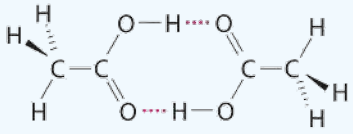
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Hydrogen bonding in ammonia between nitrogen and hydrogen. hydrogen bonding in acetic acid is between oxygen and hydrogen.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen

bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 3.1.5.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269^\circ\text{C}) < \text{Ar } (-185.7^\circ\text{C}) < N_2O\ (-88.5^\circ\text{C}) < C_{60}\ (>280^\circ\text{C}) < \text{NaCl } (1465^\circ\text{C}).$$

Exercise 3.1.5.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Example 3.1.5.5

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 3.1.5.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid, or the liquid and gas phases, are due to changes in intermolecular interactions, but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules; their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones, because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cage like structure that is less dense than liquid water.

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3.1.6: Intermolecular Forces in Action- Surface Tension, Viscosity, and Capillary Action

Learning Objectives

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action, and
- viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29 x 10^{-2} J/m^2 (at 20°C), while mercury with metallic bonds has as surface tension that is 15 times higher: 4.86 x 10^{-1} J/m^2 (at 20°C).

Figure **3.1.6.1** presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

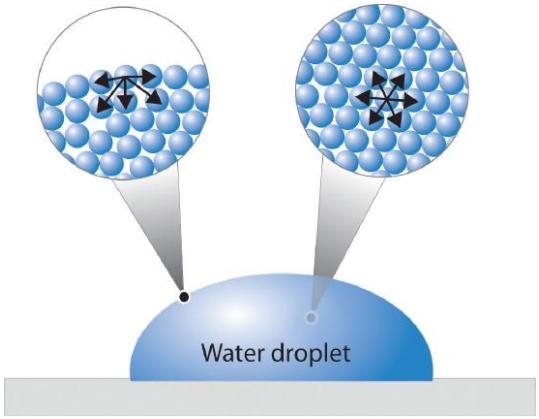


Figure **3.1.6.1**: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even

observable in the zero gravity conditions of space as shown in Figure **3.1.6.2** (and more so in the video link) where water wrung from a wet towel continues to float along the towel's surface!



Figure **3.1.6.2**: The Effects of the High Surface Tension of Liquid Water. The full video can be found at www.youtube.com/watch?v=9jB7rOC5kG8.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table **3.1.6.1**. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table **3.1.6.1**: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or

surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure **3.1.6.3**. When a glass capillary is is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

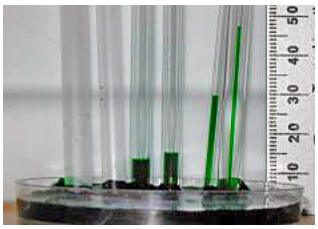


Figure **3.1.6.3**: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

- Cohesive forces bind molecules of the same type together
- Adhesive forces bind a substance to a surface

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure **3.1.6.4**). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure **3.1.6.4**).

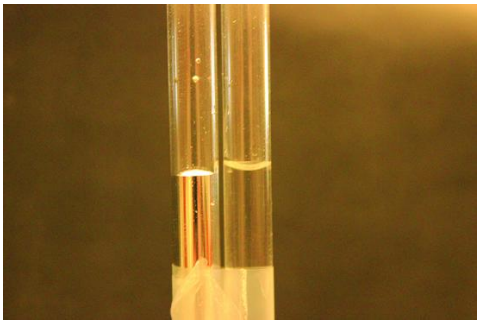


Figure **3.1.6.4**: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

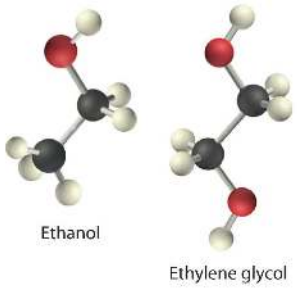
Polar substances are drawn up a glass capillary and generally have a concave meniscus.

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported

from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*



Video Discussing Surface Tension and Viscosity. Video Link: Surface Tension, Viscosity, & Melting Point, YouTube(opens in new window) [youtu.be]

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.



Figure **3.1.6.5**: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure **3.1.6.5**). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Example 3.1.6.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.

B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

? Exercise 3.1.6.1

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

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3.1.E: Gases and the Kinetic-Molecular Theory (Exercises)

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SECTION OVERVIEW

3.2: LIQUID STATE

LIQUID STATE

3.2.1: Vaporization and Vapor Pressure

3.2.2: Sublimation and Fusion

3.2.3: Heating Curve for Water

3.2.4: Phase Diagrams

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3.2.1: Vaporization and Vapor Pressure

Learning Objectives

- To know how and why the vapor pressure of a liquid varies with temperature.
- To understand that the equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- To understand that the relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressure of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (*KE*) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure **3.2.1.1**), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization), where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure.

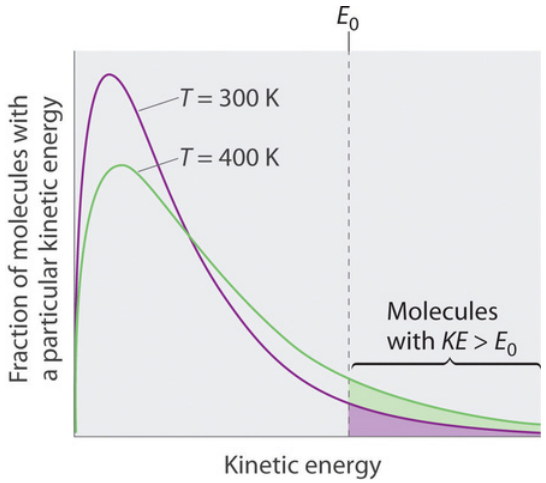


Figure **3.2.1.1**: The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures. Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature. (CC BY-SA-NC; Anonymous by request)

Graph of fraction of molecules with a particular kinetic energy against kinetic energy. Green line is temperature at 400 kelvin, purple line is temperature at 300 kelvin.

To understand the causes of vapor pressure, consider the apparatus shown in Figure **3.2.1.2**. When a liquid is introduced into an evacuated chamber (part (a) in Figure **3.2.1.2**), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase.

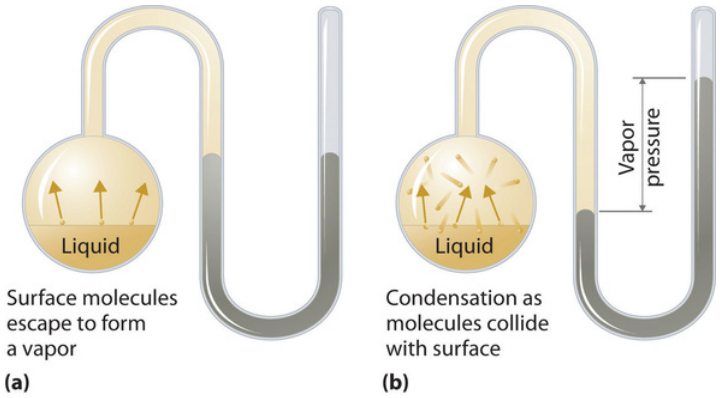


Figure **3.2.1.2**: Vapor Pressure. (a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant. (CC BY-SA-NC; Anonymous by request)

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensation (part (b) in Figure **3.2.1.2**). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure **3.2.1.3**.

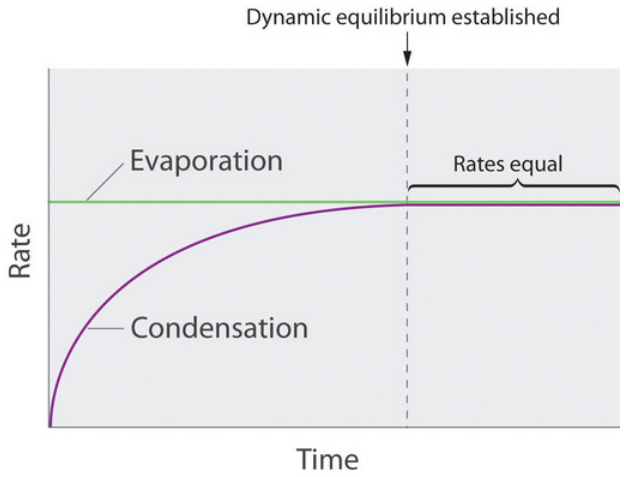


Figure **3.2.1.3**: The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber. The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation. (CC BY-SA-NC; Anonymous by request)

Graph of rate against time. The green line is evaporation while the pruple line is condensation. Dynamic equilibrium is established when the evaporation and condensation rates are equal.

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibrium. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressure of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has "disappeared." The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquids have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Figure **3.2.1.4**) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

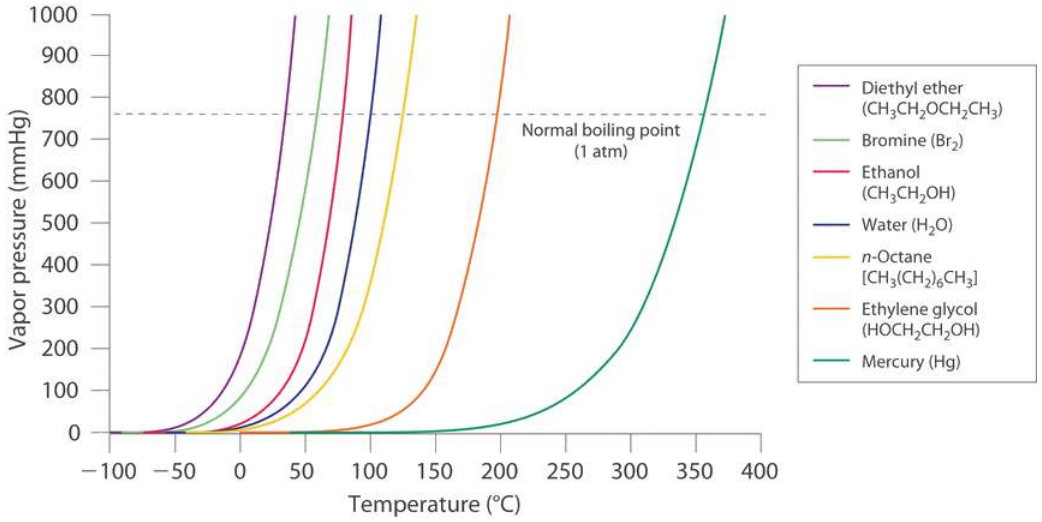


Figure **3.2.1.4**: The Vapor Pressures of Several Liquids as a Function of Temperature. The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid. (CC BY-SA-NC; Anonymous by request)

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure **3.2.1.4**. Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

> *Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.*



A Video Discussing Vapor Pressure and Boiling Points. Video Source: Vapor Pressure & Boiling Point(opens in new window) [youtu.be]

The exponential rise in vapor pressure with increasing temperature in Figure **3.2.1.4** allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$\boxed{\ln P = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C} \tag{3.2.1.1}$$

where

- $\ln P$ is the natural logarithm of the vapor pressure,
- ΔH_{vap} is the enthalpy of vaporization,
- R is the universal gas constant [8.314 J/(mol•K)],
- T is the temperature in kelvins, and
- C is the y-intercept, which is a constant for any given line.

Plotting $\ln P$ versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation **3.2.1.1**, called the Clausius–Clapeyron Equation, can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at **two** temperatures and insert the values of P and T for these points into Equation **3.2.1.2**, which is derived from the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3.2.1.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation **3.2.1.2** to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example **3.2.1.1**.



A Video Discussing the Clausius-Clapeyron Equation. Video Link: The Clausius-Clapeyron Equation(opens in new window) [youtu.be]

Example 3.2.1.1: Vapor Pressure of Mercury

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

experimentally measured vapor pressures of liquid Hg at four temperatures

T (°C)	80.0	100	120	140
P (torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 3.2.1.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.

B. Substitute the calculated value of ΔH_{vap} into Equation 3.2.1.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 3.2.1.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 3.2.1.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvin because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 3.2.1.2 gives

$$\ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

$$\ln(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right)$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$\ln\left(\frac{P_2}{0.0888\ torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\ K} - \frac{1}{(80.0+273)\ K}\right)$$

Using the relationship $e^{\ln x} = x$, we have

$$\ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5$$

$$P_2 = 4.21 Torr$$

At 160°C, liquid Hg has a vapor pressure of 4.21 torr, substantially greater than the pressure at 80.0°C, as we would expect.

? Exercise 3.2.1.1: Vapor Pressure of Nickel

The vapor pressure of liquid nickel at 1606°C is 0.100 torr, whereas at 1805°C, its vapor pressure is 1.000 torr. At what temperature does the liquid have a vapor pressure of 2.500 torr?

Answer

1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point of the liquid. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure **3.2.1.4** are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Table **3.2.1.1**: The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (mmHg)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 mmHg, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 mmHg in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table **3.2.1.1** lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

> *As pressure increases, the boiling point of a liquid increases and vice versa.*

✓ Example 3.2.1.2: Boiling Mercury

Use Figure **3.2.1.4** to estimate the following.

a. the boiling point of water in a pressure cooker operating at 1000 mmHg
b. the pressure required for mercury to boil at 250°C



Mercury boils at 356 °C at room pressure. To see video go to www.youtube.com/watch?v=0iizsbXWYoo

Given: Data in Figure **3.2.1.4**, pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 mmHg, refer to Figure **3.2.1.4** and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

a. **A** The vapor pressure curve of water intersects the P = 1000 mmHg line at about 110°C; this is therefore the boiling point of water at 1000 mmHg.

b. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ mmHg. Hence this is the pressure required for mercury to boil at 250°C.

? Exercise 3.2.1.2: Boiling Ethlyene Glycol

Ethylene glycol is an organic compound primarily used as a raw material in the manufacture of polyester fibers and fabric industry, and polyethylene terephthalate resins (PET) used in bottling. Use the data in Figure **3.2.1.4** to estimate the following.

a. the normal boiling point of ethylene glycol

b. the pressure required for diethyl ether to boil at 20°C.

Answer a

200°C

Answer b

450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

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3.2.2: Sublimation and Fusion

Sublimation

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as sublimation. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure **3.2.2.6**). The reverse of sublimation is called deposition, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.



This figure shows a test tube. In the bottom is a dark substance which breaks up into a purple gas at the top.

Figure **3.2.2.6**: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔHsub, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g) \quad \Delta H_{\mathrm{sub}} = 26.1\ \mathrm{kJ/mol} \tag{3.2.2.1}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO_2}(s) \quad \Delta H_{\mathrm{dep}} = -\Delta H_{\mathrm{sub}} = -26.1\ \mathrm{kJ/mol} \tag{3.2.2.2}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law.

$$\begin{array}{l} \mathrm{solid} \longrightarrow \mathrm{liquid} \quad \Delta H_{\mathrm{fus}} \\ \underline{\mathrm{liquid} \longrightarrow \mathrm{gas} \quad \Delta H_{\mathrm{vap}}} \\ \mathrm{solid} \longrightarrow \mathrm{gas} \quad \Delta H_{\mathrm{sub}} = \Delta H_{\mathrm{fus}} + \Delta H_{\mathrm{vap}} \end{array} \tag{3.2.2.3}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure **3.2.2.7**. For example:

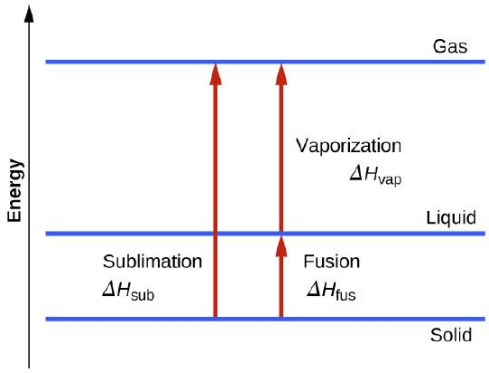


***Figure* 3.2.2.7**: *For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.*

An energy level diagram is shown with three horizontal lines representing states of solid, liquid, and gas in increasing energy levels. The enthalpy of fusion is shown by arrow pointing from solid to liquid. Enthalpy of vaporization is shown with arrow pointing from liquid to gas. The enthalpy of sublimation points from solid to gas and has the same length as the arrows for fusion and vaporization combined.

Fusion

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure \(\PageIndex{5}\).



Figure **3.2.2.5**: (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott).

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal process of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H_{fus} = 6.01 \text{ kJ/mol} \tag{3.2.2.4}$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$H_2O_{(l)} \rightarrow H_2O_{(s)} \quad \Delta H_{frz} = -\Delta H_{fus} = -6.01 \text{ kJ/mol} \tag{3.2.2.5}$$

Selected molar enthalpies of fusion are tabulated in Table **3.2.2.1**. Solids like ice which have strong intermolecular forces have much higher values than those like CH_4 with weak ones. Note that the enthalpies of fusion and vaporization change with temperature.

Table **3.2.2.1**: Molar Enthalpies of Fusion and Vaporization of Selected Substances.

Substance	Formula	ΔH(fusion) / kJ mol[1]	Melting Point / K	ΔH(vaporization) / kJ mol^{-1}	Boiling Point / K	($\Delta H_v/T_b$) / JK^{-1} mol^{-1}
Neon	Ne	0.33	24	1.80	27	67
Oxygen	O_2	0.44	54	6.82	90.2	76
Methane	CH_4	0.94	90.7	8.18	112	73
Ethane	C_2H_6	2.85	90.0	14.72	184	80
Chlorine	Cl_2	6.40	172.2	20.41	239	85
Carbon tetrachloride	CCl_4	2.67	250.0	30.00	350	86
Water*	H_2O	6.00678 at 0°C, 101kPa 6.354 at 81.6 °C, 2.50 MPa	273.1	40.657 at 100 °C, 45.051 at 0 °C, 46.567 at -33 °C	373.1	109
n-Nonane	C_9H_{20}	19.3	353	40.5	491	82
Mercury	Hg	2.30	234	58.6	630	91
Sodium	Na	2.60	371	98	1158	85
Aluminum	Al	10.9	933	284	2600	109
Lead	Pb	4.77	601	178	2022	88

*www1.lsbu.ac.uk/water/data.html

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3.2.3: Heating Curve for Water

Freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure **3.2.3.3** shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

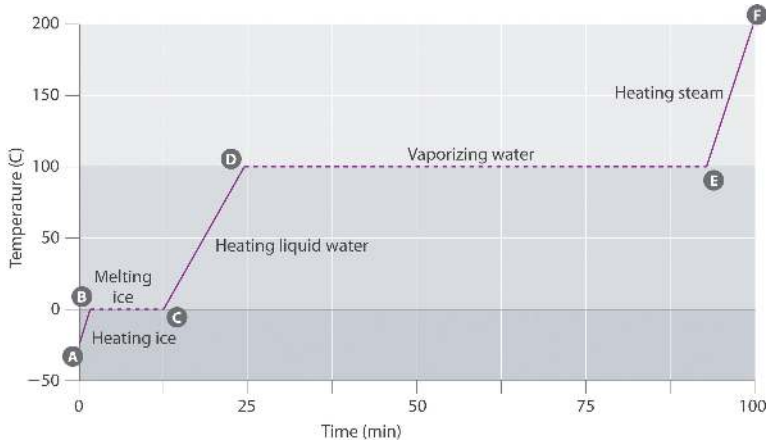


Figure **3.2.3.1**: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure **3.2.3.3**, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure **3.2.3.3**, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is

heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or "bump" the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a "boiling chip") in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure **3.2.3.4** plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure **3.2.3.3**, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

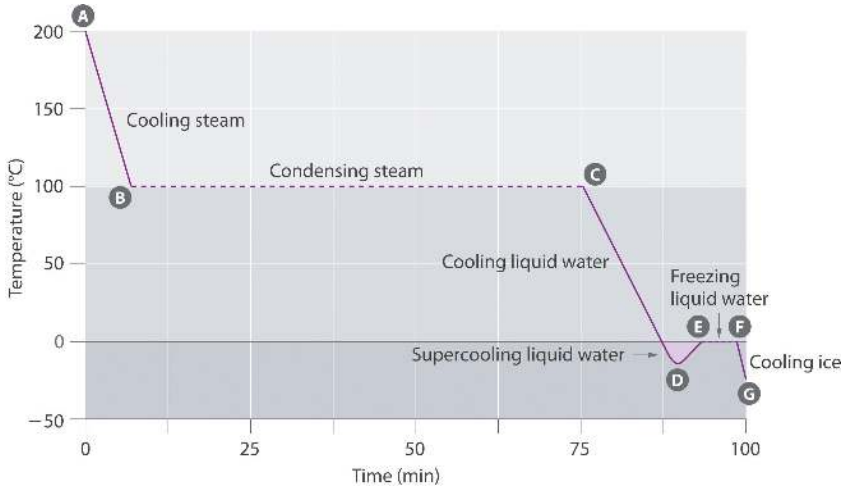


Figure **3.2.3.2**: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

Example 3.2.3.1: Cooling Hot Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy:

Substitute the values given into the general equation relating heat gained to heat lost (Equation 5.39) to obtain the final temperature of the mixture.

Solution:

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T \tag{3.2.3.1}$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

Exercise 3.2.3.1: Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example **3.2.3.1**

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

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3.2.4: Phase Diagrams

Learning Objectives

- To understand the basics of a one-component phase diagram as a function of temperature and pressure in a closed system.
- To be able to identify the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical fluid.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

Introduction

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure **3.2.4.1**). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure **3.2.4.1**) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

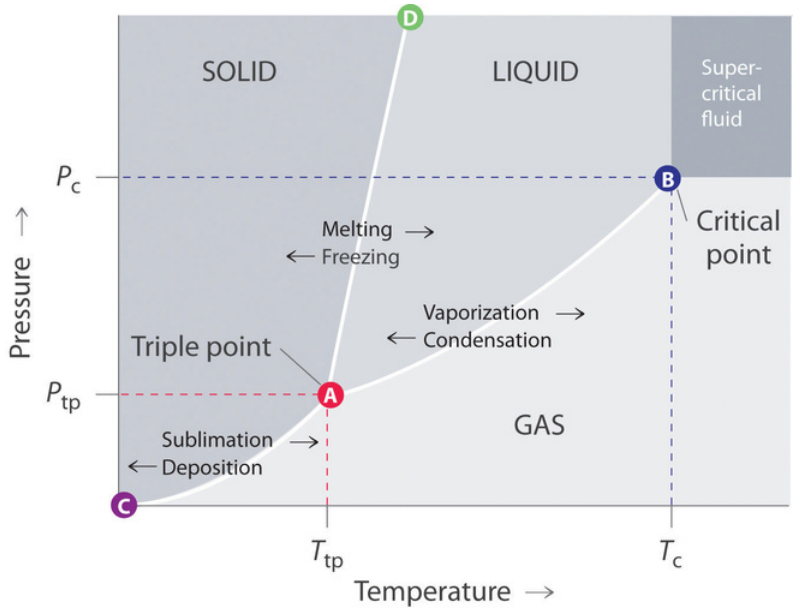


Figure **3.2.4.1**: A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure **3.2.4.1**, the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 11.5. It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple point; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure **3.2.4.1**, is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a

substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure **3.2.4.2** shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

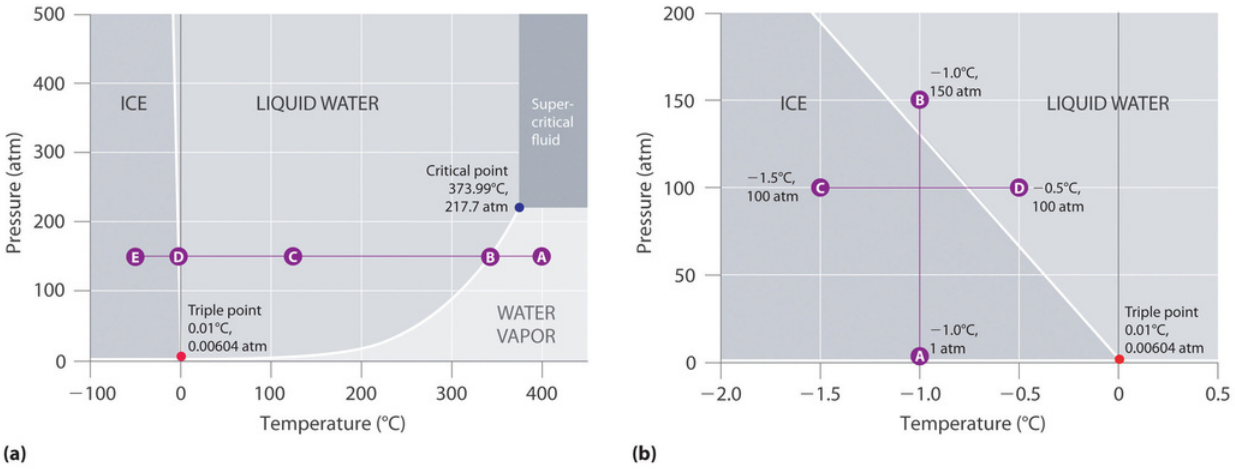


Figure **3.2.4.2**: Two Versions of the Phase Diagram of Water. (a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example **3.2.4.1**).

The phase diagram for water illustrated in Figure **3.2.4.2*b*** shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure **3.2.4.1**; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

In Figure **3.2.4.2*b*** point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Ice Skating: An Incorrect Hypothesis of Phase Transitions

Until recently, many textbooks described ice skating as being possible because the pressure generated by the skater's blade is high enough to melt the ice under the blade, thereby creating a lubricating layer of liquid water that enables the blade to slide across the ice. Although this explanation is intuitively satisfying, it is incorrect, as we can show by a simple calculation.



Pressure from ice skates on ice. from wikihow.com.

Recall that pressure (P) is the force (F) applied per unit area (A):

$$P = \frac{F}{A}$$

To calculate the pressure an ice skater exerts on the ice, we need to calculate only the force exerted and the area of the skate blade. If we assume a 75.0 kg (165 lb) skater, then the force exerted by the skater on the ice due to gravity is

$$F = mg$$

where m is the mass and g is the acceleration due to Earth's gravity (9.81 m/s^2). Thus the force is

$$F = (75.0\ kg)(9.81\ m/s^2) = 736\ (kg \bullet m)/s^2 = 736N$$

If we assume that the skate blades are 2.0 mm wide and 25 cm long, then the area of the bottom of each blade is

$$A = (2.0 \times 10^{-3}\ m)(25 \times 10^{-2}\ m) = 5.0 \times 10^{-4} m^2$$

If the skater is gliding on one foot, the pressure exerted on the ice is

$$P = \frac{736\ N}{5.0 \times 10^{-4}\ m^2} = 1.5 \times 10^6\ N/m^2 = 1.5 \times 10^6\ Pa = 15\ atm$$

The pressure is much lower than the pressure needed to decrease the melting point of ice by even 1°C, and experience indicates that it is possible to skate even when the temperature is well below freezing. Thus pressure-induced melting of the ice cannot explain the low friction that enables skaters (and hockey pucks) to glide. Recent research indicates that the surface of ice, where the ordered array of water molecules meets the air, consists of one or more layers of almost liquid water. These layers, together with melting induced by friction as a skater pushes forward, appear to account for both the ease with which a skater glides and the fact that skating becomes more difficult below about −7°C, when the number of lubricating surface water layers decreases.

✔ Example 3.2.4.1: Water

Referring to the phase diagram of water in Figure **3.2.4.2**:

a. predict the physical form of a sample of water at 400°C and 150 atm.
b. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A. Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.
B. Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

a. **A** Locate the starting point on the phase diagram in part (a) in Figure **3.2.4.2**. The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at T = 400°C and P = 150 atm is a gas.

b. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure **3.2.4.2**. At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

? Exercise 3.2.4.2

Referring to the phase diagram of water in Figure **3.2.4.2**, predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer

The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure **3.2.4.3**) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed.



Dry ice ($CO_2(s)$) sublimed in air under room temperature and pressure. from Wikipedia.

Also notice the critical point at 30.98°C and 72.79 atm. Supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

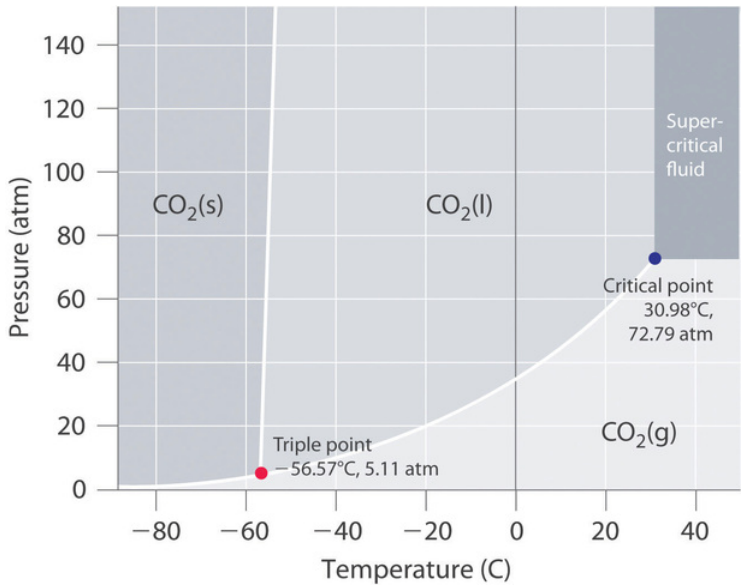


Figure **3.2.4.3**: The Phase Diagram of Carbon Dioxide. Note the critical point, the triple point, and the normal sublimation temperature in this diagram.

The triple point is at -57.57 degrees C and 5.11 atm. The critical point is at 30.98 degree C and 72.79 atm.

The Critical Point

As the phase diagrams above demonstrate, a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c), the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c), the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical point. The critical temperatures and pressures of several common substances are listed in Figure **3.2.4.1**.

Figure **3.2.4.1**: Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.



A Video Discussing Phase Diagrams. Video Source: Phase Diagrams(opens in new window) [youtu.be]

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SECTION OVERVIEW

3.3: CRYSTALS

CRYSTALS

3.3.1: X-Ray Crystallography

3.3.2: Unit Cells and Basic Structures

3.3.3: The Fundamental Types of Crystalline Solids

3.3.4: The Structure of Ionic Solids

3.3.5: Network Covalent Atomic Solids- Carbon and Silicates

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3.3.1: X-Ray Crystallography

4.7: X-Ray Diffraction

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3.3.2: Unit Cells and Basic Structures

Learning Objectives

Make sure you thoroughly understand the following essential ideas:

- The difference between square and hexagonal packing in two dimensions.
- The definition and significance of the unit cell.
- Sketch the three Bravais lattices of the cubic system, and calculate the number of atoms contained in each of these unit cells.
- Show how alternative ways of stacking three close-packed layers can lead to the hexagonal or cubic close packed structures.
- Explain the origin and significance of octahedral and tetrahedral holes in stacked close-packed layers, and show how they can arise.

Close-Packing of Identical Spheres

Crystals are of course three-dimensional objects, but we will begin by exploring the properties of arrays in two-dimensional space. This will make it easier to develop some of the basic ideas without the added complication of getting you to visualize in 3-D — something that often requires a bit of practice. Suppose you have a dozen or so marbles. How can you arrange them in a single compact layer on a table top? Obviously, they must be in contact with each other in order to minimize the area they cover. It turns out that there are two efficient ways of achieving this:



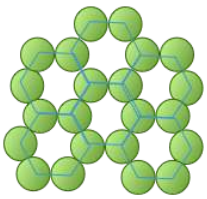
The essential difference here is that any marble within the interior of the square-packed array is in contact with four other marbles, while this number rises to six in the hexagonal-packed arrangement. It should also be apparent that the latter scheme covers a smaller area (contains less empty space) and is therefore a more efficient packing arrangement. If you are good at geometry, you can show that square packing covers 78 percent of the area, while hexagonal packing yields 91 percent coverage.

If we go from the world of marbles to that of atoms, which kind of packing would the atoms of a given element prefer?



If the atoms are identical and are bound together mainly by dispersion forces which are completely non-directional, they will favor a structure in which as many atoms can be in direct contact as possible. This will, of course, be the hexagonal arrangement.

Directed chemical bonds between atoms have a major effect on the packing. The version of hexagonal packing shown at the right occurs in the form of carbon known as *graphite* which forms 2-dimensional sheets. Each carbon atom within a sheet is bonded to three other carbon atoms. The result is just the basic hexagonal structure with some atoms missing.



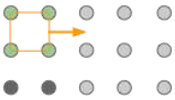
The coordination number of 3 reflects the sp^2-hybridization of carbon in graphite, resulting in plane-trigonal bonding and thus the sheet structure. Adjacent sheets are bound by weak dispersion forces, allowing the sheets to slip over one another and giving rise to the lubricating and flaking properties of graphite.

Lattices

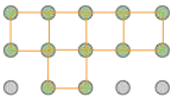
The underlying order of a crystalline solid can be represented by an array of regularly spaced points that indicate the locations of the crystal's basic structural units. This array is called a crystal lattice. Crystal lattices can be thought of as being built up from repeating units containing just a few atoms. These repeating units act much as a rubber stamp: press it on the paper, move ("translate") it by an amount equal to the lattice spacing, and stamp the paper again.



The gray circles represent a square array of lattice points.

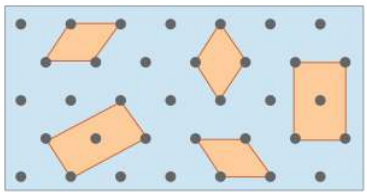


The orange square is the simplest unit cell that can be used to define the 2-dimensional lattice.



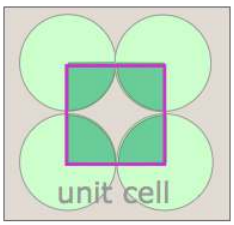
Building out the lattice by moving ("translating") the unit cell in a series of steps,

Although real crystals do not actually grow in this manner, this process is conceptually important because it allows us to classify a lattice type in terms of the simple repeating unit that is used to "build" it. We call this shape the *unit cell*. Any number of primitive shapes can be used to define the unit cell of a given crystal lattice. The one that is actually used is largely a matter of convenience, and it may contain a lattice point in its center, as you see in two of the unit cells shown here. In general, the best unit cell is the simplest one that is capable of building out the lattice.

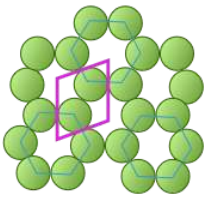




Shown above are unit cells for the close-packed square and hexagonal lattices we discussed near the start of this lesson. Although we could use a hexagon for the second of these lattices, the rhombus is preferred because it is simpler.



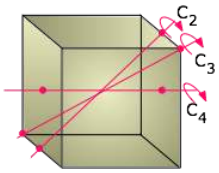
Notice that in both of these lattices, the corners of the unit cells are centered on a lattice point. This means that an atom or molecule located on this point in a real crystal lattice is shared with its neighboring cells. As is shown more clearly here for a two-dimensional square-packed lattice, a single unit cell can claim "ownership" of only one-quarter of each molecule, and thus "contains" 4 × ¼ = 1 molecule.



The unit cell of the graphite form of carbon is also a rhombus, in keeping with the hexagonal symmetry of this arrangement. Notice that to generate this structure from the unit cell, we need to shift the cell in both the *x*- and *y*- directions in order to leave empty spaces at the correct spots. We could alternatively use regular hexagons as the unit cells, but the *x*+*y* shifts would still be required, so the simpler rhombus is usually preferred. As you will see in the next section, the empty spaces within these unit cells play an important role when we move from two- to three-dimensional lattices.

Cubic crystals

In order to keep this lesson within reasonable bounds, we are limiting it mostly to crystals belonging to the so-called *cubic* system. In doing so, we can develop the major concepts that are useful for understanding more complicated structures (as if there are not enough complications in cubics alone!) But in addition, it happens that cubic crystals are very commonly encountered; most metallic elements have cubic structures, and so does ordinary salt, sodium chloride.

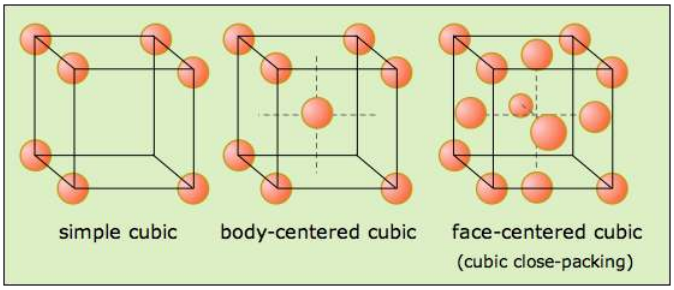


We usually think of a cubic shape in terms of the equality of its edge lengths and the 90° angles between its sides, but there is another way of classifying shapes that chemists find very useful. This is to look at what *geometric transformations* (such as rotations around an axis) we can perform that leave the appearance unchanged. For example, you can rotate a cube 90° around an axis perpendicular to any pair of its six faces without making any apparent change to it. We say that the cube possesses three mutually perpendicular *four-fold rotational axes*, abbreviated C_4 axes. But if you think about it, a cube can also be rotated around the axes that extend between opposite corners; in this case, it takes three 120° rotations to go through a complete circle, so these axes (also four in number) are three-fold or C_3 axes.

Cubic crystals belong to one of the seven crystal systems whose lattice points can be extended indefinitely to fill three-dimensional space and which can be constructed by successive translations (movements) of a primitive unit cell in three dimensions. As we will see below, the cubic system, as well as some of the others, can have variants in which additional lattice points can be placed at the center of the unit or at the center of each face.

The three types of cubic lattices

The three Bravais lattices which form the cubic crystal system are shown here.



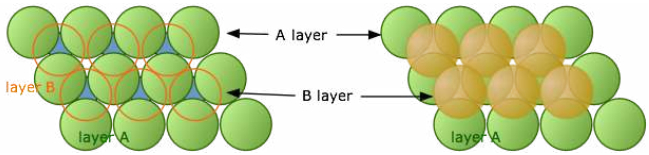
Structural examples of all three are known, with body- and face-centered (BCC and FCC) being much more common; most metallic elements crystallize in one of these latter forms. But although the simple cubic structure is uncommon by itself, it turns out that many BCC and FCC structures composed of ions can be regarded as interpenetrating combinations of two simple cubic

lattices, one made up of positive ions and the other of negative ions. Notice that only the FCC structure, which we will describe below, is a close-packed lattice within the cubic system.

Close-packed lattices in three dimensions

Close-packed lattices allow the maximum amount of interaction between atoms. If these interactions are mainly attractive, then close-packing usually leads to more energetically stable structures. These lattice geometries are widely seen in metallic, atomic, and simple ionic crystals.

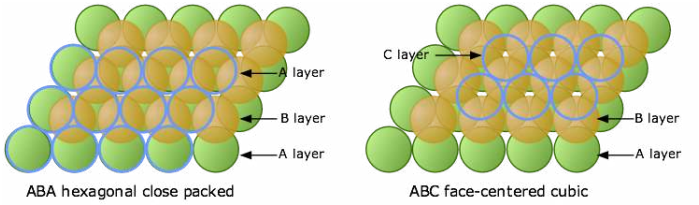
As we pointed out above, hexagonal packing of a single layer is more efficient than square-packing, so this is where we begin. Imagine that we start with the single layer of green atoms shown below. We will call this the A layer. If we place a second layer of atoms (orange) on top of the A-layer, we would expect the atoms of the new layer to nestle in the hollows in the first layer. But if all the atoms are identical, only some of these void spaces will be accessible.



In the diagram on the left, notice that there are two classes of void spaces between the A atoms; one set (colored blue) has a vertex pointing up, while the other set (not colored) has down-pointing vertices. Each void space constitutes a depression in which atoms of a second layer (the B-layer) can nest. The two sets of void spaces are completely equivalent, but only one of these sets can be occupied by a second layer of atoms whose size is similar to those in the bottom layer. In the illustration on the right above we have arbitrarily placed the B-layer atoms in the blue voids, but could just as well have selected the white ones.

Two choices for the third layer lead to two different close-packed lattice types

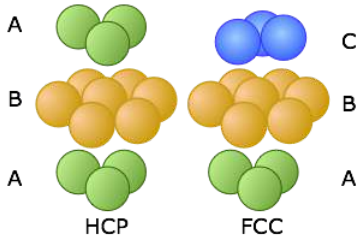
Now consider what happens when we lay down a third layer of atoms. These will fit into the void spaces within the B-layer. As before, there are two sets of these positions, but unlike the case described above, they are not equivalent.



The atoms in the third layer are represented by open blue circles in order to avoid obscuring the layers underneath. In the illustration on the left, this third layer is placed on the B-layer at locations that are directly above the atoms of the A-layer, so our third layer is just a another A layer. If we add still more layers, the vertical sequence A-B-A-B-A-B-A... repeats indefinitely.

In the diagram on the right above, the blue atoms have been placed above the white (unoccupied) void spaces in layer A. Because this third layer is displaced horizontally (in our view) from layer A, we will call it layer C. As we add more layers of atoms, the sequence of layers is A-B-C-A-B-C-A-B-C..., so we call it ABC packing.

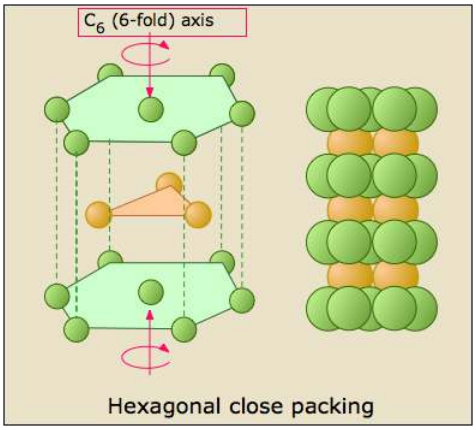
> For the purposes of clarity, only three atoms of the A and C layers are shown in these diagrams. But in reality, each layer consists of an extended hexagonal array; the two layers are simply displaced from one another.



These two diagrams that show exploded views of the vertical stacking further illustrate the rather small fundamental difference between these two arrangements— but, as you will see below, they have widely divergent structural consequences. Note the opposite orientations of the A and C layers

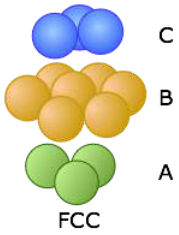
The Hexagonal closed-packed structure

The HCP stacking shown on the left just above takes us out of the cubic crystal system into the hexagonal system, so we will not say much more about it here except to point out each atom has 12 nearest neighbors: six in its own layer, and three in each layer above and below it.

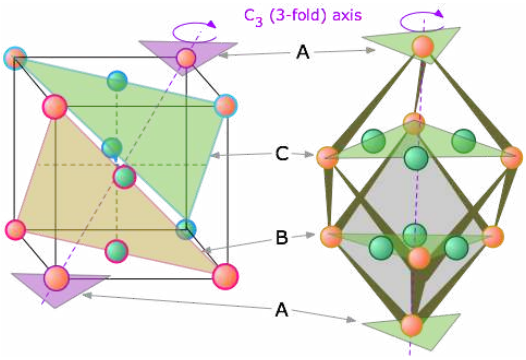


The cubic close-packed structure

Below we reproduce the FCC structure that was shown above.



You will notice that the B-layer atoms form a hexagon, but this is a *cubic* structure. How can this be? The answer is that the FCC stack is inclined with respect to the faces of the cube, and is in fact coincident with one of the three-fold axes that passes through opposite corners. It requires a bit of study to see the relationship, and we have provided two views to help you. The one on the left shows the cube in the normal isometric projection; the one on the right looks down upon the top of the cube at a slightly inclined angle.

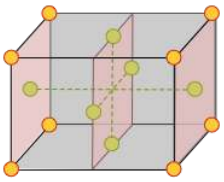


Both the CCP and HCP structures fill 74 percent of the available space when the atoms have the same size. You should see that the two shaded planes cutting along diagonals within the interior of the cube contain atoms of different colors, meaning that they

belong to different layers of the CCP stack. Each plane contains three atoms from the B layer and three from the C layer, thus reducing the symmetry to C_3, which a cubic lattice must have.

The FCC unit cell

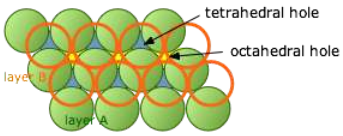
The figure below shows the the face-centered cubic unit cell of a cubic-close packed lattice.



How many atoms are contained in a unit cell? Each corner atom is shared with eight adjacent unit cells and so a single unit cell can claim only 1/8 of each of the eight corner atoms. Similarly, each of the six atoms centered on a face is only half-owned by the cell. The grand total is then (8 × 1/8) + (6 × ½) = 4 atoms per unit cell.

Interstitial Void Spaces

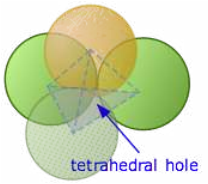
The atoms in each layer in these close-packing stacks sit in a depression in the layer below it. As we explained above, these void spaces are not completely filled. (It is geometrically impossible for more than two identical spheres to be in contact at a single point.) We will see later that these *interstitial void spaces* can sometimes accommodate additional (but generally smaller) atoms or ions.



If we look down on top of two layers of close-packed spheres, we can pick out two classes of void spaces which we call *tetrahedral* and *octahedral holes*.

Tetrahedral holes

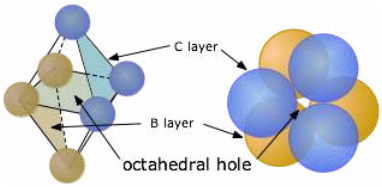
If we direct our attention to a region in the above diagram where a single atom is in contact with the three atoms in the layers directly below it, the void space is known as a *tetrahedral hole*. A similar space will be be found between this single atom and the three atoms (not shown) that would lie on top of it in an extended lattice. Any interstitial atom that might occupy this site will interact with the four atoms surrounding it, so this is also called a *four-coordinate interstitial space*.



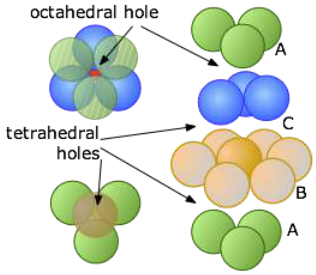
Don't be misled by this name; the boundaries of the void space are spherical sections, not tetrahedra. The tetrahedron is just an imaginary construction whose four corners point to the centers of the four atoms that are in contact.

Octahedral holes

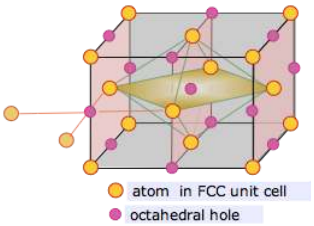
Similarly, when two sets of three trigonally-oriented spheres are in close-packed contact, they will be oriented 60° apart and the centers of the spheres will define the six corners of an imaginary octahedron centered in the void space between the two layers, so we call these *octahedral holes* or *six-coordinate interstitial sites*. Octahedral sites are larger than tetrahedral sites.



An octahedron has six corners and eight sides. We usually draw octahedra as a double square pyramid standing on one corner (left), but in order to visualize the octahedral shape in a close-packed lattice, it is better to think of the octahedron as lying on one of its faces (right).



Each sphere in a close-packed lattice is associated with one octahedral site, whereas there are only half as many tetrahedral sites. This can be seen in this diagram that shows the central atom in the B layer in alignment with the hollows in the C and A layers above and below.



The face-centered cubic unit cell contains a single octahedral hole within itself, but octahedral holes shared with adjacent cells exist at the centers of each edge. Each of these twelve edge-located sites is shared with four adjacent cells, and thus contributes (12 × ¼) = 3 atoms to the cell. Added to the single hole contained in the middle of the cell, this makes a total of 4 octahedral sites per unit cell. This is the same as the number we calculated above for the number of atoms in the cell.

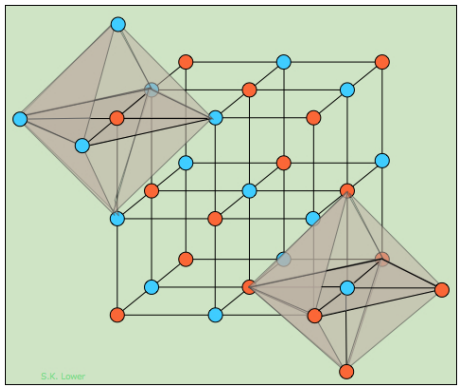
Common cubic close-packed structures

It can be shown from elementary trigonometry that an atom will fit exactly into an octahedral site if its radius is 0.414 as great as that of the host atoms. The corresponding figure for the smaller tetrahedral holes is 0.225.

Many pure metals and compounds form face-centered cubic (cubic close- packed) structures. The existence of tetrahedral and octahedral holes in these lattices presents an opportunity for "foreign" atoms to occupy some or all of these interstitial sites. In order to retain close-packing, the interstitial atoms must be small enough to fit into these holes without disrupting the host CCP lattice. When these atoms are too large, which is commonly the case in ionic compounds, the atoms in the interstitial sites will push the host atoms apart so that the face-centered cubic lattice is somewhat opened up and loses its close-packing character.

The rock-salt structure

Alkali halides that crystallize with the "rock-salt" structure exemplified by sodium chloride can be regarded either as a FCC structure of one kind of ion in which the octahedral holes are occupied by ions of opposite charge, or as two interpenetrating FCC lattices made up of the two kinds of ions. The two shaded octahedra illustrate the identical coordination of the two kinds of ions; each atom or ion of a given kind is surrounded by six of the opposite kind, resulting in a coordination expressed as (6:6).

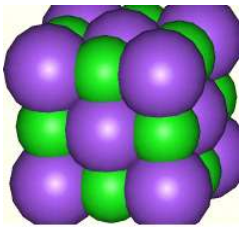


How many NaCl units are contained in the unit cell? If we ignore the atoms that were placed outside the cell in order to construct the octahedra, you should be able to count fourteen "orange" atoms and thirteen "blue" ones. But many of these are shared with adjacent unit cells.

An atom at the corner of the cube is shared by eight adjacent cubes, and thus makes a 1/8 contribution to any one cell. Similarly, the center of an edge is common to four other cells, and an atom centered in a face is shared with two cells. Taking all this into consideration, you should be able to confirm the following tally showing that there are four AB units in a unit cell of this kind.

Orange	**Blue**
8 at corners: 8 x 1/8 = 1	12 at edge centers: 12 x ¼ = 3
6 at face centers: 6 x ½ = 3	1 at body center = 1
total: 4	total: 4

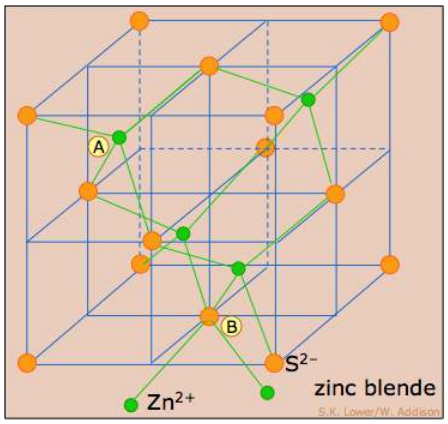
If we take into consideration the actual sizes of the ions (Na^+ = 116 pm, Cl^- = 167 pm), it is apparent that neither ion will fit into the octahedral holes with a CCP lattice composed of the other ion, so the actual structure of NaCl is somewhat expanded beyond the close-packed model.



The space-filling model on the right depicts a face-centered cubic unit cell of chloride ions (purple), with the sodium ions (green) occupying the octahedral sites.

The zinc-blende structure: using some tetrahedral holes

Since there are two tetrahedral sites for every atom in a close-packed lattice, we can have binary compounds of 1:1 or 1:2 stoichiometry depending on whether half or all of the tetrahedral holes are occupied. Zinc-blende is the mineralogical name for zinc sulfide, ZnS. An impure form known as *sphalerite* is the major ore from which zinc is obtained.

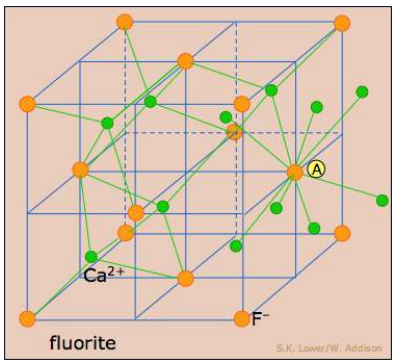


This structure consists essentially of a FCC (CCP) lattice of sulfur atoms (orange) (equivalent to the lattice of chloride ions in NaCl) in which zinc ions (green) occupy half of the tetrahedral sites. As with any FCC lattice, there are four atoms of sulfur per unit cell, and the the four zinc atoms are totally contained in the unit cell. Each atom in this structure has **four** nearest neighbors, and is thus tetrahedrally coordinated.

It is interesting to note that if all the atoms are replaced with carbon, this would correspond to the *diamond* structure.

The fluorite structure: all tetrahedral sites occupied

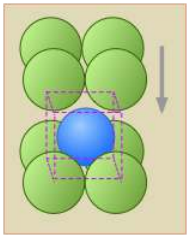
Fluorite, CaF_2, having twice as many ions of fluoride as of calcium, makes use of all eight tetrahedral holes in the CPP lattice of calcium ions (orange) depicted here. To help you understand this structure, we have shown some of the octahedral sites in the next cell on the right; you can see that the calcium ion at **A** is surrounded by eight fluoride ions, and this is of course the case for all of the calcium sites. Since each fluoride ion has four nearest-neighbor calcium ions, the coordination in this structure is described as (8:4).



Although the radii of the two ions (F^-= 117 pm, Ca^{2+} = 126 pm does not allow true close packing, they are similar enough that one could just as well describe the structure as a FCC lattice of fluoride ions with calcium ions in the octahedral holes.

Simple- and body-centered cubic structures

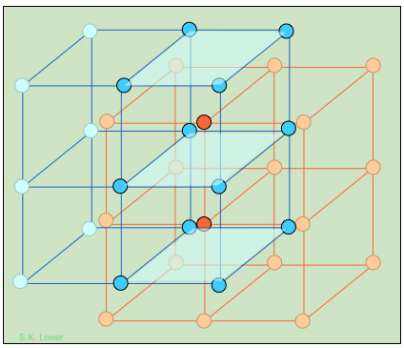
In Section 4 we saw that the only cubic lattice that can allow close packing is the face-centered cubic structure. The simplest of the three cubic lattice types, the *simple cubic lattice*, lacks the hexagonally-arranged layers that are required for close packing. But as shown in this exploded view, the void space between the two square-packed layers of this cell constitutes an octahedral hole that can accommodate another atom, yielding a packing arrangement that in favorable cases can approximate true close-packing. Each second-layer B atom (blue) resides within the unit cell defined the A layers above and below it.



The A and B atoms can be of the same kind or they can be different. If they are the same, we have a *body-centered cubic lattice*. If they are different, and especially if they are oppositely-charged ions (as in the CsCl structure), there are size restrictions: if the B atom is too large to fit into the interstitial space, or if it is so small that the A layers (which all carry the same electric charge) come into contact without sufficient A-B coulombic attractions, this structural arrangement may not be stable.

The cesium chloride structure

CsCl is the common model for the BCC structure. As with so many other structures involving two different atoms or ions, we can regard the same basic structure in different ways. Thus if we look beyond a single unit cell, we see that CsCl can be represented as two interpenetrating simple cubic lattices in which each atom occupies an octahedral hole within the cubes of the other lattice.



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3.3.3: The Fundamental Types of Crystalline Solids

Learning Objectives

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure **3.3.3.1**).

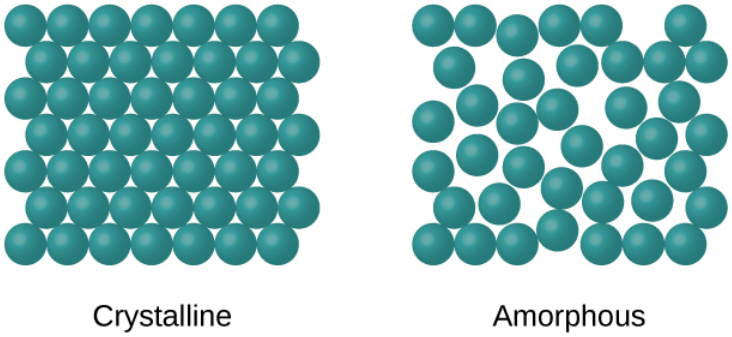


Figure **3.3.3.1**: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

The crystalline arrangement shows many circles drawn in rows and stacked together tightly. The amorphous arrangement shows many circles spread slightly apart and in no organized pattern.

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as boron oxide (Figure **3.3.3.2**), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

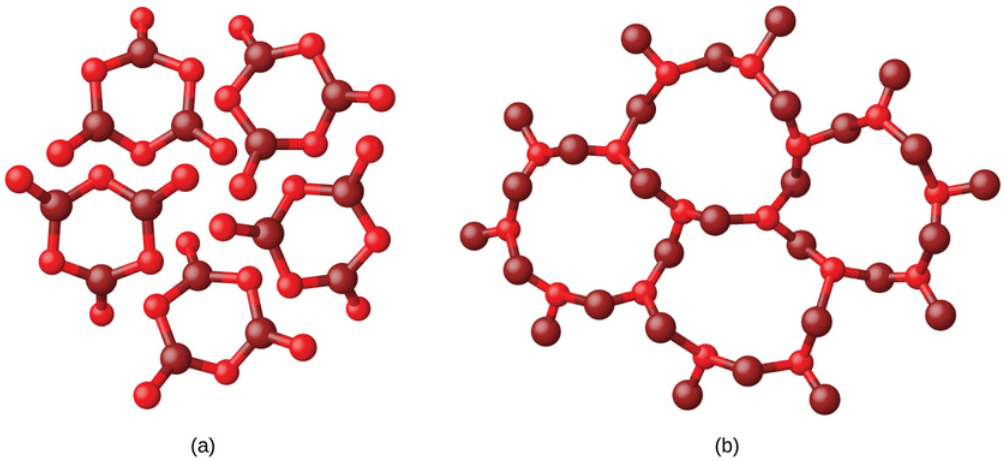


Figure **3.3.3.2**: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

The first structure of diboron trioxide shows five identical and separated hexagonal rings. The second structure of diboron trioxide shows a more interconnected structure with four large rings forming a more stable structure.

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure **3.3.3.3**). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

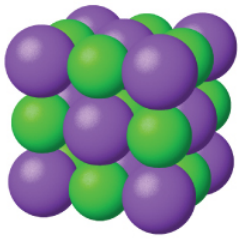


Figure **3.3.3.3**: Sodium chloride is an ionic solid.

A cube composed of purple and green spheres is shown. The cube has dimensions of three by three spheres. The purple spheres are slightly larger than the green spheres.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure **3.3.3.4**. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

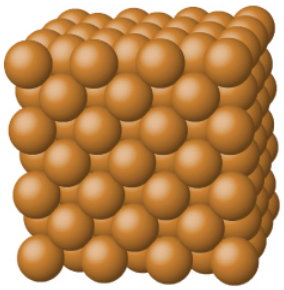


Figure **3.3.3.4**: Copper is a metallic solid.

Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure **3.3.3.5**. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

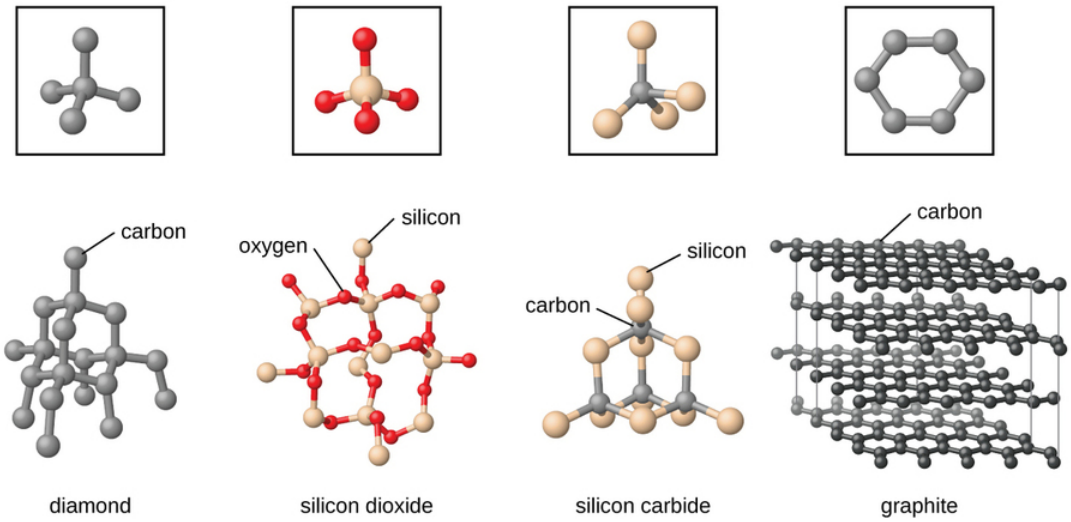


Figure **3.3.3.5**. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

The complex three dimensional structure of diamond, silicon dioxide, silicon carbide and graphite is shown along with a a smaller repeating unit of the structure shown above each structure.

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure **3.3.3.6**, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below −200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

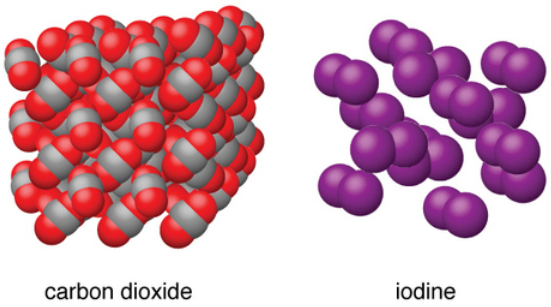


Figure **3.3.3.6**: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

On the left, many red and grey molecules are densely stacked in a 3-D drawing to represent carbon dioxide. On the right, purple molecules are scattered randomly to represent iodine.

Properties of Solids

A crystalline solid, like those listed in Table **3.3.3.1** has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table **3.3.3.1**: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure **3.3.3.7**. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

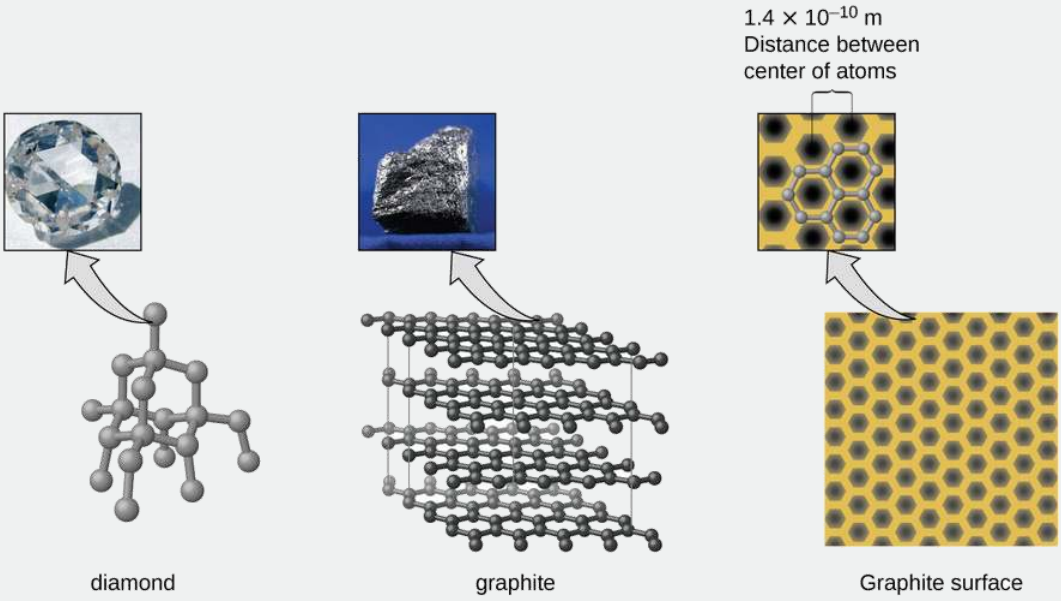


Figure **3.3.3.7**: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

A close up of a piece of diamond shows a three dimensional sturcture of a complex network of well bonded carbon atoms. A close up of a graphite shows several layers of carbon sheets. Each sheet is composed of a repeated and connected hexagonal structure of carbon atoms. The third diagram shows that the distance between the center of atoms is 1.4 times 10 to the power of negative 10 meters.

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure **3.3.3.8**, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

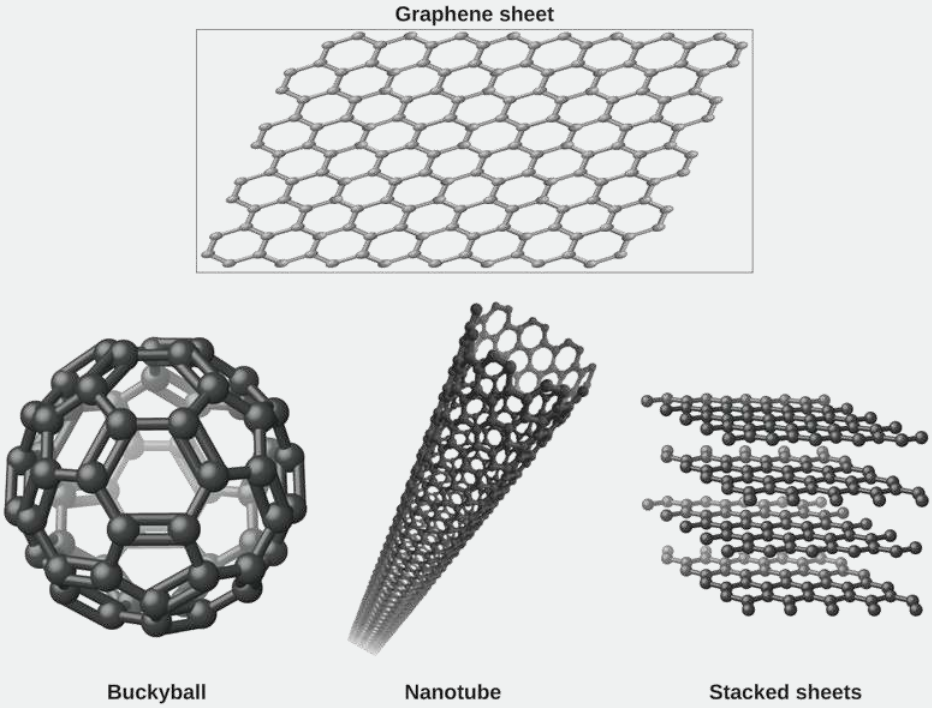


Figure **3.3.3.8**: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

A sheet of interconnected hexagonal rings is shown at the top. Below it, a bukcyball is shown which is a sphere is composed of hexagonal rings. In the lower middle image, a nanotube is shown that is made by rolling a graphene sheet into a tube. In the lower right image, stacked sheets made up of four horizontal sheets composed of joined, hexagonal rings is shown.

Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure **3.3.3.9**. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

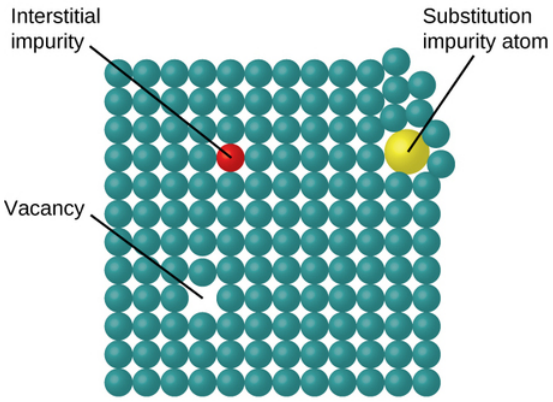


Figure **3.3.3.9**: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic

solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Glossary

amorphous solid

(also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid

solid whose particles are held together by covalent bonds

crystalline solid

solid in which the particles are arranged in a definite repeating pattern

interstitial sites

spaces between the regular particle positions in any array of atoms or ions

ionic solid

solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid

solid composed of metal atoms

molecular solid

solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy

defect that occurs when a position that should contain an atom or ion is vacant

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3.3.4: The Structure of Ionic Solids

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above.

- What is an ionic solid, what are its typical physical properties, and what kinds of elements does it contain?
- Define the lattice energy of an ionic solid in terms of the energetic properties of its component elements.
- Make a rough sketch that describes the structure of solid sodium chloride.
- Describe the role that the relative ionic radii play in contributing to the stability of an ionic solids.
- Give examples of some solids that can form when ionic solutions are evaporated, but which do not fall into the category of "ionic" solids.

In this section we deal mainly with a very small but important class of solids that are commonly regarded as composed of ions. We will see how the relative sizes of the ions determine the energetics of such compounds. And finally, we will point out that not all solids that are formally derived from ions can really be considered "ionic" at all.

Ionic Solids

The idealized ionic solid consists of two interpenetrating lattices of oppositely-charged point charges that are held in place by a balance of coulombic forces. But because real ions occupy space, no such "perfect" ionic solid exists in nature. Nevertheless, this model serves as a useful starting point for understanding the structure and properties of a small group of compounds between elements having large differences in electronegativity.

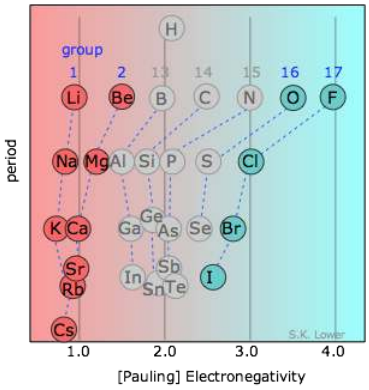


Figure **3.3.4.1**

Chemists usually apply the term "ionic solid" to binary compounds of the metallic elements of Groups 1-2 with one of the halogen elements or oxygen. As can be seen from the diagram, the differences in electronegativity between the elements of Groups 1-2 and those of Group 17 (as well as oxygen in Group 16) are sufficiently great that the binding in these solids is usually dominated by Coulombic forces and the crystals can be regarded as built up by aggregation of oppositely-charged ions.

Sodium Chloride (rock-salt) Structure

The most well known ionic solid is sodium chloride, also known by its geological names as *rock-salt* or *halite*. We can look at this compound in both structural and energetic terms.



Rock Salt

Structurally, each ion in sodium chloride is surrounded and held in tension by six neighboring ions of opposite charge. The resulting crystal lattice is of a type known as *simple cubic*, meaning that the lattice points are equally spaced in all three dimensions and all cell angles are 90°.

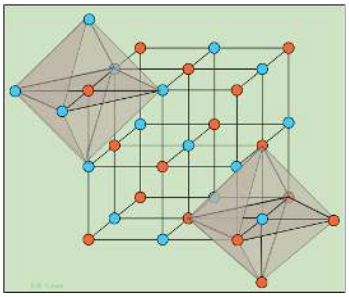


Figure **3.3.4.2**: The differently-colored circles represent the Na^+ and Cl^- ions; because their locations are geometrically equivalent, it does not matter which color is assigned to which ion.

In Figure **3.3.4.2**, we have drawn two imaginary octahedra centered on ions of different kinds and extending partially into regions outside of the diagram. (We could equally well have drawn them at any of the lattice points, but show only two in order to reduce clutter.) Our object in doing this is to show that each ion is surrounded by six other ions of opposite charge; this is known as *(6,6) coordination*. Another way of stating this is that each ion resides in an *octahedral hole* within the cubic lattice.

How can one sodium ion surrounded by six chloride ions (or *vice versa*) be consistent with the simplest formula NaCl? The answer is that each of those six chloride ions also sits at the center of its own octahedron defined by another six sodium ions. You might think that this corresponds to Na_6Cl_6, but note that the central sodium ion shown in the diagram can claim only a one-sixth share of each of its chloride ion neighbors, so the formula NaCl is not just the simplest formula, but correctly reflects the 1:1 stoichiometry of the compound. But of course, as in all ionic structures, there are no distinguishable "molecular" units that correspond to the NaCl simplest formula. Bear in mind that large amount of empty space in diagrams depicting a crystal lattice structure can be misleading, and that the ions are really in direct contact with each other to the extent that this is geometrically possible.

Sodium Chloride Energetics

Sodium chloride, like virtually all salts, is a more energetically favored configuration of sodium and chlorine than are these elements themselves; in other words, the reaction

$$Na_{(s)} + \tfrac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(s)} \tag{3.3.4.1}$$

is accompanied by a release of energy in the form of heat. How much heat, and why? To help us understand, we can imagine the formation of one mole of sodium chloride from its elements proceeding in these hypothetical steps in which we show the energies explicitly:

Step 1: *Atomization* of sodium (breaking one mole of metallic sodium into isolated sodium atoms)

$$\mathrm{Na\,(s) + 108\,kJ \longrightarrow Na\,(g)} \tag{3.3.4.2}$$

Step 2: Same thing with chlorine. This requires more energy because it involves breaking a covalent bond.

$$\mathrm{\tfrac{1}{2}Cl_2\,(g) + 127\ \ kJ \longrightarrow Cl\,(g)} \tag{3.3.4.3}$$

Step 3: We strip an electron from one mole of sodium atoms (this costs a lot of energy!)

$$\mathrm{Na\,(g) + 496\ \ kJ \longrightarrow Na^+\,(g) + e^-} \tag{3.3.4.4}$$

Step 4: Feeding these electrons to the chlorine atoms gives most of this energy back.

$$\mathrm{Cl\,(g) + e^- \longrightarrow Cl^-\,(g) + 348\ \ kJ} \tag{3.3.4.5}$$

Step 5: Finally, we bring one mole of the ions together to make the crystal lattice — with a huge release of energy.

$$\mathrm{Na^+\,(g) + Cl^-\,(g) \longrightarrow NaCl\,(s) + 787\ \ kJ} \tag{3.3.4.6}$$

If we add all of these equations together, we get

$$\mathrm{Na\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \longrightarrow NaCl\,(s) + 404\ kJ} \tag{3.3.4.7}$$

In other words, the formation of solid sodium chloride from its elements is highly *exothermic*. As this energy is released in the form of heat, it spreads out into the environment and will remain unavailable to push the reaction in reverse. We express this by saying that "sodium chloride is more *stable* than its elements".

Looking at the equations above, you can see that Equation 3.3.4.6 constitutes the big payoff in energy. The 787 kj/mol noted there is known as the NaCl *lattice energy*. Its large magnitude should be no surprise, given the strength of the coulombic force between ions of opposite charge.

It turns out that it is the lattice energy that renders the gift of stability to all ionic solids.Note that this lattice energy, while due principally to coulombic attraction between each ion and its eight nearest neighbors, is really the sum of *all* the interactions with the crystal. Lattice energies cannot be measured directly, but they can be estimated fairly well from the energies of the other processes described in the table immediately above.

How Geometry and Periodic Properties Interact

The most energetically stable arrangement of solids made up of identical molecular units (as in the noble gas elements and pure metals) are generally those in which there is a minimum of empty space; these are known as *close-packed* structures, and there are several kinds. In the case of ionic solids of even the simplest 1:1 stoichiometry, the positive and negative ions usually differ so much in size that packing is often much less efficient. This may cause the solid to assume lattice geometries that differ from the one illustrated above for sodium chloride.

By way of illustration, consider the structure of cesium chloride (the spelling *cæsium* is also used), CsCl. The radius of the Cs^+ ion is 168 pm compared to 98 pm for Na^+ and cannot possibly fit into the octahedral hole of a simple cubic lattice of chloride ions. The CsCl lattice therefore assumes a different arrangement.

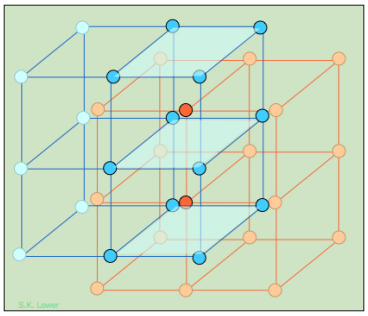


Figure **3.3.4.3**: The CsCl structure, like that of NaCl, can be regarded as two interpenetrating lattices of the oppositely-charged ions. In CsCl, however, the metal ions, instead of being surrounded by six chloride ions, are shifted into the center of each cubic element of the Cl–-ion lattice.

Figure **3.3.4.3** focuses on two of these cubic lattice elements whose tops and bottoms are shaded for clarity. It should be easy to see that each cesium ion now has eight nearest-neighbor chloride ions. Each chloride ion is also surrounded by eight cesium ions, so all the lattice points are still geometrically equivalent. We therefore describe this structure as having *(8,8) coordination*.

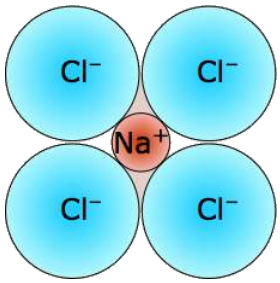
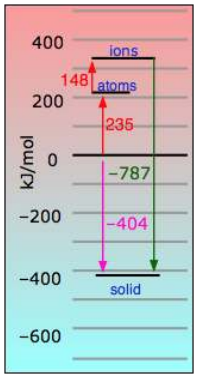
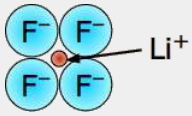
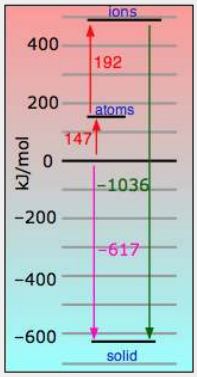
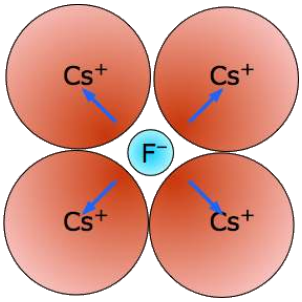
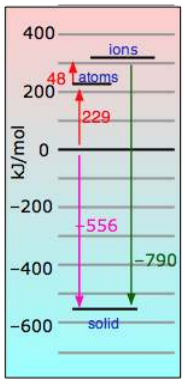
The two kinds of lattice arrangements exemplified by NaCl ("rock salt") and CsCl are found in a large number of other 1:1 ionic solids, and these names are used generically to describe the structures of these other compounds. There are of course many other

fundamental lattice arrangements (not all of them cubic), but the two we have described here are sufficient to illustrate the point that the *radius ratio* (the ratio of the radii of the positive to the negative ion) plays an important role in the structures of simple ionic solids.

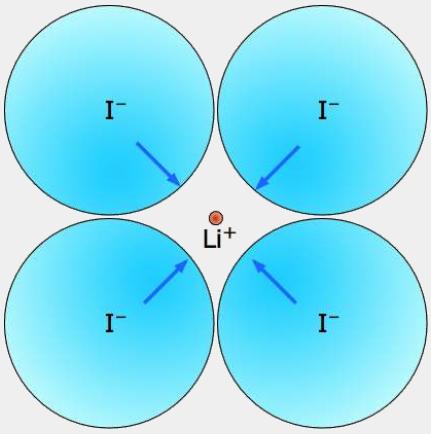
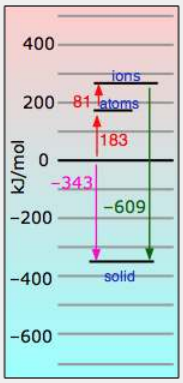
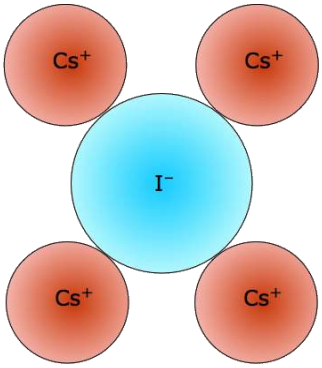
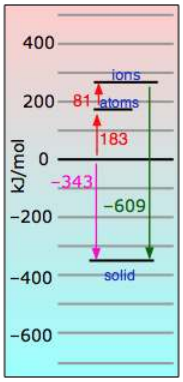
The Alkali Halides

The interaction of the many atomic properties that influence ionic binding are nicely illustrated by looking at a series of alkali halides, especially those involving extreme differences in atomic radii. The latter are all drawn to the same scale. On the energetic

plots at the right, the lattice energies are shown in green. We will start with the one you already know very well.

Sodium chloride - NaCl ("rock-salt") mp/bp 801/1413 °C; coordination (6,6)		
Lithium Fluoride - LiF - mp/bp 846/1676 °C, rock-salt lattice structure (6,6). Tiny-tiny makes strong-strong! This is the most "ionic" of the alkali halides, with the largest lattice energy and highest melting and boiling points. The small size of these ions (and consequent high charge densities) together with the large electronegativity difference between the two elements places a lot of electronic charge between the atoms. Even in this highly ionic solid, the electron that is "lost" by the lithium atom turns out to be closer to the Li nucleus than when it resides in the 2*s* shell of the neutral atom.		
Cesium Fluoride, CsF - mp/bp 703/1231 °C, (8,8) coordination. With five shells of electrons shielding its nucleus, the Cs^+ ion with its low charge density resembles a big puff-ball which can be distorted by the highly polarizing fluoride ion. The resulting ion-induced dipoles (blue arrows) account for much of the lattice energy here. The reverse of this would be a tiny metal ion trying to hold onto four relatively huge iodide ions like Lithium iodide.		

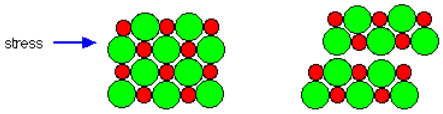
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Lithium iodide, LiI - mp/bp 745/1410 °C. Negative ions can make even bigger puff-balls. The tiny lithium ion can't get very close to any of the iodides to generate a very strong coulombic binding, but does polarize them to create an ion-induced dipole component. It does not help that the negative ions are in contact with each other. The structural geometry is the same (6,6) coordination as NaCl.		
Cesium iodide, CsI - mp/bp 626/1280 °C. Even with the (8,8) coordination afforded by the CsCl structure, this is a pretty sorry combination owing to the low charge densities. The weakness of coulombic- compared to van der Waals interactions makes this the least-"ionic" of all the alkali halide solids.		

Conclusion: Many of the alkali halide solids are not all that "ionic" in the sense that coulombic forces are the predominant actors; in many, such as the CsI illustrated above, ion-induced dipole forces are more important.

Some Properties of Ionic Solids

As noted above, ionic solids are generally hard and brittle. Both of these properties reflect the strength of the coulombic force. *Hardness* measures resistance to *deformation*. Because the ions are tightly bound to their oppositely-charged neighbors and, a mechanical force exerted on one part of the solid is resisted by the electrostatic forces operating over an extended volume of the crystal.



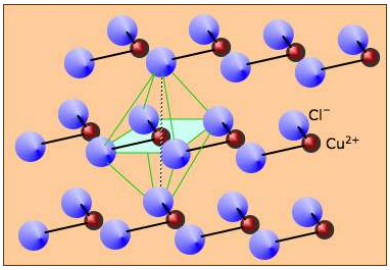
But by applying sufficient force, one layer of ions can be made to slip over another; this is the origin of *brittleness*. This slippage quickly propagates along a plane of the crystal (more readily in some directions than in others), weakening their attraction and leading to physical *cleavage*. Because the "ions" in ionic solids lack *mobility*, the solids themselves are **electrical insulators**.

Not all ion-derived solids are "ionic".

Even within the alkali halides, the role of coulombic attraction diminishes as the ions become larger and more polarizable or differ greatly in radii. This is especially true of the anions, which tend to be larger and whose electron clouds are more easily distorted. In solids composed of polyatomic ions such as $(NH_4)_2SO_4$, $SrClO_4$, NH_4CO_3, ion-dipole and ion-induced dipole forces may actually be stronger than the coulombic force. Higher ionic charges help, especially if the ions are relatively small. This is especially evident in the extremely high melting points of the Group 2 and higher oxides:

MgO (magnesia)	CaO (lime)	SrO (strontia)	Al2O3 (alumina)	ZrO2 (zirconia)
2830 °C	2610 °C	2430 °C	2050 °C	2715 °C

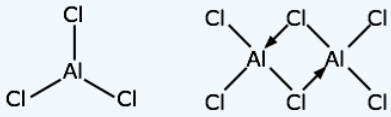
These substances are known as *refractories*, meaning that they retain their essential properties at high temperatures. Magnesia, for example, is used to insulate electric heating elements and, in the form of fire bricks, to line high-temperature furnaces. No boiling points have been observed for these compounds; on further heating, they simply dissociate into their elements. Their crystal structures can be very complex, and some (notably Al_2O_3) can have several solid forms. Even in the most highly ionic solids there is some electron sharing, so the idea of a “pure” ionic bond is an abstraction.



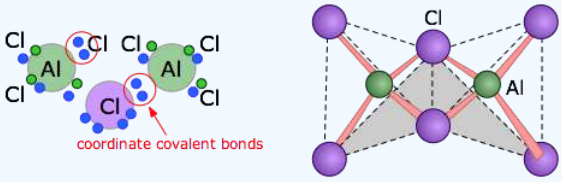
Many solids that are formally derived from ions cannot really be said to form "ionic" solids at all. For example, anhydrous copper(II) chloride consists of layers of copper atoms surrounded by four chlorine atoms in a square arrangement. Neighboring chains are offset so as to create an octahedral coordination of each copper atom. Similar structures are commonly encountered for other salts of transition metals. Similarly, most oxides and sulfides of metals beyond Group 2 tend to have structures dominated by other than ion-ion attractions.

Aluminum Halides

The trihalides of aluminum offer another example of the dangers of assuming ionic character of solids that are formally derived from ions. Aqueous solutions of what we assume to be AlF_3, $AlCl_3$, $AlBr_3$, and AlI_3 all exhibit the normal properties ionic solutions (they are electrically conductive, for example), but the solids are quite different: the melting point of AlF_3 is 1290°C, suggesting that it is indeed ionic. But $AlCl_3$ melts at 192°C — hardly consistent with ionic bonding, and the other two halides are also rather low-melting. Structural studies show that when $AlCl_3$ vaporizes or dissolves in a non-polar solvent it forms a dimer Al_2Cl_6. The two other halides exist only as dimers in all states.



The structural formula of the Al_2Cl_6 molecule shows that the aluminum atoms are bonded to four chlorines, two of which are shared between the two metal atoms. The arrows represent coordinate covalent bonds in which the bonding electrons both come from the same atom (chlorine in this case.)



As shown at the right above, the aluminum atoms can be considered to be located at the centers of two tetrahedra that possess one edge in common.

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3.3.5: Network Covalent Atomic Solids- Carbon and Silicates

Covalent Network Solids

Covalent solids are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure **3.3.5.1**, consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.

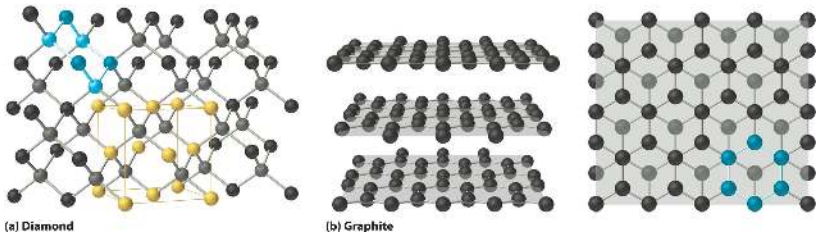


Figure **3.3.5.1**: The Structures of Diamond and Graphite. (a) Diamond consists of sp3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer.

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 12.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 12.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure **3.3.5.1**. It contains planar networks of six-membered rings of sp2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized 2pz orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 9. In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons. Table **3.3.5.2** compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table **3.3.5.2**: A Comparison of Intermolecular (ΔHsub) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226
iodine (s)	62.42	149

Carbon: An example of an Covalent Network Solid

In network solids, conventional chemical bonds hold the chemical subunits together. The bonding between chemical subunits, however, is identical to that within the subunits, resulting in a continuous network of chemical bonds. One common examples of network solids are diamond (a form of pure carbon) Carbon exists as a pure element at room temperature in three different forms: graphite (the most stable form), diamond, and fullerene.

Diamonds

The structure of diamond is shown at the right in a "ball-and-stick" format. The balls represent the carbon atoms and the sticks represent a covalent bond. Be aware that in the "ball-and-stick" representation the size of the balls do not accurately represent the size of carbon atoms. In addition, a single stick is drawn to represent a covalent bond irrespective of whether the bond is a single, double, or triple bond or requires resonance structures to represent. In the diamond structure, all bonds are single covalent bonds (σ bonds). The "space-filling" format is an alternate representation that displays atoms as spheres with a radius equal to the van der Waals radius, thus providing a better sense of the size of the atoms.

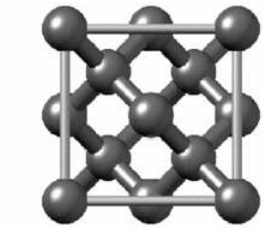


Figure **3.3.5.2**: Rotating model of diamond cubic. Figure used with permission from Wikipedia

Notice that diamond is a network solid. The entire solid is an "endless" repetition of carbon atoms bonded to each other by covalent bonds. (In the display at the right, the structure is truncated to fit in the display area.)

Questions to consider:

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in diamond?
- The diamond structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- Diamond are renowned for its hardness. Explain why this property is expected on the basis of the structure of diamond.

Graphite

The most stable form of carbon is graphite. Graphite consists of sheets of carbon atoms covalently bonded together. These sheets are then stacked to form graphite. Figure **3.3.5.3** shows a ball-and-stick representation of graphite with sheets that extended "indefinitely" in the xy plane, but the structure has been truncated for display purposed. Graphite may also be regarded as a network solid, even though there is no bonding in the z direction. Each layer, however, is an "endless" bonded network of carbon atoms.

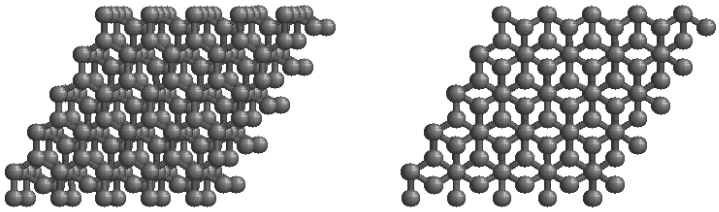


Figure **3.3.5.3**: Animation of a rotating graphite structure. This is a stereogram and can be viewed in 3D if a viewer's eyes are crossed slightly to overlap the two panels. Images used with permission from Wikipedia.

Questions to consider:

- What is the bonding geometry around each carbon?
- What is the hybridization of carbon in graphite?
- The a layer of the graphite structure consists of a repeating series of rings. How many carbon atoms are in a ring?
- What force holds the carbon sheets together in graphite?
- Graphite is very slippery and is often used in lubricants. Explain why this property is expected on the basis of the structure of graphite.
- The slipperiness of graphite is enhanced by the introduction of impurities. Where would such impurities be located and why would they make graphite a better lubricant?

Fullerenes

Until the mid 1980's, pure carbon was thought to exist in two forms: graphite and diamond. The discovery of C_{60} molecules in interstellar dust in 1985 added a third form to this list. The existence of C_{60}, which resembles a soccer ball, had been hypothesized by theoretians for many years. In the late 1980's synthetic methods were developed for the synthesis of C_{60}, and the ready availability of this form of carbon led to extensive research into its properties.

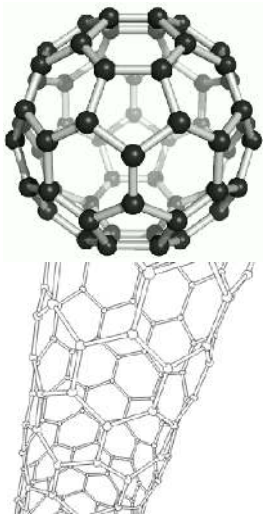


Figure **3.3.5.4**: Example of fullerenes: a buckyball (*C_{60} on left and an extended bucktube. Images used with permission from Wikipedia.*

The C_{60} molecule (Figure **3.3.5.4**; left), is called buckminsterfullerene, though the shorter name fullerene is often used. The name is a tribute to the American architect R. Buckminster Fuller, who is famous for designing and constructing geodesic domes which bear a close similarity to the structure of C_{60}. As is evident from the display, C_{60} is a sphere composed of six-member and five-member carbon rings. These balls are sometimes fondly referred to as "Bucky balls". It should be noted that fullerenes are an entire class of pure carbon compounds rather than a single compound. A distorted sphere containing more than 60 carbon atoms have also been found, and it is also possible to create long tubes (Figure **3.3.5.4**; right). All of these substances are pure carbon.

to Consider

- What is the bonding geometry around each carbon? (Note that this geometry is distorted in C_{60}.)
- What is the hybridization of carbon in fullerene?
- A single crystal of C60 falls into which class of crystalline solids?
- It has been hypothesized that C60 would make a good lubricant. Why might C60 make a good lubricant?

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SECTION OVERVIEW

3.4: SOLUTIONS

SOLUTIONS

3.4.1: Thermodynamics of Mixing

3.4.2: Partial Molar Volume

3.4.3: Colligative Properties

3.4.4: Solubility

3.4.5: Non-ideality in Solutions - Activity

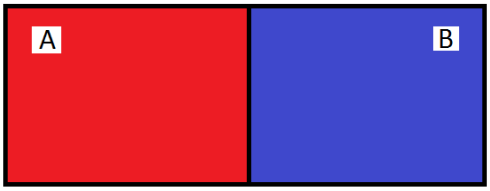
3.4.E: Mixtures and Solutions (Exercises)

3.4.S: Mixtures and Solutions (Summary)

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3.4.1: Thermodynamics of Mixing

A natural place to begin a discussion of mixtures is to consider a mixture of two gases. Consider samples of the two gases filling two partitions in a single container, both at the same pressure, temperature, having volumes V_A and V_B.



After being allowed to mix isothermally, the partial pressures of the two gases will drop by a factor of 2 (although the total pressure will still be the original value) and the volumes occupied by the two gases will double.



Enthalpy of Mixing

Assuming ideal behavior, so that interactions between individual gas molecules are unimportant, it is fairly easy to calculate \(Delta H) for each gas, as it is simply an isothermal expansion. The total enthalpy of mixing is then given by

$$\Delta H_{mix} = \Delta H_A + \Delta H_B$$

And since the enthalpy change for an **isothermal expansion of an ideal gas is zero**,

$$\Delta H_{mix} = 0$$

is a straight-forward conclusion. This will be the criterion for an **ideal mixture**.

In general, real mixtures will deviate from this limiting ideal behavior due to interactions between molecules and other concerns. Also, many substances undergo chemical changes when they mix with other substances. But for now, we will limit ourselves to discussing mixtures in which no chemical reactions take place.

Entropy of Mixing

The entropy change induced due to isothermal mixing (assuming again no interactions between the molecules in the gas mixture) is again going to be the sum of the contributions from isothermal expansions of the two gases. Fortunately, entropy changes for isothermal expansions are easy to calculate for ideal gases.

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

If we use the initial volumes V_A and V_B for the initial volumes of gases A and B, the total volume after mixing is $V_A + V_B$, and the total entropy change is

$$\Delta S_{mix} = n_A R\ln\left(\frac{V_A + V_B}{V_A}\right) + n_A R\ln\left(\frac{V_A + V_B}{V_B}\right)$$

Noting that the term

$$\frac{V_A + V_B}{V_A} = \frac{1}{\chi_A}$$

where χ_A is the mole fraction of A after mixing, and that n_A can be expresses as the product of χ_A and the total number of moles, the expression can be rewritten

$$\Delta S_{mix} = n_{tot} R\left[-\chi_A \ln(\chi_A) - \chi_B \ln(\chi_B)\right]$$

It should be noted that because the mole fraction is always between 0 and 1, that $\ln(\chi_B) < 0$. As such, the entropy change for a system undergoing isothermal mixing is always positive, as one might expect (since mixing will make the system less ordered).

> *The entropy change for a system undergoing isothermal mixing is always positive.*

Free Energy of Mixing

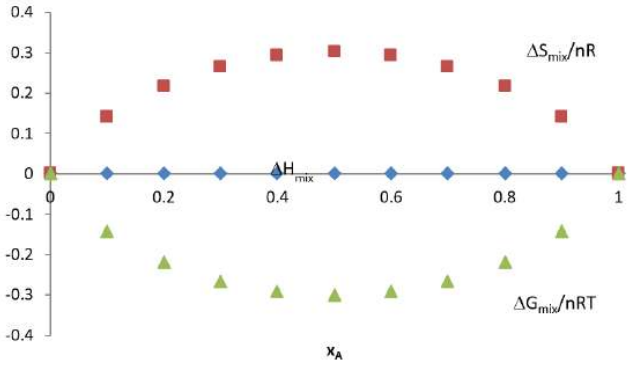
Calculating ΔG_{mix} should be no more difficult than calculating ΔS_{mix}. For *isothermal mixing* and constant total pressure

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

and so it follows from above that for the isothermal mixing of two gases at constant total pressure

$$\Delta G_{mix} = n_{tot} RT\left[-\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)\right]$$

The relationships describing the isothermal mixing of two ideal gases A and B is summarized in the graph below.



Again, because $\ln(\chi_i) < 0$, then $\Delta G_{mix} < 0$ implying that mixing is **always** a spontaneous process for an *ideal solution*. This is true for gases. But for many combinations of liquids or solids, the strong intermolecular forces may make mixing unfavorable (for example in the case of vegetable oil and water). Also, these interactions may make the volume non-additive as well (as in the case of ethanol and water).

> *Mixing is always a spontaneous process for an ideal solution.*

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3.4.2: Partial Molar Volume

The **partial molar volume** of compound A in a mixture of A and B can be defined as

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B}$$

Using this definition, a change in volume for the mixture can be described using the total differential of V:

$$dV = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,n_B} dn_A + \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A} dn_B$$

or

$$dV = V_a\, dn_A + V_b\, dn_B$$

and integration yields

$$V = \int_0^{n_A} V_a\, dn_A + \int_0^{n_B} V_b\, dn_B$$

$$V = V_a\, n_A + V_b\, n_B$$

This result is important as it demonstrates an important quality of partial molar quantities. Specifically, if ξ_i represents the partial molar property X for component i of a mixture, The total property X for the mixture is given by

$$X = \sum_i \xi_i n_i$$

It should be noted that while the volume of a substance is never negative, the partial molar volume can be. An example of this appears in the dissolution of a strong electrolyte in water. Because the water molecules in the solvation sphere of the ions are physically closer together than they are in bulk pure water, there is a volume decrease when the electrolyte dissolves. This is easily observable at high concentrations where a larger fraction of the water in the sample is tied up in solvation of the ions.

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3.4.3: Colligative Properties

Colligative properties are important properties of **solutions** as they describe how the properties of the **solvent** will change as **solute** (or solutes) is (are) added. Before discussing these important properties, let us first review some definitions.

- **Solution** – a homogeneous mixture.
- **Solvent** – The component of a solution with the largest mole fraction
- **Solute** – Any component of a solution that is not the solvent.

Solutions can exist in solid (alloys of metals are an example of solid-phase solutions), liquid, or gaseous forms. For the most part, this discussion will focus on liquid-phase solutions.

Freezing Point Depression

In general (and as will be discussed in Chapter 8 in more detail) a liquid will freeze when

$$\mu_{solid} \leq \mu_{liquid}$$

As such, the freezing point of the solvent in a solution will be affected by anything that changes the chemical potential of the solvent. As it turns out, the chemical potential of the solvent is reduced by the presence of a solute.

In a mixture, the chemical potential of component A can be calculated by

$$\mu_A = \mu_A^o + RT \ln \chi_A \tag{3.4.3.1}$$

And because χ_A is always less than (or equal to) 1, the chemical potential is always reduced by the addition of another component.

The condition under which the solvent will freeze is

$$\mu_{A,solid} = \mu_{A,liquid}$$

where the chemical potential of the liquid is given by Equation 3.4.3.1, which rearrangement to

$$\frac{\mu_A - \mu_A^o}{RT} = \ln \chi_A$$

To evaluate the temperature dependence of the chemical potential, it is useful to consider the temperature derivative at constant pressure.

$$\left[\frac{\partial}{\partial T}\left(\frac{\mu_A - \mu_A^o}{RT}\right)\right]_p = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

$$-\frac{\mu_A - \mu_A^o}{RT^2} + \frac{1}{RT}\left[\left(\frac{\partial \mu_A}{\partial T}\right)_p - \left(\frac{\partial \mu_A^o}{\partial T}\right)_p\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{3.4.3.2}$$

Recalling that

$$\mu = H = TS$$

and

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S$$

Equation 3.4.3.2 becomes

$$-\frac{(H_A - TS_A - H_A^o + TS_A^o)}{RT^2} + \frac{1}{RT}\left[-S_A + S_A^o\right] = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p \tag{3.4.3.3}$$

And noting that in the case of the solvent freezing, H_A^o is the enthalpy of the pure solvent in solid form, and H_A is the enthalpy of the solvent in the liquid solution. So

$$H_A^o - H_a = \Delta H_{fus}$$

Equation 3.4.3.3 then becomes

$$\frac{\Delta H_{fus}}{RT^2} - \cancel{\frac{-S_A + S_A^o}{RT}} + \cancel{\frac{-S_A + S_A^o}{RT}} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

or

$$\frac{\Delta H_{fus}}{RT^2} = \left(\frac{\partial \ln \chi_A}{\partial T}\right)_p$$

Separating the variables puts the equation into an integrable form.

$$\int_{T^o}^{T} \frac{\Delta H_{fus}}{RT^2} dT = \int d \ln \chi_A \tag{3.4.3.4}$$

where T^o is the freezing point of the pure solvent and T is the temperature at which the solvent will begin to solidify in the solution. After integration of Equation 3.4.3.4:

$$-\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T^o}\right) = \ln \chi_A \tag{3.4.3.5}$$

This can be simplified further by noting that

$$\frac{1}{T} - \frac{1}{T^o} = \frac{T^o - T}{TT^o} = \frac{\Delta T}{TT^o}$$

where ΔT is the difference between the freezing temperature of the pure solvent and that of the solvent in the solution. Also, for small deviations from the pure freezing point, TT^o can be replaced by the approximate value $(T^o)^2$. So the Equation 3.4.3.5 becomes

$$-\frac{\Delta H_{fus}}{R(T^o)^2}\Delta T = \ln \chi_A \tag{3.4.3.6}$$

Further, for dilute solutions, for which χ_A, the mole fraction of the solvent is very nearly 1, then

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

where χ_B is the mole fraction of the solute. After a small bit of rearrangement, this results in an expression for freezing point depression of

$$\Delta T = \left(\frac{R(T^o)^2}{\Delta H_{fus}}\right)\chi_B$$

The first factor can be replaced by K_f:

$$\frac{R(T^o)^2}{\Delta H_{fus}} = K_f$$

which is the **cryoscopic constant** for the solvent.

ΔT gives the magnitude of the reduction of freezing point for the solution. Since ΔH_{fus} and T^o are properties of the solvent, the freezing point depression property is independent of the solute and is a property based solely on the nature of the solvent. Further, since χ_B was introduced as $(1 - \chi_A)$, it represents the sum of the mole fractions of all solutes present in the solution.

It is important to keep in mind that for a real solution, freezing of the solvent changes the composition of the solution by decreasing the mole fraction of the solvent and increasing that of the solute. As such, the magnitude of ΔT will change as the freezing process continually removes solvent from the liquid phase of the solution.

Boiling Point Elevation

The derivation of an expression describing boiling point elevation is similar to that for freezing point depression. In short, the introduction of a solute into a liquid solvent lowers the chemical potential of the solvent, cause it to favor the liquid phase over the

vapor phase. As sch, the temperature must be increased to increase the chemical potential of the solvent in the liquid solution until it is equal to that of the vapor-phase solvent. The increase in the boiling point can be expressed as

$$\Delta T = K_b \chi_B$$

where

$$\frac{R(T^o)^2}{\Delta H_{vap}} = K_b$$

is called the **ebullioscopic constant** and, like the cryoscopic constant, is a property of the solvent that is independent of the solute or solutes. A very elegant derivation of the form of the models for freezing point depression and boiling point elevation has been shared by F. E. Schubert (Schubert, 1983).

Cryoscopic and ebullioscopic constants are generally tabulated using molality as the unit of solute concentration rather than mole fraction. In this form, the equation for calculating the magnitude of the freezing point decrease or the boiling point increase is

$$\Delta T = K_f m$$

or

$$\Delta T = K_b m$$

where m is the concentration of the solute in moles per kg of solvent. Some values of K_f and K_b are shown in the table below.

Substance	K_f (°C kg mol-1)	T_f^o (°C)	K_b (°C kg mol-1)	T_b^o (°C)
Water	1.86	0.0	0.51	100.0
Benzene	5.12	5.5	2.53	80.1
Ethanol	1.99	-114.6	1.22	78.4
CCl_4	29.8	-22.3	5.02	76.8

Example 3.4.3.1:

The boiling point of a solution of 3.00 g of an unknown compound in 25.0 g of CCl_4 raises the boiling point to 81.5 °C. What is the molar mass of the compound?

Solution

The approach here is to find the number of moles of solute in the solution. First, find the concentration of the solution:

$$(85.5\,°C - 76.8\,°C) = (5.02\,°C\,Kg/mol)\,m$$

$$m = 0.936\,mol/kg$$

Using the number of kg of solvent, one finds the number for moles of solute:

$$\left(0.936\,mol/\cancel{kg}\right)(0.02\,\cancel{kg}) = 0.0234\,mol$$

The ratio of mass to moles yields the final answer:

$$\frac{3.00\,g}{0.0234} = 128 g/mol$$

Vapor Pressure Lowering

For much the same reason as the lowering of freezing points and the elevation of boiling points for solvents into which a solute has been introduced, the vapor pressure of a volatile solvent will be decreased due to the introduction of a solute. The magnitude of this decrease can be quantified by examining the effect the solute has on the chemical potential of the solvent.

In order to establish equilibrium between the solvent in the solution and the solvent in the vapor phase above the solution, the chemical potentials of the two phases must be equal.

$$\mu_{vapor} = \mu_{solvent}$$

If the solute is not volatile, the vapor will be pure, so (assuming ideal behavior)

$$\mu^o_{vap} + RT \ln \frac{p'}{p^o} = \mu^o_A + RT \ln \chi_A \tag{3.4.3.7}$$

Where p' is the vapor pressure of the solvent over the solution. Similarly, for the pure solvent in equilibrium with its vapor

$$\mu^o_A = \mu^o_{vap} + RT \ln \frac{p_A}{p^o} \tag{3.4.3.8}$$

where p^o is the standard pressure of 1 atm, and p_A is the vapor pressure of the pure solvent. Substituting Equation 3.4.3.8 into Equation 3.4.3.7 yields

$$\cancel{\mu^o_{vap}} + RT \ln \frac{p'}{p^o} = \left(\cancel{\mu^o_{vap}} + RT \ln \frac{p_A}{p^o} \right) + RT \ln \chi_A$$

The terms for μ^o_{vap} cancel, leaving

$$RT \ln \frac{p'}{p^o} = RT \ln \frac{p_A}{p^o} + RT \ln \chi_A$$

Subtracting $RT \ln(P_A/P^o)$ from both side produces

$$RT \ln \frac{p'}{p^o} - RT \ln \frac{p_A}{p^o} = RT \ln \chi_A$$

which rearranges to

$$RT \ln \frac{p'}{p_A} = RT \ln \chi_A$$

Dividing both sides by RT and then exponentiating yields

$$\frac{p'}{p_A} = \chi_A$$

or

$$p' = \chi_A p_A \tag{3.4.3.9}$$

This last result is Raoult's Law. A more formal derivation would use the fugacities of the vapor phases, but would look essentially the same. Also, as in the case of freezing point depression and boiling point elevations, this derivation did not rely on the nature of the solute! However, unlike freezing point depression and boiling point elevation, this derivation did not rely on the solute being dilute, so the result should apply the entire range of concentrations of the solution.

Example 3.4.3.2:

Consider a mixture of two volatile liquids A and B. The vapor pressure of pure A is 150 Torr at some temperature, and that of pure B is 300 Torr at the same temperature. What is the total vapor pressure above a mixture of these compounds with the mole fraction of B of 0.600. What is the mole fraction of B in the vapor that is in equilibrium with the liquid mixture?

Solution

Using Raoult's Law (Equation 3.4.3.9)

$$p_A = (0.400)(150\,Toor) = 60.0\,Torr$$

$$p_B = (0.600)(300\,Toor) = 180.0\,Torr$$

$$p_{tot} = p_A + p_B = 240\,Torr$$

To get the mole fractions in the gas phase, one can use Dalton's Law of partial pressures.

$$\chi_A = \frac{p_A}{p_{tot}} = \frac{60.0\,Torr}{240\,Torr} = 0.250$$

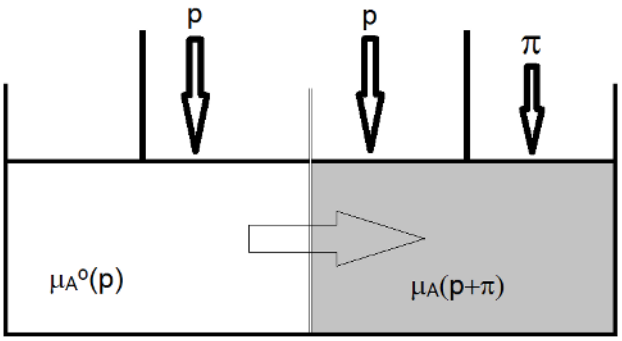
$$\chi_B = \frac{p_B}{p_{tot}} = \frac{180.0\,Torr}{240\,Torr} = 0.750$$

And, of course, it is also useful to note that the sum of the mole fractions is 1 (as it must be!)

$$\chi_A + \chi_B = 1$$

Osmotic Pressure

Osmosis is a process by which solvent can pass through a semi-permeable membrane (a membrane through which solvent can pass, but not solute) from an area of low solute concentration to a region of high solute concentration. The **osmotic pressure** is the pressure that when exerted on the region of high solute concentration will halt the process of osmosis.



The nature of osmosis and the magnitude of the osmotic pressure can be understood by examining the chemical potential of a pure solvent and that of the solvent in a solution. The chemical potential of the solvent in the solution (before any extra pressure is applied) is given by

$$\mu_A = \mu_A^o + RT \ln \chi_A$$

And since $x_A < 1$, the chemical potential is of the solvent in a solution is always lower than that of the pure solvent. So, to prevent osmosis from occurring, something needs to be done to raise the chemical potential of the solvent in the solution. This can be accomplished by applying pressure to the solution. Specifically, the process of osmosis will stop when the chemical potential solvent in the solution is increased to the point of being equal to that of the pure solvent. The criterion, therefore, for osmosis to cease is

$$\mu_A^o(p) = \mu_A(\chi_b, +\pi)$$

To solve the problem to determine the magnitude of p, the pressure dependence of the chemical potential is needed in addition to understanding the effect the solute has on lowering the chemical potential of the solvent in the solution. The magnitude, therefore, of the increase in chemical potential due to the application of excess pressure p must be equal to the magnitude of the reduction of chemical potential by the reduced mole fraction of the solvent in the solution. We already know that the chemical potential of the solvent in the solution is reduced by an amount given by

$$\mu_A^o - \mu_A = RT \ln \chi_A$$

And the increase in chemical potential due to the application of excess pressure is given by

$$\mu(p+\pi) = \mu(p) + \int_p^\pi \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

The integrals on the right can be evaluated by recognizing

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

where V is the molar volume of the substance. Combining these expressions results in

$$-RT \ln \chi_A = \int_p^{p+\pi} V \, dp$$

If the molar volume of the solvent is independent of pressure (has a very small value of κ_T – which is the case for most liquids) the term on the right becomes.

$$\int_p^{\pi} V \, dP = Vp|_p^{p+\pi} = V\pi$$

Also, for values of χ_A very close to 1

$$\ln \chi_A \approx -(1 - \chi_A) = -\chi_B$$

So, for dilute solutions

$$\chi_B RT = V\pi$$

Or after rearrangement

$$\pi \frac{\chi_B RT}{V}$$

again, where V is the molar volume of the solvent. And finally, since χ_B/V is the concentration of the solute B for cases where $n_B \ll n_A$. This allows one to write a simplified version of the expression which can be used in the case of very dilute solutions

$$\pi = [B]RT$$

When a pressure exceeding the osmotic pressure π is applied to the solution, the chemical potential of the solvent in the solution can be made to exceed that of the pure solvent on the other side of the membrane, causing reverse osmosis to occur. This is a very effective method, for example, for recovering pure water from a mixture such as a salt/water solution.

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3.4.4: Solubility

The maximum solubility of a solute can be determined using the same methods we have used to describe colligative properties. The chemical potential of the solute in a liquid solution can be expressed

$$\mu_B(solution) = \mu_B^o(liquid) + RT \ln \chi_B$$

If this chemical potential is lower than that of a pure solid solute, the solute will dissolve into the liquid solvent (in order to achieve a lower chemical potential!) So the point of saturation is reached when the chemical potential of the solute in the solution is equal to that of the pure solid solute.

$$\mu_B^o(solid) = \mu_B^o(liquid) + RT \ln \chi_B$$

Since the mole fraction at saturation is of interest, we can solve for $\ln(\chi_B)$.

$$\ln \chi_B = \frac{\mu_B^o(solid) = \mu_B^o(liquid)}{RT}$$

The difference in the chemical potentials is the molar Gibbs function for the phase change of fusion. So this can be rewritten

$$\ln \chi_B = \frac{-\Delta G_{fus}^o}{RT}$$

It would be convenient if the solubility could be expressed in terms of the enthalpy of fusion for the solute rather than the Gibbs function change. Fortunately, the Gibbs-Helmholtz equation gives us a means of making this change. Noting that

$$\left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_p = \frac{\Delta H}{T^2}$$

Differentiation of the above expression for $\ln(\chi_B)$ with respect to T at constant p yields

$$\left(\frac{\partial \ln \chi_B}{\partial T} \right)_p = \frac{1}{R} \frac{\Delta H_{fus}}{T^2}$$

Separating the variables puts this into an integrable form that can be used to see how solubility will vary with temperature:

$$\int_0^{\ln \chi_B} d \ln \chi_B = \frac{1}{R} \int_{T_f}^{T} \frac{\Delta H_{fus} dT}{T^2}$$

So if the enthalpy of fusion is constant over the temperature range of T_f to the temperature of interest,

$$\ln \chi_B = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_f} - \frac{1}{T} \right)$$

And χ_B will give the mole fraction of the solute in a saturated solution at the temperature T. The value depends on both the enthalpy of fusion, and the normal melting point of the solute.

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3.4.5: Non-ideality in Solutions - Activity

The bulk of the discussion in this chapter dealt with ideal solutions. However, real solutions will deviate from this kind of behavior. So much as in the case of gases, where fugacity was introduced to allow us to use the ideal models, **activity** is used to allow for the deviation of real solutes from limiting ideal behavior. The activity of a solute is related to its concentration by

$$a_B = \gamma \frac{m_B}{m^o}$$

where γ is the **activity coefficient**, m_B is the molaliy of the solute, and m^o is unit molality. The activity coefficient is unitless in this definition, and so the activity itself is also unitless. Furthermore, the activity coefficient approaches unity as the molality of the solute approaches zero, insuring that dilute solutions behave ideally. The use of activity to describe the solute allows us to use the simple model for chemical potential by inserting the activity of a solute in place of its mole fraction:

$$\mu_B = \mu_B^o + RT \ln a_B$$

The problem that then remains is the measurement of the activity coefficients themselves, which may depend on temperature, pressure, and even concentration.

Activity Coefficients for Ionic Solutes

For an ionic substance that dissociates upon dissolving

$$MX(s) \rightarrow M^+(aq) + X^-(aq)$$

the chemical potential of the cation can be denoted μ_+ and that of the anion as μ_-. For a solution, the total molar Gibbs function of the solutes is given by

$$G = \mu_+ + \mu_-$$

where

$$\mu = \mu^* + RT \ln a$$

where \(\mu^*\) denotes the chemical potential of an ideal solution, and a is the activity of the solute. Substituting his into the above relationship yields

$$G = \mu_+^* + RT \ln a_+ + \mu_-^* + RT \ln a_-$$

Using a molal definition for the activity coefficient

$$a_i = \gamma_i m_i$$

The expression for the total molar Gibbs function of the solutes becomes

$$G = \mu_+^* + RT \ln \gamma_+ m_+ + \mu_-^* + RT \ln \gamma_- m_-$$

This expression can be rearranged to yield

$$G = \mu_+^* + \mu_-^* + RT \ln m_+ m_- + RT \ln \gamma_+ \gamma_-$$

where all of the deviation from ideal behavior comes from the last term. Unfortunately, it impossible to experimentally deconvolute the term into the specific contributions of the two ions. So instead, we use a geometric average to define the **mean activity coefficient**, $\gamma_\pm$.

$$\gamma_\pm = \sqrt{\gamma_+ \gamma_-}$$

For a substance that dissociates according to the general process

$$M_x X_y(s) \rightarrow xM^{y+}(aq) + yX^{x-}(aq)$$

the expression for the mean activity coefficient is given by

$$\gamma_\pm = (\gamma_+^x \gamma_-^y)^{1/x+y}$$

Debeye-Hückel Law

In 1923, Debeye and Hückel (Debye & Hückel, 1923) suggested a means of calculating the mean activity coefficients from experimental data. Briefly, they suggest that

$$\log_{10}\gamma_{\pm} = \frac{1.824 \times 10^6}{(\epsilon T)^{3/2}}|z_+ + z_-|\sqrt{I}$$

where ϵ is the dielectric constant of the solvent, T is the temperature in K, z_+ and z_- are the charges on the ions, and I is the **ionic strength** of the solution. I is given by

$$I = \frac{1}{2}\frac{m_+ z_+^2 + m_- z_-^2}{m^o}$$

For a solution in water at 25 ^oC,

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3.4.E: Mixtures and Solutions (Exercises)

Q7.1

The compression factor (Z) for O_2 at 200 K is measured to have the following values:

p (atm)	Z
1.000	0.9970
4.000	0.9880
7.000	0.9788
10.000	0.9700

Using numerical integration, calculate the fugacity constant for O_2 at 200 K from these data.

Q7.2

The normal boiling point of ethanol is 78.4 ^oC. Its enthalpy of vaporization is 38.6 kJ/mol. Estimate the vapor pressure of ethanol at 24.4 ^oC.

Q7.3

When 20.0 grams of an unknown nonelectrolyte compound are dissolved in 500.0 grams of benzene, the freezing point of the resulting solution is 3.77 °C. The freezing point of pure benzene is 5.444 °C and the cryoscopic constant (K_f) for benzene is 5.12 °C/m. What is the molar mass of the unknown compound?

Q7.4

Consider a mixture of two volatile liquids, A and B. The vapor pressure of pure liquid A is 324.3 Torr and that of pure liquid B is 502.3 Torr. What is the total vapor pressure over a mixture of the two liquids for which x_B = 0.675?

Q7.5

Consider the following expression for osmotic pressure

$$\pi V = \chi_B RT \tag{3.4.E.1}$$

where π is the osmotic pressure, V is the molar volume of the solvent, χ_B is the mole fraction of the solute, R is the gas law constant, and T is the temperature (in Kelvin).

The molar volume of a particular solvent is 0.0180 L/mol. 0.200 g of a solute (B) is dissolved in 1.00 mol of the solvent. The osmotic pressure of the solvent is then measured to be 0.640 atm at 298 K. Calculate the molar mass of the solute.

Q7.6

At 300 K, the vapor pressure of HCl(g) over a solution of HCl in $GeCl_4$ are summarized in the following table. Calculate the Henry's Law constant for HCl based on these data.

χ_{HCl}	P_{HCl} (kPa)
0.005	32.0
0.012	76.9
0.019	121.8

Q7.7

Consider the mixing of 1.00 mol of hexane (C_6H_{12}) with 1.00 mole of benzene (C_6H_6). Calculate \(\Delta H\), \(\Delta S\), and \(\Delta G\) of mixing, of the mixing occurs ideally at 298 K.

Contributors and Attributions

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3.4.S: Mixtures and Solutions (Summary)

Learning Objectives

After mastering the material in this chapter, one will be able to

1. Describe the thermodynamics of mixing and calculate ΔH, ΔS, and ΔG or mixing for an ideal solution.
2. Define chemical potential, and calculate its value as a function of pressure and composition.
3. Derive expressions for the colligative properties and perform calculations using the relationships.
4. Estimate the maximum solubility of a solute in a solvent based on the concept equality of chemical potential at saturation.
5. Define fugacity and activity.
6. Calculate the mean activity coefficients of ions in solution based on the ionic strength of the solution.

Vocabulary and Concepts

- activity
- activity coefficient
- chemical potential
- cryoscopic constant
- ebullioscopic constant
- enthalpy of mixing
- fugacity
- fugacity coefficient
- Gibbs-Duhem equation
- ideal mixture
- ionic strength
- mean activity coefficient
- osmosis
- osmotic pressure
- Raoult's Law
- solute
- solution
- solvent
- the partial molar Gibbs function

References

1. Debye, P., & Hückel, E. (1923). Zur Theorie der Electrolyte. *Physikalische Zeitschrift, 24*, 185-206.
2. Schubert, F. E. (1983). Depression of Freezing Point and Elevation of Boiling Point. *Journal of Chemical Education, 60*(1), 88. doi:10.1021/ed060p87.2

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4.3.3: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

4.4: Q chases K

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SECTION OVERVIEW

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RATE

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4.1.6: 2nd order Rate Laws

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4.1.8: The Method of Half-Lives

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4.1.1: Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 4.1.1.1:

Under a certain set of conditions, the rate of the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\ M/s$$

$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\ M/s$$

$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\ M/s$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

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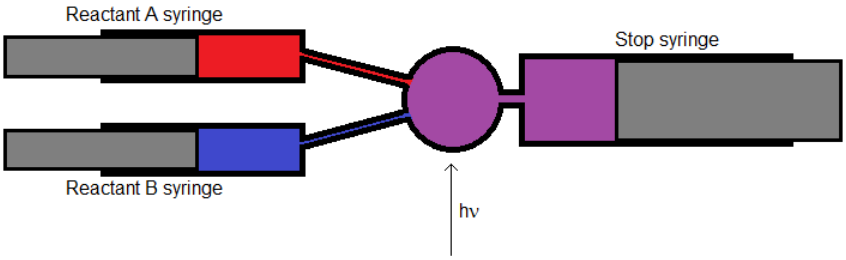
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4.1.2: Measuring Reaction Rates

There are several methods that can be used to measure chemical reactions rates. A common method is to use spectrophotometry to monitor the concentration of a species that will absorb light. If it is possible, it is preferable to measure the appearance of a product rather than the disappearance of a reactant, due to the low background interference of the measurement. However, high-quality kinetic data can be obtained either way.

The Stopped-Flow Method

The **stopped-flow method** involves using flow control (which can be provided by syringes or other valves) to control the flow of reactants into a mixing chamber where the reaction takes place. The reaction mixture can then be probed spectrophotometrically. Stopped-flow methods are commonly used in physical chemistry laboratory courses (Progodich, 2014).



Some methods depend on measuring the initial rate of a reaction, which can be subject to a great deal of experimental uncertainty due to fluctuations in instrumentation or conditions. Other methods require a broad range of time and concentration data. These methods tend to produce more reliable results as they can make use of the broad range of data to smooth over random fluctuations that may affect measurements. Both approaches (initial rates and full concentration profile data methods) will be discussed below.

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4.1.3: Rate Laws

A rate law is any mathematical relationship that relates the concentration of a reactant or product in a chemical reaction to time. Rate laws can be expressed in either derivative (or ratio, for finite time intervals) or integrated form. One of the more common general forms a rate law for the reaction

$$A + B \rightarrow products$$

may take is

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}$$

where k, α, and β are experimentally determined values. However, a rate law can take many different forms, some of which can be quite intricate and complex. The powers α and β need not be integers. For example

$$\text{rate} = k[A]^{\alpha}[B]^{1/2} \tag{4.1.3.1}$$

is a rate law that is observed for some reactions. Sometimes, the concentrations of products must be included.

$$\text{rate} = \frac{k[A]^{1/2}[B]}{[P]}$$

In some cases, the concentration for a catalyst or enzyme is important. For example, many enzyme mitigated reactions in biological systems follow the Michaelis-Menten rate law, which is of the form

$$\text{rate} = \frac{V_{max}[S]}{K_m + [S]}$$

where V_{max} and K_M are factors that are determined experimentally, and $[S]$ is the concentration of the substrate in the reaction.

Order

For those cases where the rate law can be expressed in the form

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$$

where A, B, and C are reactants (or products or catalysts, etc.) involved in the reaction, the reaction is said to be of α order in A, β order in B, and γ order in C. The reaction is said to be $\alpha + \beta + \gamma$ order overall. Some examples are shown in the following table:

Table 11.3.1: Example Rate Laws

Rate law	Order with respect to A	Order with respect to B	Order with respect to C	Overall order
$\text{rate} = k$	0	0	0	0
$\text{rate} = k[A]$	0	0	0	1
$\text{rate} = k[A]^2$	0	0	0	2
$\text{rate} = k[A][B]$	0	1	0	2
$\text{rate} = k[A]^2[B]$	0	1	0	3
$\text{rate} = k[A][B][C]$	0	1	1	3

Reaction orders can also be fractional such as for Equation 4.1.3.1 which is 1st order in A, and half order in B. The order can also be negative such as

$$\text{rate} = k\frac{[A]}{[B]}$$

which is 1st order in A, and -1 order in B. In this case, an build-up of the concentration of B will retard (slow) the reaction.

In all cases, the order of the reaction with respect to a specific reactant or product (or catalyst, or whatever) must be determined experimentally. As a general rule, the stoichiometry cannot be used to predict the form of the rate law. However, the rate law can be used to gain some insight into the possible pathways by which the reaction can proceed. That is the topic of Chapter 12. For now we will focus on three useful methods that are commonly used in chemistry to determine the rate law for a reaction from experimental data.

Empirical Methods

Perhaps the simplest of the methods to be used are the empirical methods, which rely on the qualitative interpretation of a graphical representation of the concentration vs time profile. In these methods, some function of concentration is plotted as a function of time, and the result is examined for a linear relationship. For the following examples, consider a reaction of the form

$$A + B \rightarrow products$$

in which A is one of the reactants. In order to employ these empirical methods, one must generate the forms of the integrated rate laws.

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4.1.4: 0th order Rate Law

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt} = k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A] = -k\int_{t_o}^{t} dt$$

which yields

$$[A] - [A]_o = -kt$$

or

$$[A] = [A]_o - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0th order kinetics. If they are not, other possibilities must be considered.

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4.1.5: 1st order rate law

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \qquad (4.1.5.1)$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is $\ln[A]_0$.

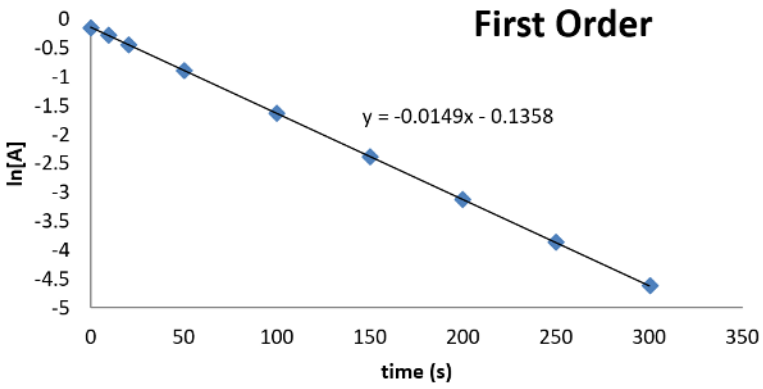
Example 4.1.5.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation 4.1.5.1) can be expressed in exponential form:

$$[A] = [A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

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4.1.6: 2nd order Rate Laws

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{4.1.6.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{4.1.6.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 4.1.6.2 is

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2nd order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A + B \rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt} = k[A][B]$$

and

$$-\frac{d[B]}{dt} = k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A] = [A]_o - [P] \tag{4.1.6.3}$$

and

$$[B] = [B]_o - [P] \tag{4.1.6.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt} = k[A][B] \tag{4.1.6.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 4.1.6.3 and 4.1.6.4) into the rate law expression (Equation 4.1.6.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{4.1.6.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o - [P])([B] = [B]_o - [P])} = k\,dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]} \frac{d[P]}{([A]_o - [P])([B]_o - [P])} = \int_{t=0}^{t} k\,dt$$

Consulting a table of integrals reveals that for $a \neq b$[1],

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0 \neq [B]_0$) results in

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right)\Bigg|_0^{[A]} = k\,t\Big|_0^t$$

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right) - \frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right) = k\,t \tag{4.1.6.7}$$

Substituting Equations 4.1.6.3 and 4.1.6.4 into Equation 4.1.6.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right) = kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m = ([B]_0 - [A]_0)k.$$

In the limit at $[A]_0 = [B]_0$, then $[A] = [B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate} = k[A]^2$$

and integrate direct like in Equation 4.1.6.1 and the integrated rate law is (as before)

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

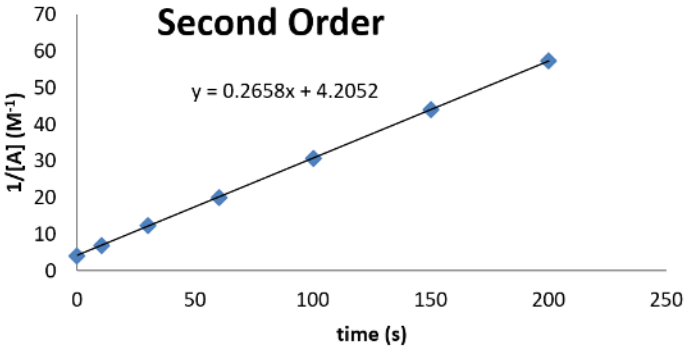
Example 4.1.6.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

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4.1.7: The Method of Initial Rates

The **method of initial rates** is a commonly used technique for deriving rate laws. As the name implies, the method involves measuring the initial rate of a reaction. The measurement is repeated for several sets of initial concentration conditions to see how the reaction rate varies. This might be accomplished by determining the time needed to exhaust a particular amount of a reactant (preferably one on which the reaction rate does not depend!) A typical set of data for a reaction

$$A + B \rightarrow products$$

might appear as follows:

Run	[A] (M)	[B] (M)	Rate (M/s)
1	0.0100	0.0100	0.0347
2	0.0200	0.0100	0.0694
3	0.0200	0.0200	0.2776

The analysis of this data involves taking the ratios of rates measured where one of the concentrations does not change. For example, assuming a rate law of the form

$$\text{rate} = k[A]^{\alpha}[B]^{\beta} \tag{4.1.7.1}$$

The ratio of runs i and j generate the following relationship.

$$\frac{\text{rate}_i}{\text{rate}_j} = \frac{k[A]_i^{\alpha}[B]_i^{\beta}}{k[A]_j^{\alpha}[B]_j^{\beta}}$$

So using runs **1** and **2**,

$$\frac{0.0347\,M/s}{0.0694\,M/s} = \frac{\cancel{k}\,(0.01\,M/s)^{\alpha}\,\cancel{(0.01\,M/s)^{\beta}}}{\cancel{k}\,(0.02\,M/s)^{\alpha}\,\cancel{(0.01\,M/s)^{\beta}}}$$

this simplifies to

$$\frac{1}{2} = \left(\frac{1}{2}\right)^{\alpha}$$

So clearly, \(\alpha = 1\) and the reaction is 1st order in A. Taking the ratio using runs 2 and 3 yields

$$\frac{0.0694\,M/s}{0.2776\,M/s} = \frac{\cancel{k}\,(0.02\,M)^{\alpha}\,\cancel{(0.01\,M)^{\beta}}}{\cancel{k}\,(0.02\,M)^{\alpha}\,\cancel{(0.02\,M)^{\beta}}}$$

This simplifies to

$$\frac{1}{4} = \left(\frac{1}{2}\right)^{\beta} \tag{4.1.7.2}$$

By inspection, one can conclude that \(\beta = 2\), and that the reaction is second order in B. But if it is not so clear (as it might not be if the concentration is not incremented by a factor of 2), the value of \(\beta\) can be determined by taking the natural logarithm of both sides of the Equation 4.1.7.2.

$$\ln\frac{1}{4} = \ln\left(\frac{1}{2}\right)^{\beta}$$

$$= \beta \ln\left(\frac{1}{2}\right)$$

dividing both sides by $\ln(1/2)$

$$\frac{\ln\left(\frac{1}{4}\right)}{\ln\left(\frac{1}{2}\right)} = \beta\frac{\ln\left(\frac{1}{2}\right)}{\ln\left(\frac{1}{2}\right)}$$

or

$$\beta = \frac{-1.3863}{-0.69315} = 2$$

And so the rate law (Equation 4.1.7.1) can be expressed as

$$\text{rate} = k[A][B]^2$$

And is 1st order in A, 2nd order in B, and 3rd order overall. The rate constant can then be evaluated by substituting one of the runs into the rate law (or using all of the data and taking an average). Arbitrarily selecting the first run for this,

$$0.0347\,M/s = k(0.01\,M/s)(0.01\,M/s)^2$$

This results in a value of k

$$k = \frac{0.0347\,M/s}{(0.01\,M/s)(0.01\,M/s)^2} = 3.47 \times 10^5\,M^{-2}s^{-1}$$

It is useful to note that the units on k are consistent with a 3rd order rate law.

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4.1.8: The Method of Half-Lives

Another method for determining the order of a reaction is to examine the behavior of the **half-life** as the reaction progresses. The half-life can be defined as the time it takes for the concentration of a reactant to fall to half of its original value. The method of half-lives involved measuring the half-life's dependence on concentration. The expected behavior can be predicted using the integrated rate laws we derived earlier.

Using the definition of the half-life, at time $t_{1/2}$ the concentration $[A]$ drops to half of its original value, $[A]_0$.

$$[A] = \frac{1}{2}[A]_o$$

at $t = t_{1/2}$.

So if the reaction is 0th order in A, after one half-life

$$\frac{1}{2}[A]_o = [A]_o - kt_{1/2}$$

Solving for $t_{1/2}$ reveals the dependence of the half-life on the initial concentration.

$$\frac{[A]_o}{2k} = t_{1/2}$$

So as the original concentration is **decreased**, the half-life of a 0th order reaction will also **decrease**.

Similarly, for a first order reaction,

$$\frac{1}{2}[A]_o = [A]_o e^{-kt_{1/2}}$$

and solving for $t_{1/2}$ results in a concentration independent expression

$$\frac{\ln 2}{k} = t_{1/2}$$

It is because the half-life of a 1st order reaction is **independent** of concentration that it is oftentimes used to describe the rate of first order processes (such as radioactive decay.)

For a 2nd order reaction, the half-life can be expressed based on the integrated rate law.

$$\frac{1}{\frac{1}{2}[A]_o} = \frac{1}{[A]_o} + kt_{1/2}$$

solving for $t_{1/2}$ yields

$$\frac{1}{t_{1/2}} = t_{1/2}$$

In the case of a second order reaction, the half-life **increases** with **decreasing** initial concentration.

Table **4.1.8.1**: Calculated half lives for Reactions following simple Rate Laws

Order	Half-life	Behavior
0th	$\frac{1}{2}[A]_o = [A]_o - kt_{1/2}$	Decreases as the reaction progresses (as [A] decreases
1st	$[\frac{\ln 2}{k} = t_{1/2}$	Remains constant as the reaction progresses (is independent of concentration)
2nd	$\frac{1}{\frac{1}{2}[A]_o} = \frac{1}{[A]_o} + kt_{1/2}$	Increases with decreasing concentration.

For reactions in which the rate law depends on the concentration of more than one species, the half-life can take a much more complex form that may depend on the initial concentrations of multiple reactants, or for that matter, products!

Example 4.1.8.1: Radiocarbon Dating

Carbon-14 decays into nitrogen-14 with first order kinetics and with a half-life of 5730 years.

$$^{14}C \rightarrow {}^{14}N$$

What is the rate constant for the decay process? What percentage of carbon-14 will remain after a biological sample has stopped ingesting carbon-14 for 1482 years?

Solution

The rate constant is fairly easy to calculate:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{5730\,yr} = 1.21 \times 10^{-4}\,yr^{-1}$$

Now the integrated rate law can be used to solve the second part of the problem.

$$[^{14}C] = [^{14}C]_o e^{-kt}$$

this can be rewritten in term of relative loss of $[^{14}C]$.

$$\frac{[^{14}C]}{[^{14}C]_o} = e^{-kt}$$

so

$$\frac{[^{14}C]}{[^{14}C]_o} = e^{-(1.21\times10^{-4}\,yr^{-1})(1482\,ys)} = 0.836$$

So after 1482 years, there is 83.6 % of ^{14}C still left.

Example 4.1.8.2:

Based on the following concentration data as a function of time, determine the behavior of the half-life as the reaction progresses. Use this information to determine if the following reaction is 0th order, 1st order, or 2nd order in A. Also, use the data to estimate the rate constant for the reaction.

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600
30	0.480
40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

Solution

If the original concentration is taken as 1.200 M, half of the original concentration is 0.600 M. The reaction takes 20 seconds to reduce the concentration to half of its original value. If the original concentration is taken as 0.800 M, it clearly takes 30 seconds for the concentration to reach half of that value. Based on this methodology, the following table is easy to generate:

$[A]_o$ (M)	1.200	0.800	0.600	0.400
$t_{1/2}$ (s)	20	30	40	60

The rate constant can be calculated using any of these values:

$$k = \frac{1}{[A]t_{1/2}} \tag{4.1.8.1}$$

$$= \frac{1}{(0.8\,M)(30\,s)} \tag{4.1.8.2}$$

$$= 0.0417\,M^{-1}s^{-1} \tag{4.1.8.3}$$

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SECTION OVERVIEW

4.2: COLLISION THEORY

COLLISION THEORY

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4.2.4: Mechanism (alt)

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4.2.S: Chemical Kinetics I (Summary)

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4.2.1: Temperature Dependence

In general, increases in temperature increase the rates of chemical reactions. It is easy to see why, since most chemical reactions depend on molecular collisions. And as we discussed in Chapter 2, the frequency with which molecules collide increases with increased temperature. But also, the kinetic energy of the molecules increases, which should increase the probability that a collision event will lead to a reaction. An empirical model was proposed by Arrhenius to account for this phenomenon. The **Arrhenius model** (Arrhenius, 1889) can be expressed as

$$k = Ae^{-E_a/RT}$$

Although the model is empirical, some of the parameters can be interpreted in terms of the energy profile of the reaction. E_a, for example, is the **activation energy**, which represents the energy barrier that must be overcome in a collision to lead to a reaction.

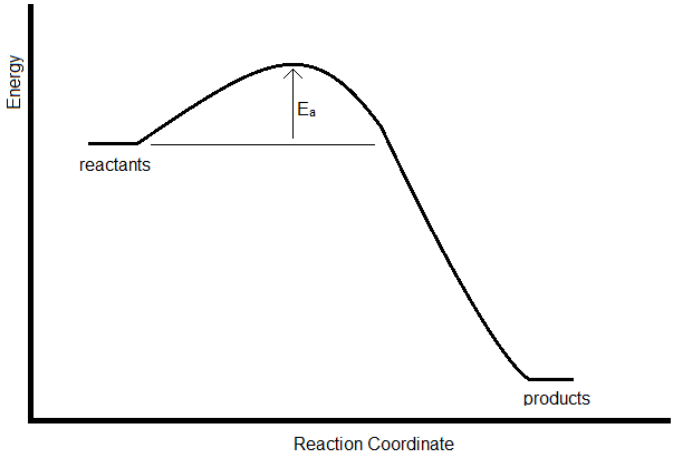


Figure 11.9.1: Reaction profile for an elementary sttep over an activated barrier of height E_a.

If the rate constant for a reaction is measure at two temperatures, the activation energy can be determined by taking the ratio. This leads to the following expression for the Arrhenius model:

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.2.1.1}$$

Example 4.2.1.1:

For a given reaction, the rate constant doubles when the temperature is increased form 25 °C to 35 °C. What is the Arrhenius activation energy for this reaction?

Solution

The energy of activation can be calculated from the Arrhenius Equation (Equation 4.2.1.1).

$$\ln\left(\frac{2k_1}{k_1}\right) = -\frac{E_a}{8.314\,\frac{J}{mol\,K}}\left(\frac{1}{308\,K} - \frac{1}{298\,K}\right)$$

From this reaction:

$$E_a = 52.9\,kJ/mol$$

Preferably, however, the rate constant is measured at several temperatures, and then the activation energy can be determined using all of the measurements, by fitting them to the expression

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

This can be done graphically by plotting the natural logarithm of the rate constant as a function of $1/T$ (with the temperature measured in K). The result should be a straight line (for a well-behaved reaction!) with a slope of $-E_a/R$.

There are some theoretical models (such as collision theory and transition state theory) which suggest the form of the Arrhenius model, but the model itself is purely empirical. A general feature, however, of the theoretical approaches is to interpret the activation energy as an energy barrier which a reaction must overcome in order to lead to a chemical reaction.

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4.2.2: Collision Theory

Collision Theory was first introduced in the 1910s by Max Trautz (Trautz, 1916) and William Lewis (Lewis, 1918) to try to account for the magnitudes of rate constants in terms of the frequency of molecular collisions, the collisional energy, and the relative orientations of the molecules involved in the collision.

The rate of a reaction, according to collision theory, can be expressed as

$$\text{rate} = Z_{ab}F \tag{4.2.2.1}$$

where Z_{AB} is the frequency of collisions between the molecules A and B involved in the reaction, and F is the fraction of those collisions that will lead to a reaction. The factor F has **two** important contributors, the energy of the collision and the orientation of the molecules when they collide. The first term, Z_{AB}, can be taken from the kinetic molecular theory discussed in Chapter 2.

$$Z_{AB} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}[A][B] \tag{4.2.2.2}$$

Where the first term is the average relative velocity in which μ is the reduced mass of the A-B collisional system, σ_{AB} is the collisional cross section, and $[A]$ and $[B]$ are the concentrations of A and B.

The factor F depends on the activation energy. Assuming a Boltzmann (or Boltzmann-like) distribution of energies, the fraction of molecular collisions that will have enough energy to overcome the activation barrier is given by

$$F = e^{-E_a/RT} \tag{4.2.2.3}$$

Combining Equations 4.2.2.2 and 4.2.2.3, the rate of the reaction (Equation 4.2.2.1) is predicted by

$$\text{rate} = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}e^{-E_a/RT}[A][B]$$

So if the rate law can be expressed as a second order rate law

$$\text{rate} = k[A][B]$$

it is clear that the rate constant k is given by

$$k = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}e^{-E_a/RT}$$

By comparison, the theory predicts the form of the **Arrhenius prefactor** to be

$$A = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2}\sigma_{AB}$$

It should be noted that collision theory appears to apply only to **bimolecular reactions**, since it takes two molecules to collide. But there are many reactions that have first order rate laws, but are initiated by bimolecular steps in the mechanisms. (Reaction mechanisms will form a large part of the discussion in Chapter 12.) Consider as an example, the decomposition of N_2O_5, which follows the reaction

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

Under a certain set of conditions, the following concentrations are observed as a function of time.

time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
0	0.0260	0.0000	0.0000
100	0.0219	0.0081	0.0016
200	0.0185	0.0150	0.0030
300	0.0156	0.0207	0.0041
400	0.0132	0.0256	0.0051
500	0.0111	0.0297	0.0059
600	0.0094	0.0332	0.0066
700	0.0079	0.0361	0.0072

Graphically, these data look as follows:

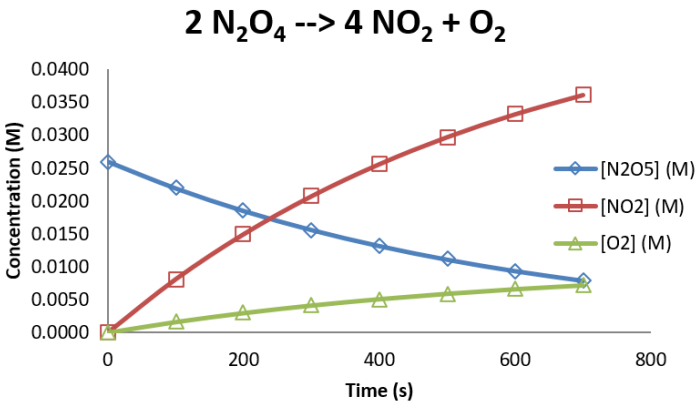
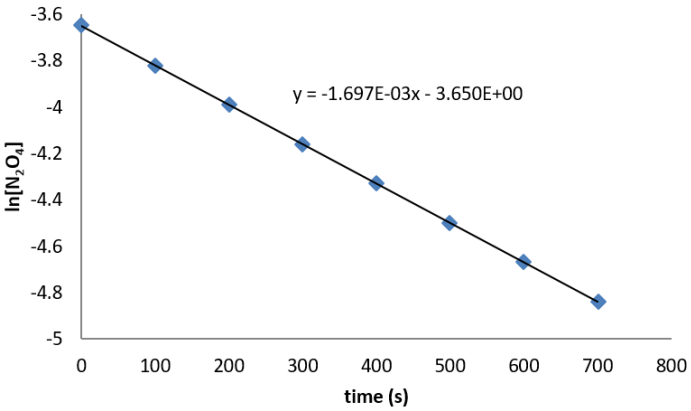


Figure 10.11.1: Concentration kinetics of the thermal decomposition reaction of N_2O_5.

The data for N_2O_5 can be analyzed empirically to show that the reaction is first order in N_2O_5, with a rate constant of 1.697 x 10^{-3} s^{-1}. (The graph is shown below.) So the rate law for the reaction is

$$\text{rate} = 1.697 \times 10^{-3} s^{-1} [N_2O_5]$$

So how can collision theory be used to understand the rate constant? As it turns out, the mechanism for the reaction involves a bimolecular initiation step.



The mechanism for the reaction has a bimolecular initiation step

$$N_2O_5 + M \rightleftharpoons N_2O_5^* + M$$

where $N_2O_5^*$ is an energetically activated form of N_2O_5 which can either relax to reform N_2O_5 or decompose to form the products of the reaction. Because the initiation step is bimolecular, collision theory *can* be used to understand the rate law, but because the product of the unimolecular step undergoes slow conversion to products unimolecularly, the overall rate is observed to be first order in N_2O_5. The analysis of reaction mechanisms, and reconciliation with observed rate laws, form the subjects of Chapter 12.

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4.2.3: Transition State Theory

Transition state theory was proposed in 1935 by Henry Erying, and further developed by Merrideth G. Evans and Michael Polanyi (Laidler & King, 1983), as another means of accounting for chemical reaction rates. It is based on the idea that a molecular collision that leads to reaction must pass through an intermediate state known as the transition state. For example, the reaction

$$A + BC \rightarrow AB + C$$

would have an intermediate (ABC) where the $B-C$ bond is partially broken, and the $A-B$ bond is partially formed.

$$A + B - C \rightarrow (A - B - C)^{\ddagger} \rightarrow A - B + C$$

So the reaction is mediated by the formation of an activated complex (denoted with the double-dagger symbol ‡) and the decomposition of that complex into the reaction products. Using this theory, the rate of reaction can be expressed as the product of two factors

$$\text{rate} = (\text{transition state concentration}) \times (\text{decomposition frequency})$$

If the formation of the activated complex is considered to reach an equilibrium,

$$K^{\ddagger} = \frac{[ABC]^{\ddagger}}{[A][BC]}$$

So the concentration of the transition state complex can be expressed by

$$[ABC]^{\ddagger} = K^{\ddagger}[A][BC]$$

Using the relationship from Chapter 9 for the equilibrium constant, $K^{\ddagger}$ can be expressed in terms of the free energy of formation of the complex (\(\Delta G^‡\))

$$K^{\ddagger} = e^{-\Delta G^{\ddagger}/RT}$$

And so the reaction rate is given by

$$\text{rate} = (\text{frequency})[A][BC]e^{-\Delta G^{\ddagger}/RT}$$

and the remaining task is to derive an expression for the frequency factor. If the frequency is taken to be equal to the vibrational frequency for the vibration of the bond being broken in the activated complex in order to form the reaction products, it can be expressed in terms of the energy of the oscillation of the bond as the complex vibrates.

$$E = h\nu = k_B T$$

or

$$\nu = \frac{k_B T}{h}$$

The reaction rate is then predicted to be

$$\text{rate} = \frac{k_B T}{h}[A][BC]e^{-\Delta G^{\ddagger}/RT}$$

And the rate constant is thus given by

$$k = \frac{k_B T}{h}e^{-\Delta G^{\ddagger}/RT}$$

An alternative description gives the transition state formation equilibrium constant in terms of the partition functions describing the reactants and the transition state:

$$K^{\ddagger} = \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}}e^{-\Delta G^{\ddagger}/RT}$$

where Q_i is the **partition function** describing the ith species. If the partition function of the transition state is expressed as a product of the partition function excluding and contribution from the vibration leading to the bond cleavage that forms the products and the partition function of that specific vibrational mode

$$Q^{\ddagger} = Q^{\ddagger'} q_v^{\ddagger}$$

In this case, $q_v^{\ddagger}$ can be expressed by

$$q_v^{\ddagger} = \frac{1}{1 - e^{-h\nu^{\ddagger}/RT}} \approx \frac{k_B T}{h\nu^{\ddagger}}$$

So the equilibrium constant can be expressed

$$K^{\ddagger} = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}} e^{-\Delta G^{\ddagger}/RT}$$

And so the rate constant, which is the product of $n^{\ddagger}$ and $K^{\ddagger}$, is given by

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A^{\ddagger} Q_{BC}^{\ddagger}} e^{-\Delta G^{\ddagger}/RT}$$

which looks very much like the Arrhenius equation proposed quite a few years earlier! Thus, if one understands the vibrational dynamics of the activated complex, and can calculate the partition functions describing the reactants and the transition state, one can, at least in theory, predict the rate constant for the reaction. In the next chapter, we will take a look at how kinetics studies can shed some light on chemical reaction mechanisms.

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4.2.4: Mechanism (alt)

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4.2.E: Chemical Kinetics I (Exercises)

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4.2.S: Chemical Kinetics I (Summary)

The results of the integration of these simple rate laws can be summarized in the following table.

Order	Elementary Reaction	Integrated rate law	Linear plot
0	-	$[A] = [A]_o - kt$	$[A]$ vs. t
1	$A \rightarrow P$	$\ln[A] = \ln [A]_o - kt$ $[[A] = [A]_o e^{-kt}$	$\ln[A]$ vs. t
2	$A + A \rightarrow P$	$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$	$\frac{1}{[A]}$ vs. t
	$A + B \rightarrow P$	$\frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B][A]_o}{[A][B]_o}\right) = kt$	$\ln\left(\frac{[B]}{[A]}\right)$ vs. t

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SECTION OVERVIEW

4.3: EQUILIBRIUM

EQUILIBRIUM

4.3.1: Reactions can also be Reversible

4.3.2: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

4.3.3: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

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4.3.1: Reactions can also be Reversible

Reversible and irreversible reactions are prevalent in nature and are responsible for reactions such as the breakdown of ammonia.

Introduction

It was believed that all chemical reactions were irreversible until 1803, when French chemist Claude Louis Berthollet introduced the concept of reversible reactions. Initially he observed that sodium carbonate and calcium chloride react to yield calcium carbonate and sodium chloride; however, after observing sodium carbonate formation around the edges of salt lakes, he realized that large amount of salts in the evaporating water reacted with calcium carbonate to form sodium carbonate, indicating that the reverse reaction was occurring.

Chemical reactions are represented by chemical equations. These equations typically have a unidirectional arrow ($\rightarrow$) to represent irreversible reactions. Other chemical equations may have a bidirectional harpoons ($\rightleftharpoons$) that represent reversible reactions (not to be confused with the double arrows $\leftrightarrow$ used to indicate resonance structures). To review the fundamentals of chemical reactions, click here: Chemical Reactions

Irreversible Reactions

A fundamental concept of chemistry is that chemical reactions occurred when reactants reacted with each other to form products. These unidirectional reactions are known as irreversible reactions, reactions in which the reactants convert to products and where the products *cannot* convert back to the reactants. These reactions are essentially like baking. The ingredients, acting as the reactants, are mixed and baked together to form a cake, which acts as the product. This cake cannot be converted back to the reactants (the eggs, flour, etc.), just as the products in an irreversible reaction cannot convert back into the reactants.

An example of an irreversible reaction is combustion. Combustion involves burning an organic compound—such as a hydrocarbon—and oxygen to produce carbon dioxide and water. Because water and carbon dioxide are stable, they do not react with each other to form the reactants. Combustion reactions take the following form:

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O \tag{4.3.1.1}$$

Reversible Reactions

In reversible reactions, the reactants and products are never fully consumed; they are each constantly reacting and being produced. A reversible reaction can take the following summarized form:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D \tag{4.3.1.2}$$

This reversible reaction can be broken into two reactions.

Reaction 1:

$$A + B \xrightarrow{k_1} C + D \tag{4.3.1.3}$$

Reaction 2:

$$C + D \xrightarrow{k_{-1}} A + B \tag{4.3.1.4}$$

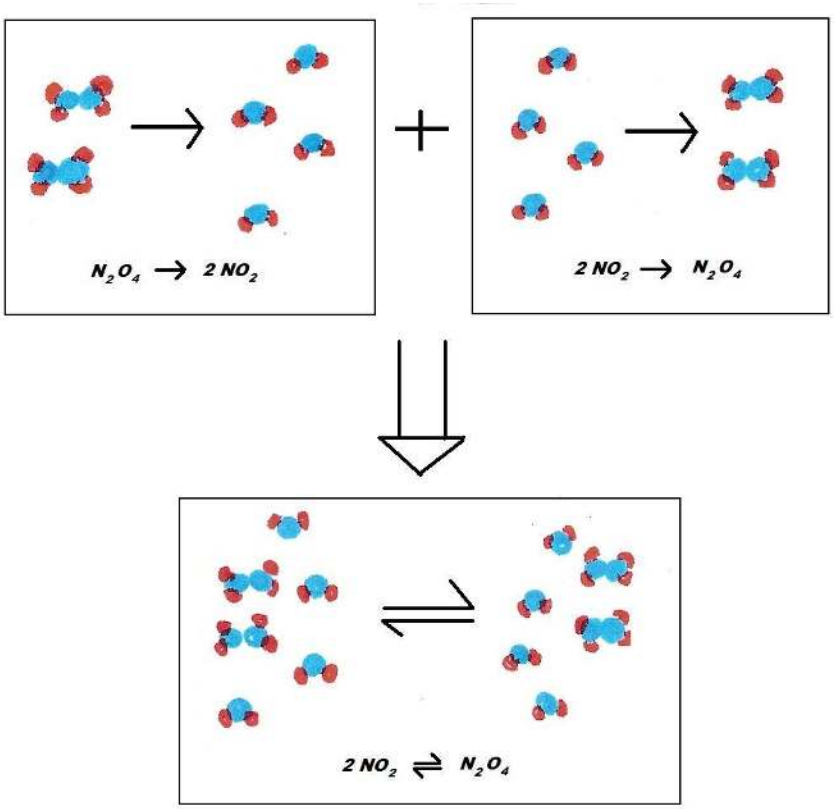
These two reactions are occurring ***simultaneously***, which means that the reactants are reacting to yield the products, as the products are reacting to produce the reactants. Collisions of the reacting molecules cause chemical reactions in a closed system. After products are formed, the bonds between these products are broken when the molecules collide with each other, producing sufficient energy needed to break the bonds of the product and reactant molecules.

Below is an example of the summarized form of a reversible reaction and a breakdown of the reversible reaction $N_2O_4 \leftrightarrow 2NO_2$

Reaction 1 and Reaction 2 happen at the same time because they are in a closed system.

Blue: Nitrogen Red: Oxygen

Reaction 1 Reaction 2



Imagine a ballroom. Let reactant A be 10 girls and reactant B be 10 boys. As each girl and boy goes to the dance floor, they pair up to become a product. Once five girls and five boys are on the dance floor, one of the five pairs breaks up and moves to the sidelines, becoming reactants again. As this pair leaves the dance floor, another boy and girl on the sidelines pair up to form a product once more. This process continues over and over again, representing a reversible reaction.

Unlike irreversible reactions, reversible reactions lead to equilibrium: in reversible reactions, the reaction proceeds in both directions whereas in irreversible reactions the reaction proceeds in only one direction. To learn more about this phenomenon, click here: Chemical Equilibrium

If the reactants are formed at the same rate as the products, a dynamic equilibrium exists. For example, if a water tank is being filled with water at the same rate as water is leaving the tank (through a hypothetical hole), the amount of water remaining in the tank remains consistent.

Connection to Biology

There are four binding sites on a hemoglobin protein. Hemoglobin molecules can either bind to carbon dioxide or oxygen. As blood travels through the alveoli of the lungs, hemoglobin molecules pick up oxygen-rich molecules and bind to the oxygen. As the hemoglobin travels through the rest of the body, it drops off oxygen at the capillaries for the organ system to use oxygen. After expelling the oxygen, it picks up carbon dioxide. Because this process is constantly carried out through the body, there are always hemoglobin molecules picking or expelling oxygen and other hemoglobin molecules that are picking up or expelling carbon dioxide. Therefore, the hemoglobin molecules, oxygen, and carbon dioxide are reactants while the hemoglobin molecules with oxygen or carbon dioxide bound to them are the products. In this closed system, some reactants convert into products as some products are changing into reactants, making it similar to a reversible reaction.

Contributors and Attributions

- Heather Yee (UCD), Mandeep Sohal (UCD)

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4.3.2: The Rate Constants of a Reversible Reaction Can Be Determined Using Relaxation Techniques

The traditional experimental methods described above all assume the possibility of following the reaction after its components have combined into a homogeneous mixture of known concentrations. But what can be done if the time required to complete the mixing process is comparable to or greater than the time needed for the reaction to run to completion?

Flow methods

Flow instruments are a rapid mixing devices used to study the chemical kinetics of fast reactions in solution. There are different flavors that can be implement depending on the nature of the reaction as discussed below.

Continuous Flow Approach

For reactions that take place in milliseconds, the standard approach since the 1950s has been to employ a flow technique of some kind. An early example was used to study fast gas-phase reactions in which one of the reactants is a free radical such as OH that can be produced by an intense microwave discharge acting on a suitable source gas mixture. This gas, along with the other reactant being investigated, is made to flow through a narrow tube at a known velocity.

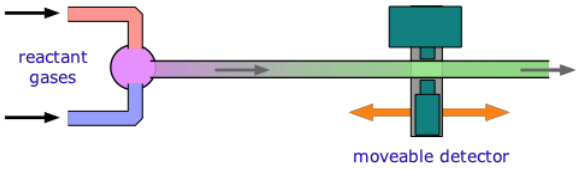


Figure **4.3.2.1**: A continuous flow fast kinetic system.

If the distance between the point at which the reaction is initiated and the product detector is known, then the time interval can be found from the flow rate. By varying this distance, the time required to obtain the maximum yield can then be determined. Although this method is very simple in principle, it can be complicated in practice.

Stopped Flow Approach

Owing to the rather large volumes required, continuous flow method is more practical for the study of gas-phase reactions than for solutions, for which the stopped-flow method described below is generally preferred. These are by far the most common means of studying fast solution-phase reactions over time intervals of down to a fraction of a millisecond. The use of reasonably simple devices is now practical even in student laboratory experiments. These techniques make it possible to follow not only changes in the concentrations of reactants and products, but also the buildup and decay of reaction intermediates.

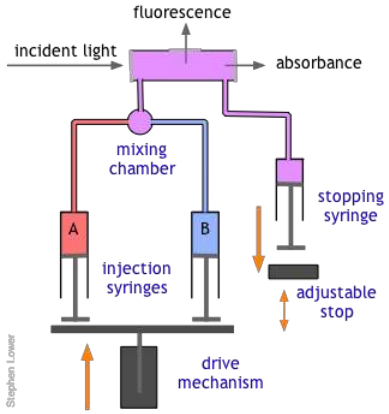


Figure **4.3.2.2**: A stop flow fast kinetic system.

The basic stopped-flow apparatus consists of two or more coupled syringes that rapidly inject the reactants into a small mixing chamber and then through an observation cell that can be coupled to instruments that measure absorption, fluorescence, light scattering, or other optical or electrical properties of the solution. As the solution flows through the cell, it empties into a stopping syringe that, when filled, strikes a backstop that abruptly stops the flow. The volume that the stopping syringe can accept is

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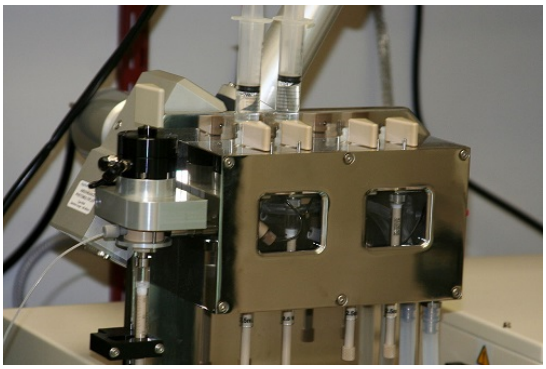


Figure **4.3.2.3**: Stop-flow equipment at a biochemistry research laboratory for measuring rapid reactions and properties such as enzyme kinetics. from Wladimir Labeikovsky.

Quenched Flow Approach

In a quenched-flow instrument, the reaction is stopped after a certain amount of time has passed after mixing. The stopping of the reaction is called quenching and it can be achieved by various means, for example by mixing with another solution, which stops the reaction (chemical quenching), quickly lowering the temperature (freeze quenching) or even by exposing the sample to light of a certain wavelength (optical quenching).

Of course, there are many reactions that cannot be followed by changes in light absorption or other physical properties that are conveniently monitored. In such cases, it is often practical to *quench* (stop) the reaction after a desired interval by adding an appropriate quenching agent. For example, an enzyme-catalyzed reaction can be stopped by adding an acid, base, or salt solution that denatures (destroys the activity of) the protein enzyme. Once the reaction has been stopped, the mixture is withdrawn and analyzed in an appropriate manner.

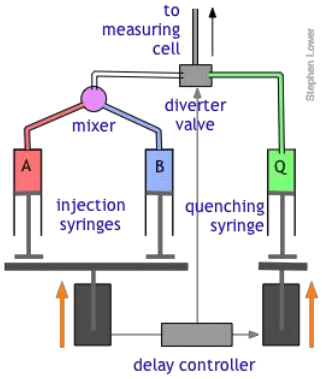


Figure **4.3.2.4**: A quench flow fast kinetic system.

The quenched-flow technique works something like the stopped-flow method described above, with a slightly altered plumbing arrangement. The reactants A and B are mixed and fed directly through the diverter valve to the measuring cell, which is not shown in this diagram. After a set interval that can vary from a few milliseconds to 200 sec or more, the controller activates the quenching syringe and diverter valve, flooding the cell with the quenching solution.

Relaxation Methods

To investigate reactions that are complete in less than a millisecond, one can start with a pre-mixed sample in which one of active reactants is generated *in situ*. Alternatively, a rapid change in pressure or temperature can alter the composition of a reaction that has already achieved equilibrium.

Flash Photolysis

Many reactions are known which do not take place without light of wavelength sufficiently short to supply the activation energy needed to break a bond, often leading to the creation of a highly reactive radical. A good example is the combination of gaseous Cl_2 with H_2, which proceeds explosively when the system is illuminated with visible light. In *flash photolysis*, a short pulse of light is used to initiate a reaction whose progress can be observed by optical or other means.

Photolysis refers to the use of light to decompose a molecule into simpler units, often ions or free radicals. In contrast to *thermolysis* (decomposition induced by high temperature), photolysis is able to inject energy into a molecule almost instantaneously and can be much "cleaner," meaning that there are fewer side reactions that often lead to complex mixtures of products. Photolysis can also be highly *specific*; the wavelength of the light that triggers the reaction can often be adjusted to activate one particular kind of molecule without affecting others that might be present.

Norrish and Porter

All this had been known for a very long time, but until the mid-1940's there was no practical way of studying the kinetics of the reactions involving the highly reactive species produced by photolysis. In 1945, Ronald Norrish of Cambridge University and his graduate student George Porter conceived the idea of using a short-duration flash lamp to generate gas-phase CH_2 radicals, and then following the progress of the reaction of these radicals with other species by means of absorption spectroscopy.

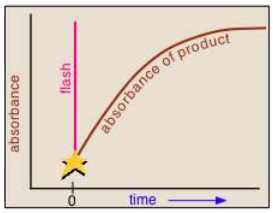


Figure **4.3.2.5**: Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

In a flash photolysis experiment, recording of the absorbance of the sample cell contents is timed to follow the flash by an interval that can be varied in order to capture the effects produced by the product or intermediate as it is formed or decays. Norrish and Porter shared the 1967 Nobel Prize in Chemistry for this work.

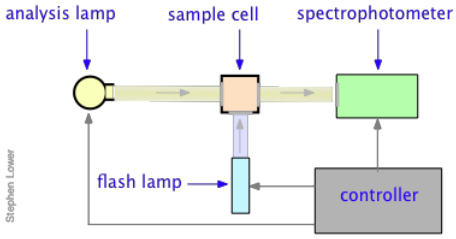


Figure **4.3.2.6**: A flash-photolysis relaxation experiment

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{4.3.2.1}$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^- \tag{4.3.2.2}$$

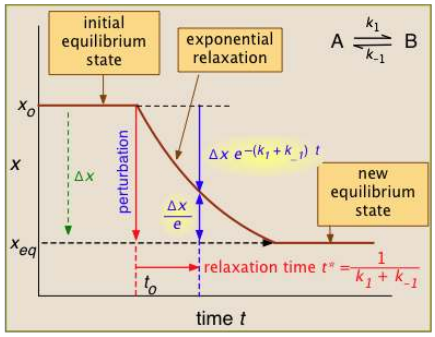
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

Temperature Jumps

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. For example, if the reaction

$$\mathbf{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} \tag{4.3.2.3}$$

is endothermic, then according to the Le Chatelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product B has a higher concentration. The composition of the system will than begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.



For the general case illustrated here, the quantity "*x*" being plotted is a measurable quantity such as light absorption or electrical conductivity that varies linearly with the composition of the system. **In a first-order process**, *x* will vary with time according to

$$x_t = x_o e^{-kt} \tag{4.3.2.4}$$

After the abrupt perturbation at time t_o, the relaxation time t^* is defined as the half-time for the return to equilibrium — that is, as the time required for x_o to decrease by \($\Delta x/e = \Delta x/2.718$\). The derivation of t^* and the relations highlighted in yellow can be found in most standard kinetics textbooks. Temperature jumps are likely most commonly used.

The rate law for the reversible reaction in Equation 4.3.2.3 can be written as

$$\frac{d[\mathbf{B}]}{dt} = k_1[\mathbf{A}] - k_{-1}[\mathbf{B}] \tag{4.3.2.5}$$

Consider a system comprising **A** and **B** that is allowed to achieve equilibrium concentrations at a temperature, T_1. After equilibrium is achieved, the temperature of the system is instantaneously lowered to T_2 and the system is allowed to achieve new equilibrium concentrations of **A** and **B**, $[\mathbf{A}]_{eq,2}$ and $[\mathbf{B}]_{eq,2}$. During the transition time from the first equilibrium state to the second equilibrium state, we can write the instantaneous concentration of **A** as

$$[\mathbf{A}] = [\mathbf{B}]_{eq,1} - [\mathbf{B}] \tag{4.3.2.6}$$

The rate of change of species **B** can then be written as

$$\frac{d[\mathbf{B}]}{dt} = k_1\left([\mathbf{B}]_{eq,1} - [\mathbf{B}]\right) - k_{-1}[\mathbf{B}] = k_1[\mathbf{B}]_{eq,1} - (k_1 + k_{-1})[\mathbf{B}] \tag{4.3.2.7}$$

At equilibrium, $d[\mathbf{B}]/dt = 0$ and $[\mathbf{B}] = [\mathbf{B}]_{eq,2}$, allowing us to write

$$k_1[\mathbf{B}]_{eq,1} = (k_1 + k_{-1})[\mathbf{B}]_{eq,2} \tag{4.3.2.8}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathbf{B}}{\left([\mathbf{B}]_{eq,2} - [\mathbf{B}]\right)} = (k_1 + k_{-1})\,dt \tag{4.3.2.9}$$

Integrating yields

$$-\ln\left([\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}\right)=-\left(k_1+k_{-1}\right)t+C \tag{4.3.2.10}$$

We can rearrange the above equation in terms of B

$$[\mathrm{B}]=Ce^{-(k_1+k_{-1})t}+[\mathrm{B}]_{\mathrm{eq},2} \tag{4.3.2.11}$$

At $t=0$, $[\mathrm{B}]=[\mathrm{B}]_{\mathrm{eq},1}$, so $C=[\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}$. Plugging the the value of C, we arrive at

$$[\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}=\left([\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}\right)e^{-(k_1+k_{-1})t} \tag{4.3.2.12}$$

which can also be expressed as

$$\Delta[\mathrm{B}]=\Delta[\mathrm{B}]_0e^{-(k_1+k_{-1})t}=\Delta[\mathrm{B}]_0e^{-t/\tau} \tag{4.3.2.13}$$

where $\Delta[\mathrm{B}]$ is the difference in the concentration of B from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta[\mathrm{B}]/\Delta[\mathrm{B}]_0\right)$ versus t will be linear with a slope of $-\left(k_1+k_{-1}\right)$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

Contributors and Attributions

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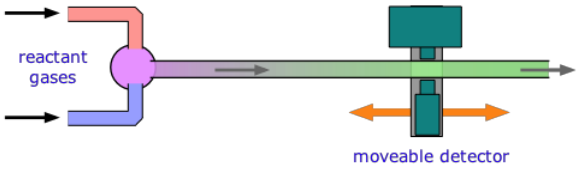


Figure **4.3.3.1**: A continuous flow fast kinetic system.

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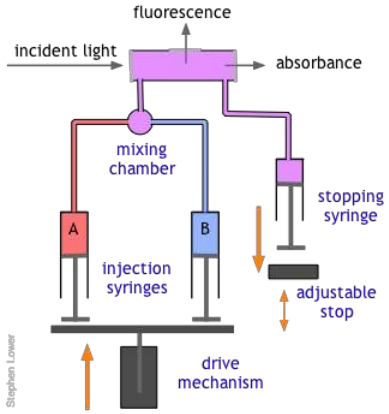


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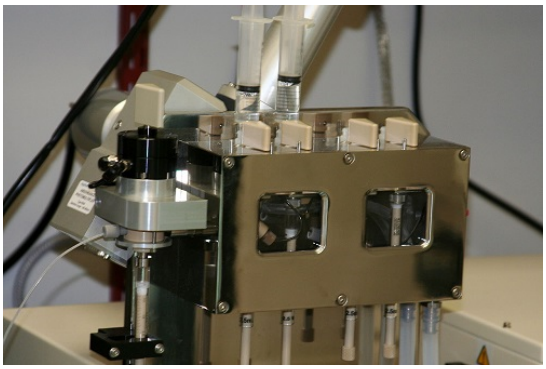


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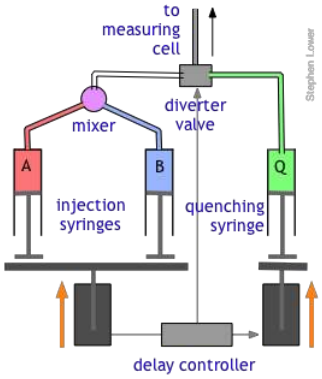


Figure **4.3.3.4**: A quench flow fast kinetic system.

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Photolysis refers to the use of light to decompose a molecule into simpler units, often ions or free radicals. In contrast to *thermolysis* (decomposition induced by high temperature), photolysis is able to inject energy into a molecule almost instantaneously and can be much "cleaner," meaning that there are fewer side reactions that often lead to complex mixtures of products. Photolysis can also be highly *specific*; the wavelength of the light that triggers the reaction can often be adjusted to activate one particular kind of molecule without affecting others that might be present.

Norrish and Porter

All this had been known for a very long time, but until the mid-1940's there was no practical way of studying the kinetics of the reactions involving the highly reactive species produced by photolysis. In 1945, Ronald Norrish of Cambridge University and his graduate student George Porter conceived the idea of using a short-duration flash lamp to generate gas-phase CH_2 radicals, and then following the progress of the reaction of these radicals with other species by means of absorption spectroscopy.

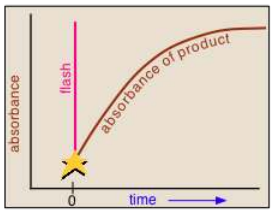


Figure **4.3.3.5**: Basic principle of a flash-photolysis relaxation experiment where an excitation pulse purturbed a system at equilibrium and the subsequent dynamics are resolved in time.

In a flash photolysis experiment, recording of the absorbance of the sample cell contents is timed to follow the flash by an interval that can be varied in order to capture the effects produced by the product or intermediate as it is formed or decays. Norrish and Porter shared the 1967 Nobel Prize in Chemistry for this work.

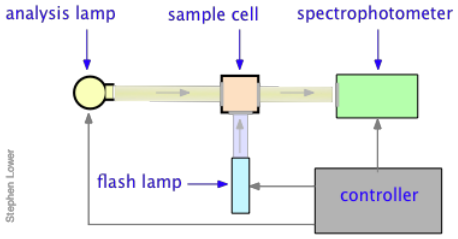


Figure **4.3.3.6**: A flash-photolysis relaxation experiment

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

$$2H_2O \rightarrow H_3O^+ + OH^- \tag{4.3.3.1}$$

and the formation of the triiodide ion in aqueous solution

$$I^- + I_2 \rightarrow I_3^- \tag{4.3.3.2}$$

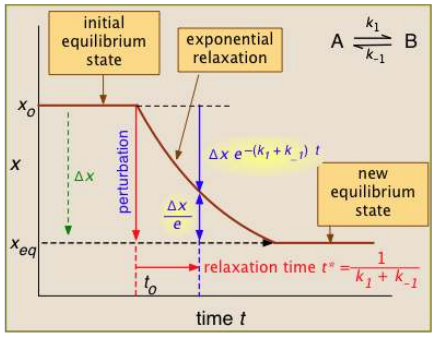
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

Temperature Jumps

The rate constants of reversible reactions can be measured using a relaxation method. In this method, the concentrations of reactants and products are allowed to achieve equilibrium at a specific temperature. Once equilibrium has been achieved, the temperature is rapidly changed, and then the time needed to achieve the new equilibrium concentrations of reactants and products is measured. For example, if the reaction

$$\mathbf{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{B} \tag{4.3.3.3}$$

is endothermic, then according to the Le Chatelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product B has a higher concentration. The composition of the system will than begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.



For the general case illustrated here, the quantity "*x*" being plotted is a measurable quantity such as light absorption or electrical conductivity that varies linearly with the composition of the system. **In a first-order process**, *x* will vary with time according to

$$x_t = x_o e^{-kt} \tag{4.3.3.4}$$

After the abrupt perturbation at time t_o, the relaxation time t^* is defined as the half-time for the return to equilibrium — that is, as the time required for x_o to decrease by \($\Delta x/e = \Delta x/2.718$\). The derivation of t^* and the relations highlighted in yellow can be found in most standard kinetics textbooks. Temperature jumps are likely most commonly used.

The rate law for the reversible reaction in Equation 4.3.3.3 can be written as

$$\frac{d[\mathbf{B}]}{dt} = k_1[\mathbf{A}] - k_{-1}[\mathbf{B}] \tag{4.3.3.5}$$

Consider a system comprising **A** and **B** that is allowed to achieve equilibrium concentrations at a temperature, T_1. After equilibrium is achieved, the temperature of the system is instantaneously lowered to T_2 and the system is allowed to achieve new equilibrium concentrations of **A** and **B**, $[\mathbf{A}]_{eq,2}$ and $[\mathbf{B}]_{eq,2}$. During the transition time from the first equilibrium state to the second equilibrium state, we can write the instantaneous concentration of **A** as

$$[\mathbf{A}] = [\mathbf{B}]_{eq,1} - [\mathbf{B}] \tag{4.3.3.6}$$

The rate of change of species **B** can then be written as

$$\frac{d[\mathbf{B}]}{dt} = k_1\left([\mathbf{B}]_{eq,1} - [\mathbf{B}]\right) - k_{-1}[\mathbf{B}] = k_1[\mathbf{B}]_{eq,1} - (k_1 + k_{-1})[\mathbf{B}] \tag{4.3.3.7}$$

At equilibrium, $d[\mathbf{B}]/dt = 0$ and $[\mathbf{B}] = [\mathbf{B}]_{eq,2}$, allowing us to write

$$k_1[\mathbf{B}]_{eq,1} = (k_1 + k_{-1})[\mathbf{B}]_{eq,2} \tag{4.3.3.8}$$

Using the above equation, we can rewrite the rate equation as

$$\frac{d\mathbf{B}}{\left([\mathbf{B}]_{eq,2} - [\mathbf{B}]\right)} = (k_1 + k_{-1})\,dt \tag{4.3.3.9}$$

Integrating yields

$$-\ln\left([\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}\right)=-\left(k_1+k_{-1}\right)t+C \tag{4.3.3.10}$$

We can rearrange the above equation in terms of B

$$[\mathrm{B}]=Ce^{-(k_1+k_{-1})t}+[\mathrm{B}]_{\mathrm{eq},2} \tag{4.3.3.11}$$

At $t=0$, $[\mathrm{B}]=[\mathrm{B}]_{\mathrm{eq},1}$, so $C=[\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}$. Plugging the the value of C, we arrive at

$$[\mathrm{B}]-[\mathrm{B}]_{\mathrm{eq},2}=\left([\mathrm{B}]_{\mathrm{eq},1}-[\mathrm{B}]_{\mathrm{eq},2}\right)e^{-(k_1+k_{-1})t} \tag{4.3.3.12}$$

which can also be expressed as

$$\Delta\left[\mathrm{B}\right]=\Delta[\mathrm{B}]_0e^{-(k_1+k_{-1})t}=\Delta[\mathrm{B}]_0e^{-t/\tau} \tag{4.3.3.13}$$

where $\Delta\left[\mathrm{B}\right]$ is the difference in the concentration of B from the final equilibrium concentration after the perturbation, and τ is the *relaxation time*. A plot of $\ln\left(\Delta\left[\mathrm{B}\right]/\Delta[\mathrm{B}]_0\right)$ versus t will be linear with a slope of $-\left(k_1+k_{-1}\right)$, where k_1 and k_{-1} are the rate constants at temperature, T_2.

Contributors and Attributions

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- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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SECTION OVERVIEW

4.4: Q chases K

Q chases K

4.4.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

4.4.2: Rate Laws Must Be Determined Experimentally

4.4.3: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

4.4.4: Different Rate Laws Predict Different Kinetics

4.4.5: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants

4.4.E: Chemical Kinetics I - Rate Laws (Exercises)

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4.4.1: The Time Dependence of a Chemical Reaction is Described by a Rate Law

The Reaction Rate

The rate of a chemical reaction (or the **reaction rate**) can be defined by the time needed for a change in concentration to occur. But there is a problem in that this allows for the definition to be made based on concentration changes for either the reactants or the products. Plus, due to stoichiometric concerns, the rates at which the concentrations are generally different! Toward this end, the following convention is used.

For a general reaction

$$aA + bB \rightarrow cC + dD$$

the reaction rate can be defined by any of the ratios

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{dt} = -\frac{1}{b}\frac{\Delta[B]}{dt} = +\frac{1}{c}\frac{\Delta[C]}{dt} = +\frac{1}{d}\frac{\Delta[D]}{dt}$$

Or for infinitesimal time intervals

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[C]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Example 4.4.1.1:

Under a certain set of conditions, the rate of the reaction

$$\mathrm{N_2 + 3\,H_2 \rightarrow 2\,NH_3}$$

the reaction rate is $6.0 \times 10^{-4}\ M/s$. Calculate the time-rate of change for the concentrations of N_2, H_2, and NH_3.

Solution:

Due to the stoichiometry of the reaction,

$$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

so

$$\frac{d[N_2]}{dt} = -6.0 \times 10^{-4}\ M/s$$
$$\frac{d[H_2]}{dt} = -2.0 \times 10^{-4}\ M/s$$
$$\frac{d[NH_3]}{dt} = 3.0 \times 10^{-4}\ M/s$$

Note: The time derivatives for the reactants are negative because the reactant concentrations are decreasing, and those of products are positive since the concentrations of products increase as the reaction progresses.

The Rate Law

As shown above, the rate of the reaction can be followed experimentally by measuring the rate of the loss of a reactant or the rate of the production of a product. The rate of the reaction is often related to the concentration of some or all of the chemical species present at a given time. An equation called the *rate law* is used to show this relationship. The rate law **cannot** be predicted by looking at the balanced chemical reaction but must be determined by experiment. For example, the rate law for the reaction

$$\mathrm{Cl_2\,(g) + CO\,(g) \longrightarrow Cl_2CO\,(g)}$$

was experimentally determined to be

$$\text{rate} = k[Cl_2]^{3/2}[CO]$$

In this equation, k is the rate constant, and $[Cl_2]$ and $[CO]$ are the molar concentrations of Cl_2 and of CO. Each exponent is called the *order* of the given species. Thus, the rate law is second order in Cl_2 and first order in CO. The sum of the individual reactant orders is called the **reaction order**. This reaction has a reaction order of two and a half.

In the next section, we will discuss methods to experimentally determine the rate law.

Contributors and Attributions

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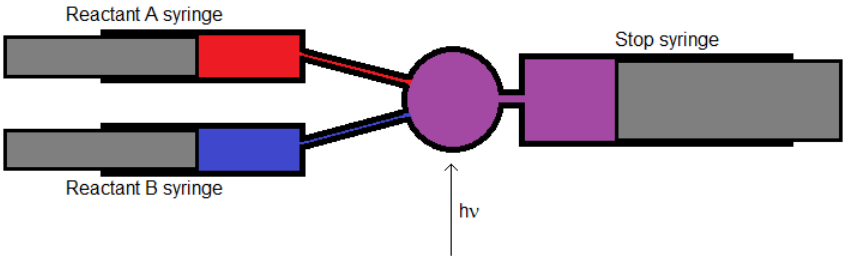
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4.4.2: Rate Laws Must Be Determined Experimentally

There are several methods that can be used to measure chemical reactions rates. A common method is to use spectrophotometry to monitor the concentration of a species that will absorb light. If it is possible, it is preferable to measure the appearance of a product rather than the disappearance of a reactant, due to the low background interference of the measurement. However, high-quality kinetic data can be obtained either way.

The Stopped-Flow Method

The **stopped-flow method** involves using flow control (which can be provided by syringes or other valves) to control the flow of reactants into a mixing chamber where the reaction takes place. The reaction mixture can then be probed spectrophotometrically. Stopped-flow methods are commonly used in physical chemistry laboratory courses (Progodich, 2014).



Some methods depend on measuring the initial rate of a reaction, which can be subject to a great deal of experimental uncertainty due to fluctuations in instrumentation or conditions. Other methods require a broad range of time and concentration data. These methods tend to produce more reliable results as they can make use of the broad range of data to smooth over random fluctuations that may affect measurements. Both approaches (initial rates and full concentration profile data methods) will be discussed below.

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4.4.3: First-Order Reactions Show an Exponential Decay of Reactant Concentration with Time

A first order rate law would take the form

$$\frac{d[A]}{dt} = k[A]$$

Again, separating the variables by placing all of the concentration terms on the left and all of the time terms on the right yields

$$\frac{d[A]}{[A]} = -k\,dt$$

This expression is also easily integrated as before

$$\int_{[A]=0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t=0}^{t=t} dt$$

Noting that

$$\frac{dx}{x} = d(\ln x)$$

The form of the integrated rate law becomes

$$\ln[A] - \ln[A]_o = kt$$

or

$$\ln[A] = \ln[A]_o - kt \qquad (4.4.3.1)$$

This form implies that a plot of the natural logarithm of the concentration is a linear function of the time. And so a plot of ln[A] as a function of time should produce a linear plot, the slope of which is -k, and the intercept of which is $\ln[A]_0$.

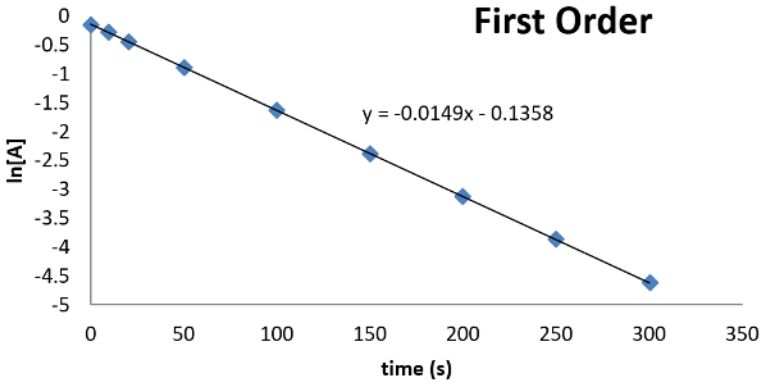
Example 4.4.3.1:

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with first order kinetics. Also, if the data are first order, determine the value of the rate constant for the reaction.

Time (s)	0	10	20	50	100	150	200	250	300
[A] (M)	0.873	0.752	0.648	0.414	0.196	0.093	0.044	0.021	0.010

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.0149 s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

It should also be noted that the integrated rate law (Equation 4.4.3.1) can be expressed in exponential form:

$$[A] = [A]_o e^{-kt}$$

Because of this functional form, 1st order kinetics are sometimes referred to as exponential decay kinetics. Many processes, including radioactive decay of nuclides follow this type of rate law.

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4.4.4: Different Rate Laws Predict Different Kinetics

Difference rate laws predict different kinetics

Zero-order Kinetics

If the reaction follows a zeroth order rate law, it can be expressed in terms of the time-rate of change of [A] (which will be negative since A is a reactant):

$$-\frac{d[A]}{dt} = k$$

In this case, it is straightforward to separate the variables. Placing time variables on the right and [A] on the left

$$d[A] = -k\,dt$$

In this form, it is easy to integrate. If the concentration of A is $[A]_0$ at time t = 0, and the concentration of A is [A] at some arbitrary time later, the form of the integral is

$$\int_{[A]_o}^{[A]} d[A] = -k\int_{t_o}^{t} dt$$

which yields

$$[A] - [A]_o = -kt$$

or

$$[A] = [A]_o - kt$$

This suggests that a plot of concentration as a function of time will produce a straight line, the slope of which is –k, and the intercept of which is $[A]_0$. If such a plot is linear, then the data are consistent with 0th order kinetics. If they are not, other possibilities must be considered.

Second Order Kinetics

If the reaction follows a second order rate law, the some methodology can be employed. The rate can be written as

$$-\frac{d[A]}{dt} = k[A]^2 \tag{4.4.4.1}$$

The separation of concentration and time terms (this time keeping the negative sign on the left for convenience) yields

$$-\frac{d[A]}{[A]^2} = k\,dt$$

The integration then becomes

$$-\int_{[A]_o}^{[A]} \frac{d[A]}{[A]^2} = \int_{t=0}^{t} k\,dt \tag{4.4.4.2}$$

And noting that

$$-\frac{dx}{x^2} = d\left(\frac{1}{x}\right)$$

the result of integration Equation 4.4.4.2 is

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

And so a plot of $1/[A]$ as a function of time should produce a linear plot, the slope of which is k, and the intercept of which is $1/[A]_0$.

Other 2nd order rate laws are a little bit trickier to integrate, as the integration depends on the actual stoichiometry of the reaction being investigated. For example, for a reaction of the type

$$A + B \rightarrow P$$

That has rate laws given by

$$-\frac{d[A]}{dt} = k[A][B]$$

and

$$-\frac{d[B]}{dt} = k[A][B]$$

the integration will depend on the decrease of [A] and [B] (which will be related by the stoichiometry) which can be expressed in terms the concentration of the product [P].

$$[A] = [A]_o - [P] \tag{4.4.4.3}$$

and

$$[B] = [B]_o - [P] \tag{4.4.4.4}$$

The concentration dependence on A and B can then be eliminated if the rate law is expressed in terms of the production of the product.

$$\frac{d[P]}{dt} = k[A][B] \tag{4.4.4.5}$$

Substituting the relationships for $[A]$ and $[B]$ (Equations 4.4.4.3 and 4.4.4.4) into the rate law expression (Equation 4.4.4.5) yields

$$\frac{d[P]}{dt} = k([A]_o - [P])([B] = [B]_o - [P]) \tag{4.4.4.6}$$

Separation of concentration and time variables results in

$$\frac{d[P]}{([A]_o - [P])([B] = [B]_o - [P])} = k\,dt$$

Noting that at time $t = 0$, $[P] = 0$, the integrated form of the rate law can be generated by solving the integral

$$\int_{[A]_o}^{[A]} \frac{d[P]}{([A]_o - [P])([B]_o - [P])} = \int_{t=0}^{t} k\,dt$$

Consulting a table of integrals reveals that for $a \neq b$[1],

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\ln\left(\frac{b-x}{a-x}\right)$$

Applying the definite integral (as long as $[A]_0 \neq [B]_0$) results in

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right)\Bigg|_0^{[A]} = k\,t\Big|_0^t$$

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0 - [P]}{[A]_0 - [P]}\right) - \frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B]_0}{[A]_0}\right) = kt \tag{4.4.4.7}$$

Substituting Equations 4.4.4.3 and 4.4.4.4 into Equation 4.4.4.7 and simplifying (combining the natural logarithm terms) yields

$$\frac{1}{[B]_0 - [A]_0}\ln\left(\frac{[B][A]_o}{[A][B]_o}\right) = kt$$

For this rate law, a plot of $\ln([B]/[A])$ as a function of time will produce a straight line, the slope of which is

$$m = ([B]_0 - [A]_0)k.$$

In the limit at $[A]_0 = [B]_0$, then $[A] = [B]$ at all times, due to the stoichiometry of the reaction. As such, the rate law becomes

$$\text{rate} = k[A]^2$$

and integrate direct like in Equation 4.4.4.1 and the integrated rate law is (as before)

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt$$

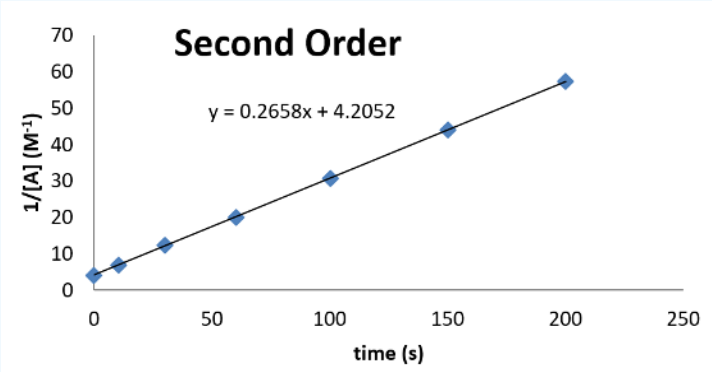
Example 4.4.4.2: Confirming Second Order Kinetics

Consider the following kinetic data. Use a graph to demonstrate that the data are consistent with second order kinetics. Also, if the data are second order, determine the value of the rate constant for the reaction.

time (s)	0	10	30	60	100	150	200
[A] (M)	0.238	0.161	0.098	0.062	0.041	0.029	0.023

Solution

The plot looks as follows:



From this plot, it can be seen that the rate constant is 0.2658 M^{-1} s^{-1}. The concentration at time $t = 0$ can also be inferred from the intercept.

[1] This integral form can be generated by using the method of partial fractions. See (House, 2007) for a full derivation.

Example 4.4.4.3

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

$$2N_2O_5\,(soln) \rightarrow 4NO_2\,(soln) + O_2\,(g)$$

This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	−3.310	27.4
600	0.0274	−3.597	36.5
1200	0.0206	−3.882	48.5
1800	0.0157	−4.154	63.7
2400	0.0117	−4.448	85.5
3000	0.00860	−4.756	116
3600	0.00640	−5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

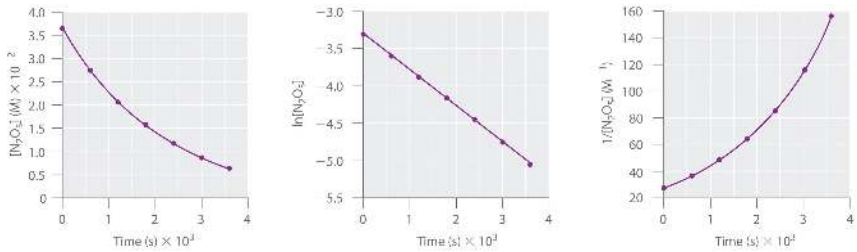
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 13.4.2 to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[N_2O_5]$ versus t, $\ln[N_2O_5]$ versus t, and $1/[N_2O_5]$ versus t:



The plot of $\ln[N_2O_5]$ versus t gives a straight line, whereas the plots of $[N_2O_5]$ versus t and $1/[N_2O_5]$ versus t do not. This means that the decomposition of N_2O_5 is first order in $[N_2O_5]$.

B The rate law for the reaction is therefore

$$rate = k\,[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus t for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[N_2O_5]$ versus t. Using the points for t = 0 and 3000 s,

$$slope = \frac{ln[N_2O_5]_{3000} - ln[N_2O_5]_0}{3000\ s - 0\ s} = \frac{[-4.756] - [-3.310]}{3000\ s} = 4.820 \times 10^{-4}\ s^{-1}$$

Thus $k = 4.820 \times 10^{-4}\ s^{-1}$.

Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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4.4.5: Transition-State Theory Can Be Used to Estimate Reaction Rate Constants

Transition State Theory

In Figure 28.8.1 , the point at which we evaluate or measure E_a serves as a dividing line (also called a *dividing surface*) between reactants and products. At this point, we do not have $\mathbf{A}+\mathbf{B}$, and we do not have $\mathbf{C}$. Rather, what we have is an activated complex of some kind called a *transition state* between reactants and products. The value of the reaction coordinate at the transition state is denoted $q^{\ddagger}$. Recall our notation $\mathbf{x}$ for the complete set of coordinates and momenta of all of the atoms in the system. Generally, the reaction coordinate q is a function $q(\mathbf{x})$ of all of the coordinates and momenta, although typically, $q(\mathbf{x})$ is a function of a subset of the coordinates and, possibly, the momenta.

As an example, let us consider two atoms $\mathbf{A}$ and $\mathbf{B}$ undergoing a collision. An appropriate reaction coordinate could simply be the distance r between $\mathbf{A}$ and $\mathbf{B}$. This distance is a function of the positions $\mathbf{r}_{\mathbf{A}}$ and $\mathbf{r}_{\mathbf{B}}$ of the two atoms, in that

$$q = r = |\mathbf{r}_{\mathbf{A}} - \mathbf{r}_{\mathbf{B}}| \tag{4.4.5.1}$$

When $\mathbf{A}$ and $\mathbf{B}$ are molecules, such as proteins, $q(\mathbf{x})$ is a much more complicated function of $\mathbf{x}$.

Now, recall that the mechanical energy $\mathcal{E}(\mathbf{x})$ is given by

$$\mathcal{E}(\mathbf{x}) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_1} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{4.4.5.2}$$

and is a sum of kinetic and potential energies. Transition state theory assumes the following:

1. The system is classical, and the time dependence of the coordinates and momenta is determined by Newton's laws of motion

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i \tag{4.4.5.3}$$

2. We start a trajectory obeying this equation of motion with an initial condition $\mathbf{x}$ that makes $q(\mathbf{x}) = q^{\ddagger}$ and such that $\dot{q}(\mathbf{x}) > 0$ so that the reaction coordinate proceeds initial to the right, i.e., toward products.
3. We follow the motion $\mathbf{x}_t$ of the coordinates and momenta in time starting from this initial condition $\mathbf{x}$, which gives us a unique function $\mathbf{x}_t(\mathbf{x})$.
4. If $q(\mathbf{x}_t(\mathbf{x})) > q^{\ddagger}$ at time t, then the trajectory is designated as "reactive" and contributes to the reaction rate.

Define a function $\theta(y)$, which is 1 if $y \geq 0$ and 0 if $y < 0$. The function $\theta(y)$ is known as a *step function*.

We now define a *flux* of reactive trajectories $k(t)$ using statistical mechanics

$$k(t) = \frac{1}{hQ_r} \int_{q(\mathbf{x})=q^{\ddagger}} d\mathbf{x}\, e^{-\beta\mathcal{E}(\mathbf{x})} |\dot{q}(\mathbf{x})| \, \theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right) \tag{4.4.5.4}$$

where h is Planck's constant. Here Q_r is the partition function of the reactants

$$Q_r = \int d\mathbf{x}\, e^{-\beta\mathcal{E}(\mathbf{x})} \theta\left(q^{\ddagger} - q(\mathbf{x})\right) \tag{4.4.5.5}$$

The meaning of Equation 4.4.5.4 is an ensemble average over a canonical ensemble of the product $|\dot{q}(\mathbf{x})|$ and $\theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right)$. The first factor in this product $|\dot{q}(\mathbf{x})|$ forces the initial velocity of the reaction coordinate to be positive, i.e., toward products, and the step function $\theta\left(q(\mathbf{x}_t(\mathbf{x})) - q^{\ddagger}\right)$ requires that the trajectory of $q(\mathbf{x}_t(\mathbf{x}))$ be reactive, otherwise, the step function will give no contribution to the flux. The function $k(t)$ in Equation 4.4.5.4 is known as the *reactive flux*. In the definition of Q_r the step function $\theta\left(q^{\ddagger} - q(\mathbf{x})\right)$ measures the total number of microscopic states on the reactive side of the energy profile.

A plot of some examples of reactive flux functions $k(t)$ is shown in Figure 28.8.2 . These functions are discussed in greater detail in *J. Chem. Phys.* **95**, 5809 (1991). These examples all show that $k(t)$ decays at first but then finally reaches a plateau value. This plateau value is taken to be the true rate of the reaction under the assumption that eventually, all trajectories that will become reactive will have done so after a sufficiently long time. Thus,

$$k = \lim_{t\to\infty} k(t) \tag{4.4.5.6}$$

gives the true rate constant. On the other hand, a common approximation is to take the value $k(0)$ as an estimate of the rate constant, and this is known as the transition *state theory approximation* to k, i.e.,

$$k^{(\mathrm{TST})} = k(0) \tag{4.4.5.7}$$

$$= \frac{1}{Q_r} \int_{q(\mathbf{x})=q^\ddagger} d\mathbf{x}\, e^{-\beta \mathcal{E}(\mathbf{x})} \left|\dot{q}(\mathbf{x})\right| \theta\left(q(\mathbf{x}) - q^\ddagger\right) \tag{4.4.5.8}$$

However, note that since we require $\dot{q}(\mathbf{x})$ to initially be toward products, then by definition, at $t = 0$, $q(\mathbf{x}) \geq q^\ddagger$, and the step function in the above expression is redundant. In addition, if $\dot{q}(\mathbf{x})$ only depends on momenta (or velocities) and not actually on coordinates, which will be true if $q(\mathbf{x})$ is not curvilinear (and is true for some curvilinear coordinates $q(\mathbf{x})$), and if $q(\mathbf{x})$ only depends on coordinates, then Equation ??? reduces to

$$k^{(\mathrm{TST})} = \frac{1}{hQ_r} \int d\mathbf{x}_\mathbf{p} e^{-\beta \sum_{i=1}^N \mathbf{p}_i^2/2m_i} \left|\dot{q}(\mathbf{p}_1, \ldots, \mathbf{p}_N)\right| \int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger} d\mathbf{x}_\mathbf{r} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)} \tag{4.4.5.9}$$

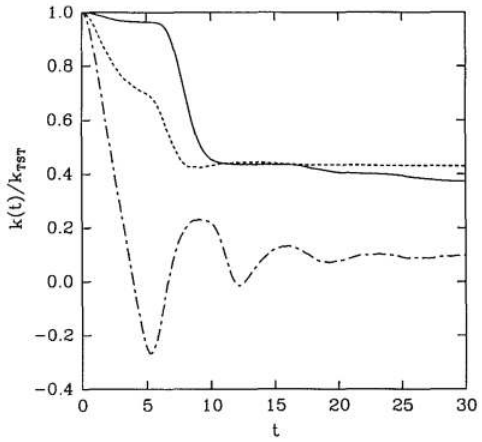


Figure 28.8.2 : Examples of the reactive flux $k(t)$.

The integral

$$Z^\ddagger = \int_{q(\mathbf{r}_1,\ldots,\mathbf{r}_N)=q^\ddagger} d\mathbf{x}_\mathbf{r} e^{-\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_N)}$$

counts the number of microscopic states consistent with the condition $q(\mathbf{r}_1, \ldots, \mathbf{r}_N) = q^\ddagger$ and is, therefore, a kind of partition function, and is denoted $Q^\ddagger$. On the other hand, because it is a partition function, we can derive a free energy $\Delta F^\ddagger$ from it

$$F^\ddagger \propto -k_B T \ln Z^\ddagger \tag{4.4.5.10}$$

Similarly, if we divide Q_r into its ideal-gas and configurational contributions

$$Q_r = Q_r^{(\mathrm{ideal})} Z_r \tag{4.4.5.11}$$

then we can take

$$Z_r = e^{-\beta F_r} \tag{4.4.5.12}$$

where F_r is the free energy of the reactants. Finally, setting $\dot{q} = p/\mu$, where μ is the associated mass, and p is the corresponding momentum of the reaction coordinate, then, canceling most of the momentum integrals between the numerator and $Q_r^{(\mathrm{ideal})}$, the momentum integral we need is

$$\int_0^\infty e^{-\beta p^2/2\mu} \frac{p}{\mu} = k_B T \tag{4.4.5.13}$$

which gives the final expression for the transition state theory rate constant

$$k^{(\mathrm{TST})} = \frac{k_B T}{h} e^{-\beta(F^\ddagger - F_r)} = \frac{k_B T}{h} e^{-\beta \Delta F^\ddagger} \tag{4.4.5.14}$$

Figure 28.8.2 actually shows $k(t)/k^{(TST)}$, which must start at 1. As the figure shows, in addition, for $t > 0$, $k(t) < k^{(TST)}$. Hence, $k^{(TST)}$ is always an upper bound to the true rate constant. Transition state theory assumes that any trajectory that initially moves toward products will be a reactive trajectory. For this reason, it overestimates the reaction rate. In reality, trajectories can cross the dividing surface several or many times before eventually proceeding either toward products *or* back toward reactants.

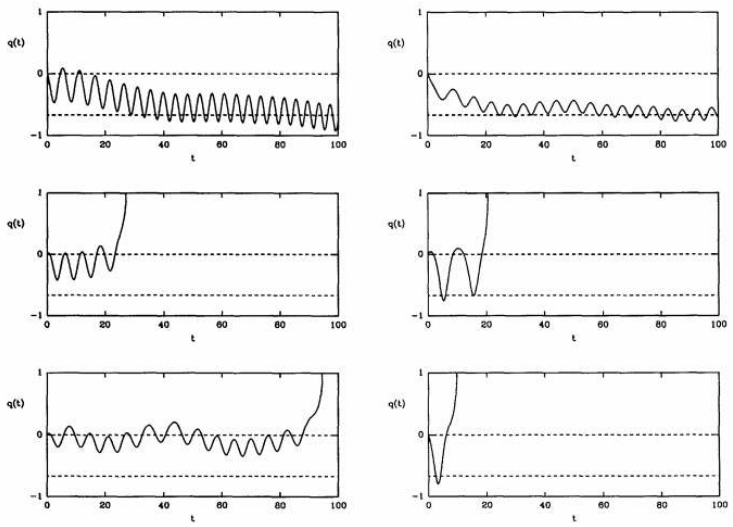


Figure 28.8.3 : Examples of the trajectories in a typical system, some of which are reactive but some of which return to reactants.

Figure 28.8.3 shows that one can obtain trajectories of both types. Here, the dividing surface lies at $q = 0$. Left, toward $q = -1$ is the reactant side, and right, toward $q = 1$ is the product side. Because some trajectories return to reactants and never become products, the true rate is always less than $k^{(TST)}$, and we can write

$$k = \kappa k^{(TST)} \tag{4.4.5.15}$$

where the factor $\kappa < 1$ is known as the *transmission factor*. This factor accounts for multiple recrossings of the dividing surface and the fact that some trajectories do not become reactive ones.

Contributors and Attributions

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4.4.E: Chemical Kinetics I - Rate Laws (Exercises)

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CHAPTER OVERVIEW

5: ACIDS

5.1: ACIDITY

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CHAPTER OVERVIEW

6: SPONTANEITY

6.1: Chemical Potential
6.2: The Gibbs-Duhem Equation

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6.1: Chemical Potential

In much the same fashion as the partial molar volume is defined, the **partial molar Gibbs function** is defined for compound i in a mixture:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}} \tag{6.1.1}$$

This particular partial molar function is of particular importance, and is called the **chemical potential**. The chemical potential tells how the Gibbs function will change as the composition of the mixture changes. And since systems tend to seek a minimum aggregate Gibbs function, the chemical potential will point to the direction the system can move in order to reduce the total Gibbs function. In general, the total change in the Gibbs function (dG) can be calculated from

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,n_{j\neq i}} dn_i$$

Or, by substituting the definition for the chemical potential, and evaluating the pressure and temperature derivatives as was done in Chapter 6:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

But as it turns out, the chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions U, H, A, or G:

Table **6.1.1**: Chemical potential can be defined as the partial molar derivative any of the four major thermodynamic functions

$dU = TdS - pdV + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}}$
$dH = TdS - VdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}}$
$dA = -pdV - TdS + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_{j\neq i}}$
$dG = Vdp - SdT + \sum_i \mu_i dn_i$	$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_{j\neq i}}$

The last definition, in which the chemical potential is defined as the partial molar Gibbs function is the most commonly used, and perhaps the most useful (Equation 6.1.1). As the partial most Gibbs function, it is easy to show that

$$d\mu = Vdp - SdT$$

where V is the molar volume, and S is the molar entropy. Using this expression, it is easy to show that

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V$$

and so at constant temperature

$$\int_{\mu^o}^{\mu} d\mu = \int_{p^o}^{p} V\, dp \tag{6.1.2}$$

So that for a substance for which the molar volume is fairly independent of pressure at constant temperature (i. e., κ_T is very small), therefore Equation 6.1.2 becomes

$$\int_{\mu^o}^{\mu} d\mu = V \int_{p^o}^{p} dp$$

$$\mu - \mu^o = V(p - p^o)$$

or

$$\mu = \mu^o + V(p - p^o)$$

Where p^o is a reference pressure (generally the standard pressure of 1 atm) and μ^o is the chemical potential at the standard pressure. If the substance is highly compressible (such as a gas) the pressure dependence of the molar volume is needed to complete the integral. If the substance is an ideal gas

$$V = \frac{RT}{p}$$

So at constant temperature, Equation 6.1.2 then becomes

$$\int_{\mu^o}^{\mu} d\mu = RTint_{p^o}^{p} \frac{dp}{p} \tag{6.1.3}$$

or

$$\mu = \mu^o + RT \ln\left(\frac{p}{p^o}\right)$$

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6.2: The Gibbs-Duhem Equation

For a system at **equilibrium**, the Gibbs-Duhem equation must hold:

$$\sum_i n_i d\mu_i = 0 \tag{6.2.1}$$

This relationship places a compositional constraint upon any changes in the chemical potential in a mixture at constant temperature and pressure for a given composition. This result is easily derived when one considers that μ_i represents the partial molar Gibbs function for component i. And as with other partial molar quantities,

$$G_{tot} = \sum_i n_i \mu_i$$

Taking the derivative of both sides yields

$$dG_{tot} = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i$$

But dG can also be expressed as

$$dG = Vdp - sdT + \sum_i \mu_i dn_i$$

Setting these two expressions equal to one another

$$\sum_i n_i d\mu_i + \cancel{\sum_i \mu_i dn_i} = Vdp - sdT + \cancel{\sum_i \mu_i dn_i}$$

And after canceling terms, one gets

$$\sum_i n_i d\mu_i = Vdp - sdT \tag{6.2.2}$$

For a system at constant temperature and pressure

$$Vdp - sdT = 0 \tag{6.2.3}$$

Substituting Equation 6.2.3 into 6.2.2 results in the **Gibbs-Duhem equation** (Equation 6.2.1). This expression relates how the chemical potential can change for a given composition while the system maintains equilibrium. So for a binary system, consisting of components A and B (the two most often studied compounds in all of chemistry)

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

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CHAPTER OVERVIEW

9: Content ToAdd

9.1: 4.2 Ionic and Covalent Compounds

9.2: 4.3 Lewis Dot Structures

9.3: 4.4 Shapes of Molecules - VSEPR Theory and Valence Bond Theory

9.4: 4.5 Electronegativity, Bond Polarity, and Molecular Polarity

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9.1: 4.2 Ionic and Covalent Compounds

Skills to Develop

- 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 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 **9.1.1**).

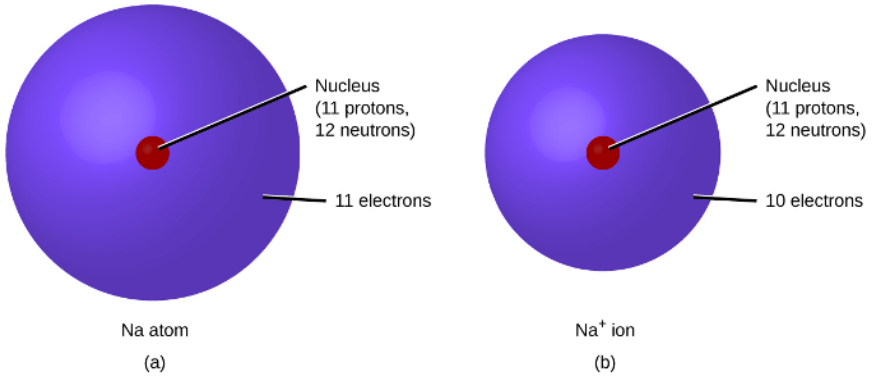


Figure* 9.1.1*: *(a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.*

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 IA) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group IIA) 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 VIIA gain one electron and form anions with a 1− charge; atoms of group VIA 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^-. (A discussion of the theory supporting the favored status of noble gas electron numbers (an octet of valence electrons) reflected in these predictive rules for ion formation exists, but is not is described in this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure **9.1.2**). 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 IA elements form 1+ ions; group IIA 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 VIIA elements (one group left of the noble gases) form 1− ions; group VIA 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.

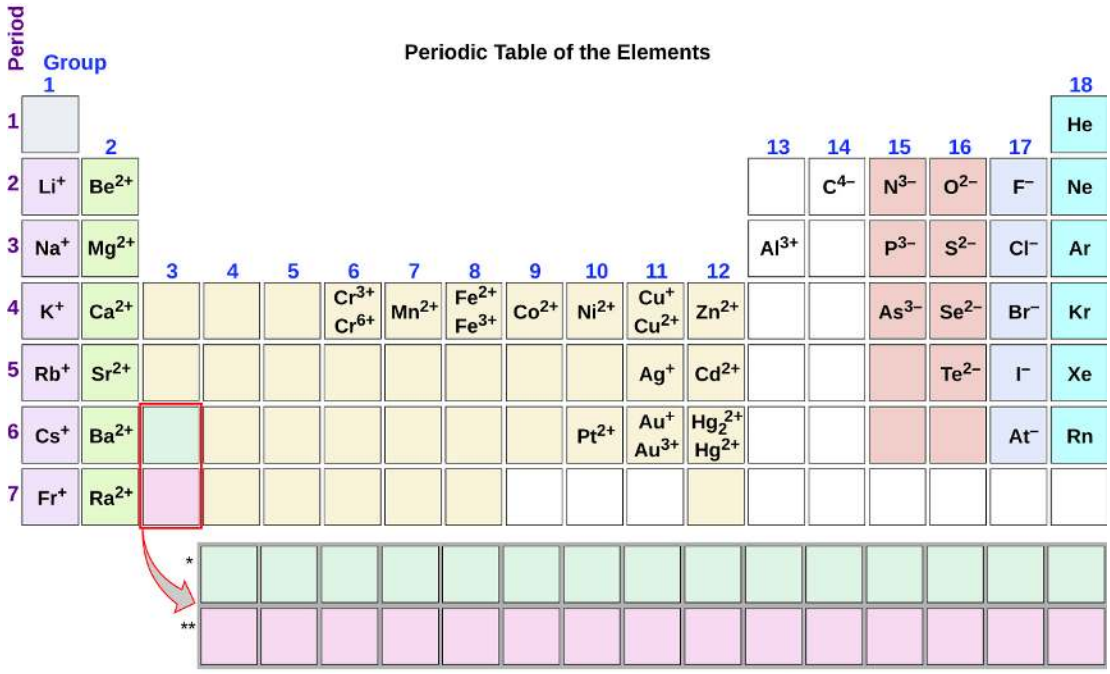


Figure* 9.1.2*: *Some elements exhibit a regular pattern of ionic charge when they form ions.*

Example 9.1.1: 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, Al^{3+}.

Exercise 9.1.1

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer

Se^{2-}, the selenide ion

Example 9.1.2: 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 IIA) 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+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group VA) 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-}, and it is called a nitride ion.

Exercise 9.1.2

Aluminum and chlorine 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.

Answer

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Chlorine will form an anion with a charge of 1−: Cl^{-}, a chloride ion.

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 a group of covalently-bonded atoms with an overall charge. Some of the more important polyatomic ions are listed in Table **9.1.1**. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Table* 9.1.1*: *Common Polyatomic Ions*

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}	hydroxide	OH^-
peroxide	O_2^{2-}		
hydroxide	OH^-	water	H_2O
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
cyanate	OCN^-	cyanic acid	$HOCN$
carbonate	CO_3^{2-}	hydrogen carbonate	HCO_3^-
hydrogen carbonate	HCO_3^-	carbonic acid	H_2CO_3
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	hydrogen sulfate	HSO_4^-
hydrogen sulfate	HSO_4^-	sulfuric acid	H_2SO_4
sulfite	SO_3^{2-}	hydrogen sulfite	HSO_3^-
hydrogen sulfite	HSO_3^-	sulfurous acid	H_2SO_3
phosphate	PO_4^{3-}	hydrogen phosphate	HPO_4^{2-}
hydrogen phosphate	HPO_4^{2-}	dihydrogen phospahte	$H_2PO_4^-$
dihydrogen phosphate	$H_2PO_4^-$	phosphoric acid	H_3PO_4
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

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 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.

9.1.1: 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 ionically-bonded as a pure compound, but does form ions when dissolved in water).

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 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °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 **9.1.3**).

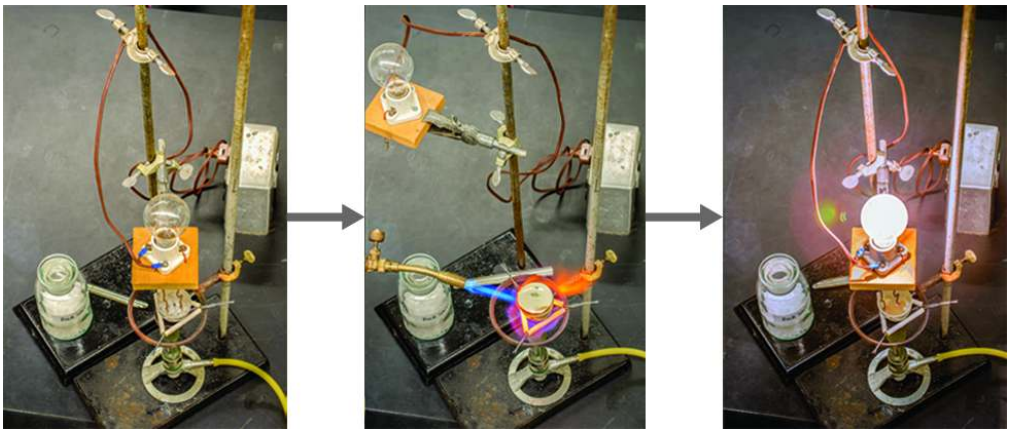


Figure* 9.1.3*: *Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)*

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 9.1.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure **9.1.4**) 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?



Figure* 9.1.4*: *Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)*

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.

Exercise 9.1.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table **9.1.1**) 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 $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $(\mathbf{PO_4^{3-}})$ groups. The $\mathbf{PO_4^{3-}}$ 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.

Example 9.1.4: 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 $\mathbf{H_2PO_4^-}$. 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 $\mathbf{H_2PO_4^-}$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise 9.1.4

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, $\mathbf{O_2^{2-}}$ (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer

Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it cannot 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 in this chapter. 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 $\mathbf{C_2O_4^{2-}}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-

possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

9.1.2: 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 in a later chapter of this text. 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 9.1.5: 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 IA) is a metal, and iodine (group VIIA) is a nonmetal; KI is predicted to be ionic.
b. Hydrogen (group IA) is a nonmetal, and oxygen (group VIA) is a nonmetal; H_2O_2 is predicted to be molecular.
c. Carbon (group IVA) is a nonmetal, hydrogen (group IA) is a nonmetal, and chlorine (group VIIA) is a nonmetal; $CHCl_3$ is predicted to be molecular.
d. Lithium (group IA) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

Exercise 9.1.5

Using the periodic table, predict whether the following compounds are ionic or covalent:

a. SO_2
b. CaF_2
c. N_2H_4
d. $Al_2(SO_4)_3$

Answer a

molecular

Answer b

ionic

Answer c

molecular

Answer d

ionic

9.1.3: Summary

Metals (particularly those in groups IA and IIA) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups VIA and VIIA, and, to a lesser extent, those in Group VA) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two or more nonmetals.

9.1.4: Glossary

covalent bond
attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound
(also, molecular compound) composed of molecules formed by atoms of two or more different elements covalently bonded together

ionic bond
electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound
compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound
(also, covalent compound) composed of molecules formed by atoms of two or more different elements covalently bonded together

monatomic ion
ion composed of a single atom

polyatomic ion
ion composed of more than one atom

oxyanion
polyatomic anion composed of a central atom bonded to oxygen atoms

9.1.5: Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).
- Modified by Tom Neils (Grand Rapids Community College)

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9.2: 4.3 Lewis Dot Structures

Skills to Develop

- To use Lewis dot symbols to explain the stoichiometry of a compound

9.2.1: Using Lewis Dot Symbols to Describe Covalent Bonding

It is usually easier to figure out a problem if you can draw a picture, either mental or real, of what is happening. This is often done in physics and mathematics, and it is especially helpful when looking at the bonding, structure, physical properties, and reactivity of compounds.

The most common picture, or model, of elements and compounds used is the Lewis Dot Structure. These pictures show you the type(s) of atom(s) involved, their position in the molecule, and where their valence electrons are situated.

To draw structures of substances you need to know:

1. the electronegativities of the elements so that you can decide if the atoms form ionic bonds or covalent bonds.
2. the number of valence electrons so that you can determine what ions will likely form (if the bonding will be ionic) or how many electrons will need to be shared in bonds (if the bonding will be covalent.)

9.2.1.0.1: GENERAL TERMS FOR LEWIS DOT STRUCTURES:

1. Dot • one dot represents one valence electron (found on odd-electron particles)

2. Pair of Dots •• a pair of dots represents a nonbonding (lone) pair of electrons that are **not** involved in a covalent bond and "belong to" only one atom

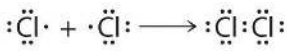
3. Dash each dash represents two electrons that are shared between two atoms as a covalent bond.

   One dash — a single bond; one set of two electrons shared; also a sigma (σ) bond

   Two dashes = a double bond; two sets of two electrons shared; one sigma (σ) and one pi (π) bond

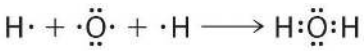
   Three dashes ≡ a triple bond: three sets of two electrons shared; one sigma and two pi (π) bonds

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



In CHM 110, you should always use lines to represent bonds. The use of dots will be reserved for non-bonding (lone) electron pairs.

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

Skills to Develop

9.2.1.0.1: THE EASY METHOD PROCEDURE TO DETERMINE A LEWIS DOT STRUCTURE

In this process, the basic concept of this method is that all valence electrons present will be taken away from the individual atoms and pooled together. They will first be doled out to form the requisite number of bonds. The remaining valence electrons will then be added to individual atoms as lone pairs to complete the octet of each atom.

1. Calculate the total number of valence electrons required for each atom to have an octet, or eight valence electrons. The major exception to this rule is that hydrogen wants only two (2) valence electrons. The other two most commonly-occurring exceptions are Be (4) and B (6) valence electrons.

Thus, the process for step one is 2 x (# of H atoms) + 8 x (# of most other atoms) = valence electrons needed

2. Calculate the total number of valence electrons in the given species.

If you have a **polyatomic anion**, you must add the number of '-' charges because there are extra valence electrons.

If you have a **polyatomic cation**, you must subtract the number of '+' charges because there are missing valence electrons.

3. Subtract result **2** from result **1**. This is the number of valence electrons lacking for each atom to have its own octet. This number of electrons will have to be shared in bonds.

4. Divide result **3** by two, because there are two electrons per bond. This is the number of covalent bonds you must use!

5. Connect the atoms in the formula together with the number of bonds from result **4**. Helpful hints:

i) H atoms form only one bond.

ii) The first atom in the formula is usually the central atom to which the other atoms bond

iii) If the particle has only three atoms, and each atom is of a different element, the atom in the middle of the formula is usually in the middle of the structure.

iv) species are as symmetrical as possible when there are several central atoms

v) For **neutral** species:

Group IV atoms usually form four bonds

Group V atoms usually form three bonds

Group VI atoms usually form two bonds

Group VII atoms usually form one bond

6. Add in electrons as **non-bonding pairs** or **lone pairs (groups of two)**, so that each atom has eight electrons around it.

7. Count the total number of electrons in the structure. The number should be equal to the number of electrons in result **2**.

CAUTIONS:

1. Never put a lone pair on an H atom.

2. The only common substances that have a lone pair on a C atom are CO and CN^-. Other than those two particles, you should not put a lone pair on a C atom.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

9.2.1.1: The H_2O Molecule

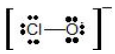
1. (1 O atom) x (8) + (2 H atoms) x (2) = 12 valence electrons needed
2. (1 O atom) x (6) + (2 H atoms) x (1) = 8 valence electrons present.
3. 12-8 = 4 electrons short, thus 4 electrons must be shared
4. 4 shared electrons/ 2 electrons per bond = 2 bonds
5. Connect the each of the two H atoms to the O atom with one single bond each.
6. Add the remaining 4 electrons to the oxygen (as two lone pairs) to give the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

9.2.1.2: The OCl^- Ion

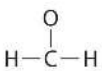
1. (1 O atom) x (8) + (1 Cl atom) x (8) = 16 valence electrons needed
2. (1 O atom) x (6) + (1 Cl atom) x (7) + 1 = 14 valence electrons present.
3. 16 - 14 = 2 electrons short, thus 2 electrons must be shared
4. 2 shared electrons/ 2 electrons per bond = 1 bond
5. Connect the two atoms with one single bond .
6. Add the remaining 12 electrons as lone pairs, with 3 pairs on the O atom and 3 pairs on the Cl atom, giving the following structure:



Each atom now has an octet of electrons. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

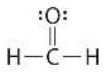
9.2.1.3: The CH_2O Molecule

1. (1 O atom) x (8) + (1 C atom) x (8) + (2 H atoms) x (2) = 20 valence electrons needed
2. (1 O atom) x (6) + (1 C atom) x (4) + (2 H atoms) x (1) = 12 valence electrons present.
3. 20 - 12 = 8 electrons short, thus 8 electrons must be shared
4. 8 shared electrons/ 2 electrons per bond = 4 bonds
5. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. Connect the two H atoms and the O atom to the C atom with with one single bond each, giving the structure:



6. There is still one more bond that you must use in the structure. At this point, the C atom has only three bonds and the O atom has only one bond. Thus, putting one more bond between the C and the O, creating a double bond, will satisfy all bonding requirements.

7. Add the remaining 4 electrons as two lone pairs on the O atom, giving the following structure:



Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 9.2.1

Write the Lewis electron structure for each species.

a. NCl_3
b. S_2^{2-}
c. NOCl

Given: chemical species

Asked for: Lewis electron structures

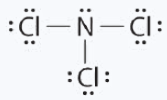
Strategy:

Use the six-step procedure to write the Lewis electron structure for each species.

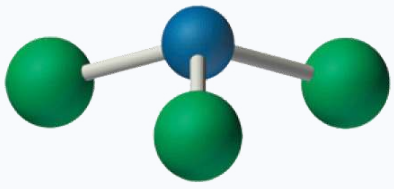
Solution:

a. NCl_3 Determine number of bonds needed

1. (1 N atom) x (8) + (3 Cl atoms) x (8) = 32 valence electrons needed
2. (1 N atom) x (5) + (3 Cl atoms) x (7) = 26 valence electrons present.
3. 32 - 26 = 6 electrons short, thus 6 electrons must be shared
4. 6 shared electrons/ 2 electrons per bond = 3 bonds
5. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. Connect the three Cl atoms with the central N atom with three single bonds.
6. You have used 6 electrons. Add the remaining 20 electrons on to the structure as lone pairs, to ensure that each atom has an octet (1 lone pair for N, and 3 lone pairs for each Cl.)



Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



Nitrogen trichloride

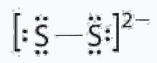
b. S_2^{2-} ion Determine number of bonds needed

1. (2 S atoms) x (8) = 16 valence electrons needed
2. (2 S atoms) x (6) + 2 = 14 valence electrons present.
3. 16-14 = 2 electrons short, thus 2 electrons must be shared

4. 2 shared electrons/ 2 electrons per bond = 1 bond

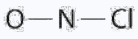
5. Connect the each of the two S atoms with one single bond each.

6. You have used two electrons. Add the remaining 12 electrons to the S atoms (as three lone pairs per S atom) to give the following structure:



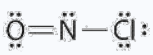
c. NOCl Determine number of bonds needed

1. (1 N atom) x (8) + (1 O atom) x (8) + (1 Cl atom) x (8) = 24 valence electrons needed
2. (1 N atom) x (5) + (1 O atom) x (6) + (1 Cl atom) x (7)= 18 valence electrons present.
3. 24-18 = 6 electrons short, thus 6 electrons must be shared
4. 6 shared electrons/ 2 electrons per bond = 3 bonds
5. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. Also, this molecule falls into the category of a particle that has only three atoms, and each atom is of a different element, so the atom in the middle of the formula is usually in the middle of the structure. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



6. There is still one more bond that you must use in the structure. At this point, the N atom has only two bonds and the O atom has only one bond. Thus, putting one more bond between the N and the O, creating a double bond, will satisfy all bonding requirements. The Cl, as a halogen, is stable with just one bond.

7. You have used 6 electrons. Add the remaining 12 electrons as two lone pairs on the O atom, one lone pair on the N atom, and three lone pairs ion the Cl atom giving the following structure:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.



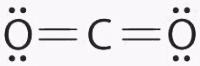
Nitrosyl chloride

Exercise 9.2.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer:

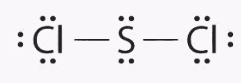
1.



2.



Carbon dioxide

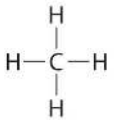




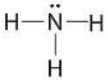
Sulfur dichloride

9.2.2: Using Lewis Electron Structures to Explain Stoichiometry

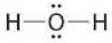
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of Group VIIA (the halogens), this number is one; for the elements of Group VIA (the chalcogens), it is two; for Group VA elements, three; and for Group IVA elements four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Group 14



Group 15

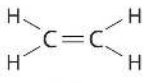


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Lewis structures explain why the elements of groups IVA–VIIA form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. Diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches,

fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure **9.2.3**). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

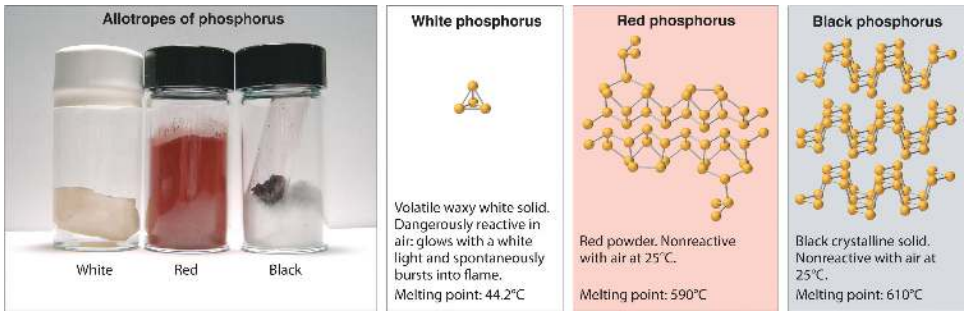


***Figure* 9.2.3**: *The Three Allotropes of Phosphorus: White, Red, and Black. ll three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.*

9.2.3: Summary

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group IVA elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group VA elements typically contain three bonds.

9.2.4: Contributors

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9.3: 4.4 Shapes of Molecules - VSEPR Theory and Valence Bond Theory

9.3.1: VSEPR Theory

Valence **S**hell **E**lectron **P**air **R**epulsion Theory uses the basic idea that electron pairs are mutually repulsed to predict the arrangement of electron pairs around a central atom (an atom that has at least two other atoms bonded directly to it). The key to correctly applying VSEPR Theory is to start with a correct Lewis dot structure. From a correct Lewis dot structure, it is a straightforward process to determine the shape of a molecule or polyatomic ion by determining the arrangement of electron pairs around every central atom in the molecule or polyatomic ion.

The step-by-step process to determine the shape around each central atom is

1. Draw the Lewis dot structure.

2. Apply the following analysis to each separate, central atom (where a central atom is an atom with two or more other atoms bonded directly to it.)

a) Find the number of "things attached" to the central atom, where a "thing attached" is either an atom or a non-bonding electron pair.

(Actually, you are counting the number of hybrid orbitals on the central atom, but that is the next theory to be discussed.)

It is important to remember that you are **not** counting bonds!

b) Find the **Electron Pair Arrangement (EPA)** in the table below

# of Things Attached	Electron Pair Arrangement	Ideal Bond Angle
2	line (linear shape)	180
3	trigonal plane(trigonal planar shape)	120
4	tetrahedron (tetrahedral shape)	109.5

c) Find the **Molecular Geometry (MG)** of the particle, determined by counting up the number of atoms and the number of lone pairs and using this table:

# of atoms attached	Electron pair geometry
2	Linear
3	trigonal planar
2	angular

4		tetrahedron
3		trigonal pyramid
2		tetrahedron

Example 9.3.1

Determine the Electron Pair Arrangement and Molecular Geometry about the central atom(s) in a) OF_2 and b) CH_3CN.

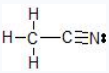
Solution

a) The Lewis dot structure of OF_2 is  (leaving off the lone pairs on the non-central F atoms.)

There are 2 atoms and 2 lone pairs attached to the central O atom, for a total of 4 "things attached."

From the two tables above, we can see that the O atom must have an EPA of a tetrahedron, and its MG is bent.

b) The Lewis dot structure of CH_3CN is



There are 4 atoms and 0 lone pairs attached to the central C atom on the left, for a total of 4 "things attached."

From the two tables above, we can see that this C atom must have an EPA of a tetrahedron, and its MG is also a tetrahedron.

There are 2 atoms and 0 lone pairs attached to the central C atom on the right, for a total of 2 "things attached."

From the two tables above, we can see that this C atom must have an EPA of a line, and its MG is also a line.

Exercise 9.3.1

Determine the Electron Pair Arrangement and Molecular Geometry about the central atom(s) in a) PF_3 and b) CH_2NH.

Answer

a) The Lewis dot structure of PF_3 is  (leaving off the lone pairs on the non-central F atoms.)

There are 3 atoms and 1 lone pair attached to the central P atom, for a total of 4 "things attached."

From the two tables above, we can see that the P atom must have an EPA of a tetrahedron, and its MG is a trigonal pyramid.

b)The Lewis dot structure of CH_2NH is



There are 3 atoms and 0 lone pairs attached to the central C atom on the left, for a total of 3 "things attached."

From the two tables above, we can see that this C atom must have an EPA of a trigonal plane, and its MG is also a trigonal plane.

There are 2 atoms and 1 lone pair attached to the central N atom on the right, for a total of 3 "things attached."

From the two tables above, we can see that this N atom must have an EPA of a trigonal plane, and its MG is bent.

Example 9.3.1

Use the VSEPR model to predict the number of atoms and lone pairs attached, the electron pair arrangement, and molecular geometry of the central atom in each compound.

a. H_2S
b. $CHCl_3$

Given: two chemical compounds

Asked for: number of atoms and lone pairs attached, the electron pair arrangement and molecular geometry

Strategy:

A. Using the VSEPR approach to determine the number of atoms and lone pairs attached, the electron pair arrangement, and the molecular geometry of the central atom in each molecule.

Solution:

a. H_2S has two atoms and two lone pairs attached to the sulfur atom, so the VSEPR model predicts an electron pair arrangement of a tetrahedron and a molecular geometry that is bent, or V shaped.

b. The central C atom in the $CHCl_3$ molecule has four atoms attached and no lone pairs. The carbon atom has an electron pair arrangement of a tetrahedron, and the molecular geometry is a tetrahedral shape.

Exercise 9.3.1

Use the VSEPR model to predict the number of atoms and lone pairs attached, the electron pair arrangement, and molecular geometry for the central atom(s) in each compound. and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF_4^- ion

b. hydrazine ($H_2N–NH_2$)

Answer a

B has four atoms attached and no lone pairs, so it forms an electron pair arrangement of a tetrahedron. The molecular geometry is tetrahedral shape.

Answer b

Each N atom has three other atoms attached and one lone pair attached. The electron pair arrangement is a tetrahedron. The molecular geometry about each N is a trigonal pyramidal shape.

9.3.1.1: Contributors

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9.4: 4.5 Electronegativity, Bond Polarity, and Molecular Polarity

Skills to Develop

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, whereas the bonding electron pair is shared equally in the covalent bond in Cl_2, in $NaCl$ the one valence electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. As demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally or nearly equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

9.4.1: Percent Ionic Character of a Covalent polar Bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure **9.4.4** compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

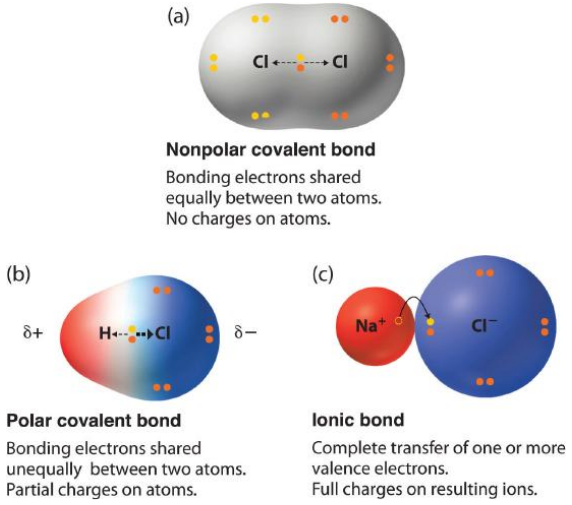


Figure* 9.4.4*: *The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.*

One method for calculating the percent ionic character of a bond is to use the following equation:

$$\%\ \text{ionic character} = \frac{EN_{higher} - EN_{lower}}{EN_{higher}} \times 100$$

≥ 50% means the bond is ionic

> 5% but < 50% means the bond is polar covalent

≤ 5% means the bond is pure (non-polar) covalent

Table of Pauling Electronegativities

H 2.20																	
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	
K 0.82	Ca 1.00	Sc 1.2	Ti 1.3	V 1.5	Cr 1.6	Mn 1.6	Fe 1.6	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.7	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	
Rb 0.82	Sr 0.95	Y 1.1	Zr 1.2	Nb 1.2	Mo 1.3	Tc 1.4	Ru 1.6	Rh 1.4	Pd 1.4	Ag 1.4	Cd 1.5	In 1.78	Sn 1.96	Sb 2.05	Te 2.2	I 2.66	
Cs 0.79	Ba 0.89	La 1.1	Hf 1.2	Ta 1.3	W 1.4	Re 1.5	Os 1.5	Ir 1.6	Pt 1.4	Au 1.4	Hg 1.4	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.20	

Example 9.4.1

What is the % ionic character of a P-S bond?

Solution

Add text here.

Exercise 9.4.1

Add exercises text here.

Answer

Add texts here. Do not delete this text first.

9.4.2: Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\text{less electronegative}}{A}} - \underset{\delta^-}{\overset{\text{more electronegative}}{B}} \tag{9.4.1}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: χ_{Cl} = 3.16, χ_H = 2.20, and χ_{Na} = 0.93. Cl_2 must be nonpolar because the electronegativity difference (Δχ) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, Δχ is 2.23. This high value is typical of an ionic compound (Δχ ≥ ≈1.5) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, Δχ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl} \tag{9.4.2}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

9.4.3: Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges.

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure **9.4.4**).

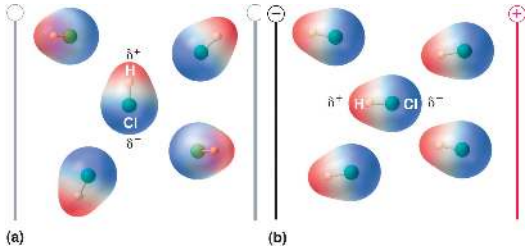


Figure* 9.4.5*: *Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.*

The measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl} \tag{9.4.3}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta+}{H} - \overset{0.18\delta-}{Cl} \tag{9.4.4}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure **9.4.6** shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure **9.4.6** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example **9.4.2**.

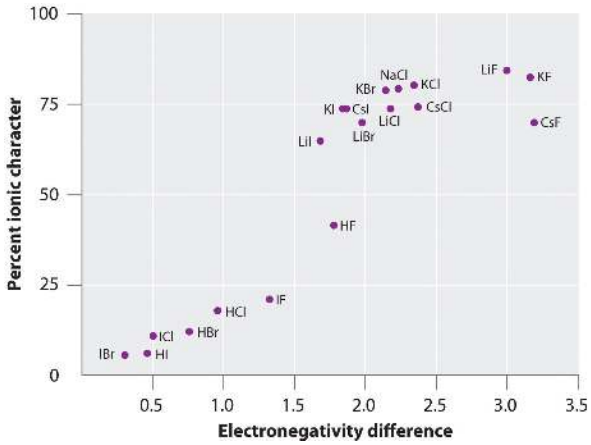


Figure* 9.4.6*: *A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.*

9.4.4: Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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