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Introduction to Gases

Gases represent a state of matter that has no fixed shape or fixed volume, which consist of tiny, energetic particles, i.e., atoms or molecules, that are widely spaced (Figure 1.1). Compared to the other states of matter, solids and liquids, gases have a much lower density, i.e., they have a small mass per unit volume, because there is a great deal of empty space between gas particles. At room temperature and pressure, the gas inside a container occupies only 0.1% of the total container volume. The other 99.9% of the total volume is empty space (whereas in liquids and solids, about 70% of the volume is occupied by particles). Gas particles move very fast and collide with one another, causing them to diffuse, or spread out, until they are evenly distributed throughout the volume of their container. You will never see only half of a balloon filled with air.

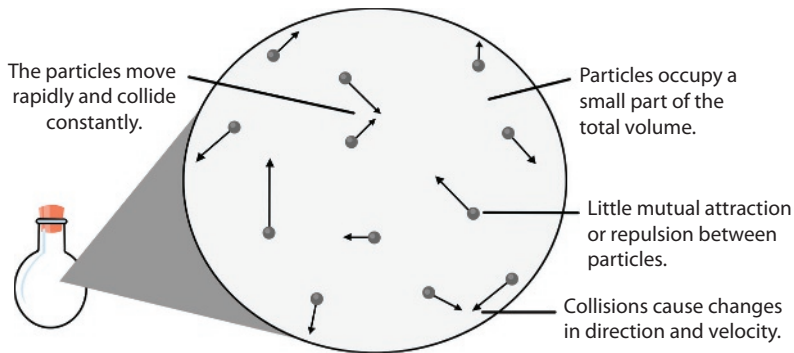


Figure 1.1 Gas atoms or molecules are constantly moving and colliding with one another.

Although both liquids and gases take the shape of their containers, gases differ from liquids in that there is so much space between gas molecules that they offer little resistance to motion and can be compressed to smaller and smaller volumes. As seen in Figure 1.2, as a gas is compressed, the molecules making up the gas get closer together and create a higher internal pressure.

Hydrogen is the lightest known gas. Any balloon filled with hydrogen gas will float in air if the total mass of its container is not too great. Helium gas is also lighter than air and has 92% of the lifting power of hydrogen. Today all airships, i.e., blimps, use helium instead of hydrogen because it offers almost the same lifting power and is not flammable.

Gases can be monatomic, diatomic, and polyatomic. Monatomic gases are gases composed of single atoms, diatomic gases are those composed of two atom molecules, and polyatomic gases are those made up of molecules with more than two atoms. Noble gases such as helium, neon, argon, etc., are normally found as single atoms, since they are chemically inert. Gases such as nitrogen (N_2), oxygen (O_2), and carbon monoxide (CO) tend to be found as diatomic molecules (Figure 1.3). Carbon dioxide (CO_2), and methane (CH_4) are examples of polyatomic gas molecules (Figure 1.3).

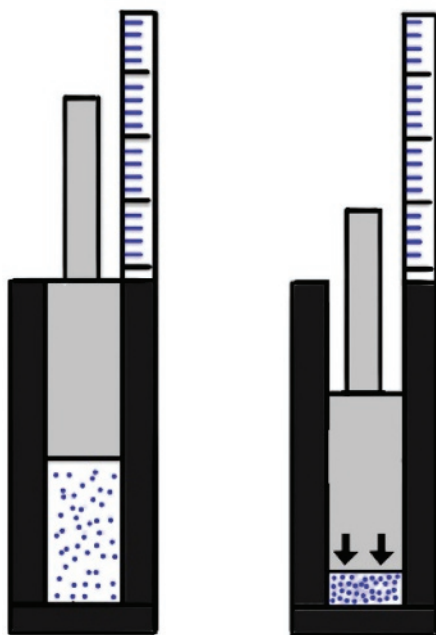


Figure 1.2 As gas is compressed, the gas molecules get closer together.

Gases can be found all around us. In fact, the earth's atmosphere is a blanket of gases composed of nitrogen (78%), oxygen (21%), argon (1%), and then trace amounts of carbon dioxide, neon, helium, methane, krypton, hydrogen, nitrous oxide, xenon, ozone, iodine, carbon monoxide, and ammonia.

Because of the large distances between gas particles, the attractions or repulsions among them are weak. The particles in a gas are in rapid and continuous motion. For example, the average velocity of nitrogen molecules, N_2 , at 68 °F is about 1640 ft/s. As the temperature of a gas increases, the particles' velocity increases. The average velocity of nitrogen molecules at 212 °F is about 1886 ft/s. The particles in a gas are constantly colliding with the walls of the container and with each other. Because of these collisions, the gas particles are constantly changing their direction of motion and their velocity. In a typical situation, a gas particle moves a very short distance between collisions. For example, oxygen, O_2 , molecules at normal temperatures

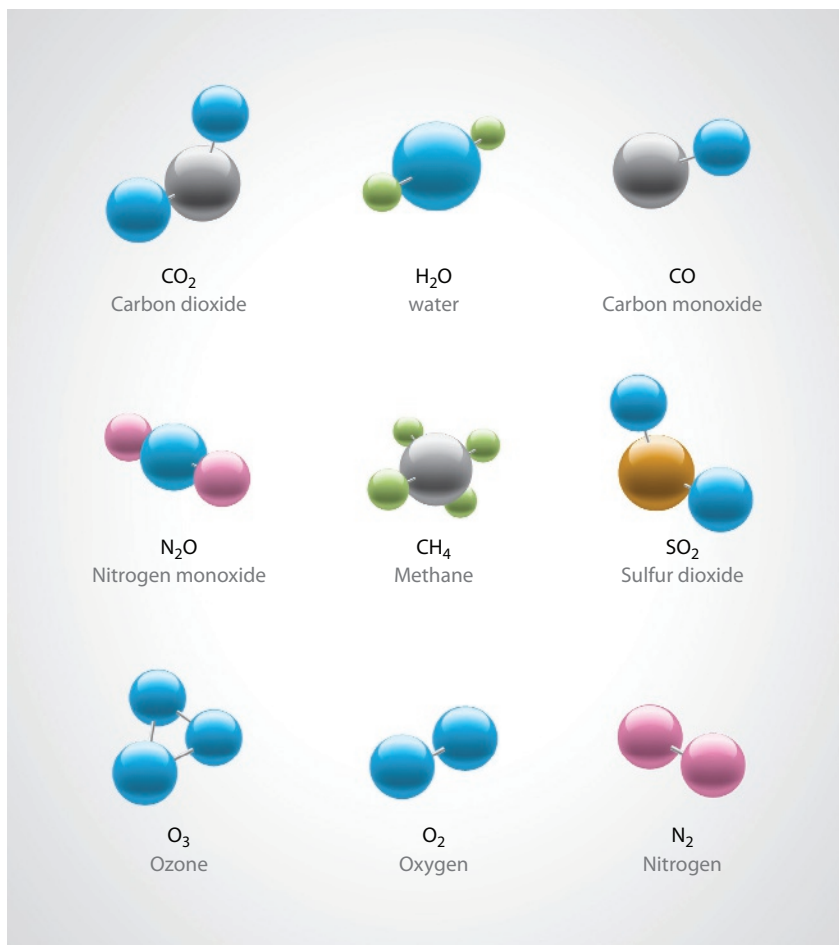


Figure 1.3 Oxygen, nitrogen, and carbon monoxide are examples of diatomic molecules. Carbon dioxide, water, nitrogen monoxide, methane, sulfur dioxide, and ozone are examples of polyatomic molecules.

and pressures move an average of 0.000003937 inches between collisions.

1.1 Ideal Gases

Scientists often simplify the model of gases by imagining the behavior of an ideal gas. An ideal gas differs from a real gas in

that the particles are assumed to be point masses, that is, particles that have a mass but occupy no volume. It is also assumed that there are no attractive or repulsive forces at all between the particles. When all these assumptions are incorporated into a gas model, the “ideal gas model” is obtained. As the name implies, the ideal gas model describes an “ideal” of gas behavior that is only approximated by reality. Nevertheless, the model has been proven to reasonably explain and predict the behavior of typical gases under typical conditions.

Note: Under ordinary conditions, the properties of gases predicted by the ideal gas law are within 5% of their actual values.

1.2 Properties of Gases

The ideal gas model is used to predict changes in four related gas properties: volume, number of particles, temperature, and pressure. Volumes of gases are usually described in cubic feet, ft^3 , or cubic meters, m^3 , and numbers of particles are usually described in moles.

1.3 Temperature

Temperature is a physical quantity expressing how hot or cold a system of atoms or physical object is. Technically, temperature is the proportional measure of the average kinetic energy related to the random motions of the constituent particles of matter in a system. Temperature is an important property of a system because it is an indication of the direction in which heat energy will spontaneously flow. Remember that heat energy always flows from a hotter body (one at a higher temperature) to a colder body (one at a lower temperature).

Temperature is a measure of the total heat energy in a system.

Gas temperatures can be measured with thermometers, infrared guns, and thermocouples. Readings can be reported

in degrees Fahrenheit, °F, or Celsius, °C. However, engineers generally use Rankine, or Kelvin temperatures for calculations.

1.4 Pressure

Remember that gases have no definite shape or volume; they tend to fill whatever container they are in. They can compress and expand and have extremely low densities when compared to a liquid or solid. Combinations of gases tend to mix together spontaneously; that is, they form gas mixtures. Air, for example, is a solution of mostly nitrogen and oxygen. Any understanding of the properties of gases must be able to explain the properties of gas mixture.

The kinetic theory of gases indicates that gas particles are always in motion and are colliding with other particles and the walls of the container holding them. Although collisions with container walls are elastic (i.e., there is no net energy gain or loss because of the collision), a gas particle does exert a force on the wall during the collision. Each time a gas particle collides with and ricochets off one of the walls of its container, it exerts a tiny force against the wall. The accumulation of all these forces distributed over the area of the walls of the container causes something we call pressure. Pressure (P) is defined as the force of all the gas particle-wall collisions divided by the area of the wall:

$$\text{Pressure} = \text{force/area}$$

In English units, pressure is measured in psi, or pounds per square in. The formal, SI-approved unit of pressure is the pascal (Pa), which is defined as 1 N/m² (one newton of force over an area of one square meter). However, this is usually too small in magnitude to be useful. A common unit of pressure is the atmosphere (atm), which was originally defined as the average atmospheric pressure at sea level.

1.5 Gas Laws

When seventeenth-century scientists began studying the physical properties of gases, they noticed simple relationships between some of the measurable properties of gases. For example, scientists noted that for a given quantity of gas, usually expressed in units of moles, i.e., number of molecules $[n]$ in a system, if the temperature (T) of the gas is kept constant, pressure and volume are related: as one variable increases, the other variable decreases. Conversely, as one variable decreases, the other variable increases. Therefore, we say that *pressure and volume are inversely related*.

take pressure (P) and volume (V), for example:

There is more to it, however: pressure and volume of a given amount of gas at a constant temperature are numerically related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{constant at constant } n(\text{moles}) \text{ and } T(\text{temperature}) \quad (1.1)$$

If either volume or pressure changes while the amount and temperature stays the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labelled P_1 and V_1 and the new conditions are labelled P_2 and V_2 , we have

$$P_1 V_1 = \text{constant} = P_2 V_2 \quad (1.2)$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply:

$$P_1 V_1 = P_2 V_2 \text{ at constant } n \text{ and } T \quad (1.3)$$

This equation is an example of a gas law. A gas law is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called *Boyle's Law*, after the English scientist Robert Boyle, who first announced it in 1662. Figure 1.4 shows two representations of what Boyle's Law describes.

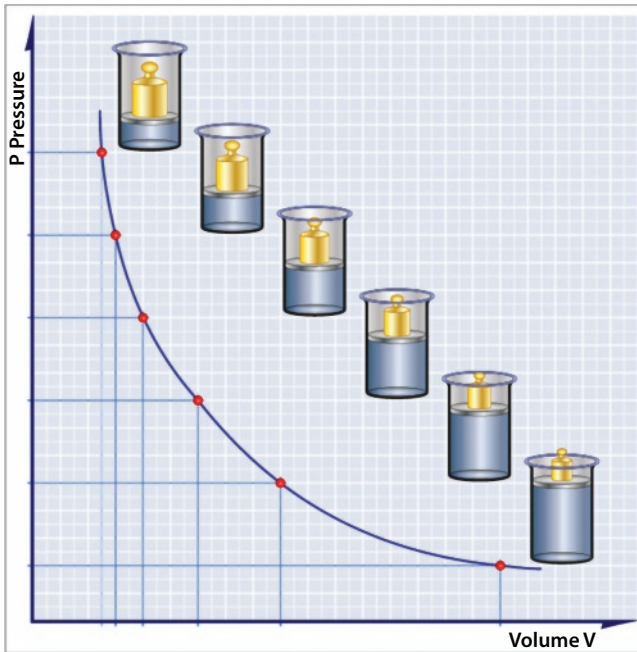


Figure 1.4 Starting with a piston having a given pressure and volume (far right piston), the volume continuously decreases as the applied pressure increases. If you plot pressure (P) as a function of the volume (V) for a given amount of gas at a certain temperature, you will get a plot that looks like the one shown here.

Boyle's law example:

A tire with a volume of 11.41 L (0.4029 ft³) reads 44 psia (pounds per square inch absolute) on the tire gauge. What is the new tire pressure if you compress the tire to a new volume of 10.6 L (0.3743 ft³)?

Answer:

First, we write out Boyle's Law:

$$P_1 V_1 = P_2 V_2 \quad (1.4)$$

Solving for P₂ we get:

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{44 \text{ psi} \times 0.4029 \text{ ft}^3}{0.3743 \text{ ft}^3} = 47.36 \text{ psi}$$

$$P_2 = 47.39 \text{ psia}$$

Here is a listing of all the ideal gas laws along with what each one means:

Avogadro's Law states that equal volumes of all ideal gases (at the same temperature and pressure) contain the same number of molecules.

Boyle's Law states that equal pressure is inversely proportional to volume (when temperature is constant).

Charles's Law states that volume is proportional to temperature (when pressure is constant). Remember that temperature must be measured in Kelvin.

Gay-Lussac's Law states that pressure is proportional to temperature (when volume is constant).

Combining Charles's Law, Boyle's Law, and Gay-Lussac's Law gives us the combined law:

$$\frac{P \times V}{T} = \text{constant} \quad (1.5)$$

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2} \quad (1.6)$$

If we consider Avogadro's Law, we can combine all four gas properties into one equation:

$$\frac{P \times V}{n \times T} = R \quad (1.7)$$

The constant R in this equation is called the Universal Gas Constant.

The ideal gas law in this form is the most useful and should be memorized by those dealing with gases on a regular basis.

n = number of gas particles in a container

P = Pressure

T = Temperature

V = volume of the container

Keep in mind that these gas laws only apply during isothermal compression, i.e., compression occurring at a constant temperature, inside lab devices that move slowly and are poorly insulated. We'll discuss why this is important a little later in this chapter.

1.6 Gas Mixtures

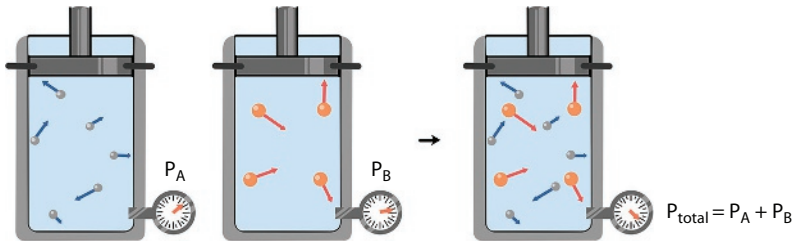
1.6.1 Dalton's Law of Partial Pressures

Most gaseous systems contain a mixture of gases. For example, air is a mixture of nitrogen gas, oxygen gas, xenon gas, carbon dioxide gas, and many others. A typical “neon” light on a Las Vegas marquee contains argon gas as well as neon. When working with a mixture of gases, we are sometimes interested in the total pressure exerted by all the gases together, and sometimes we are interested in the portion of the total pressure that is exerted by only one of the gases in the mixture. The portion of the total pressure that one gas in a mixture of gases contributes is called the partial pressure of the gas. Partial pressure is defined as the pressure exerted by one of the gases in a mixture if it occupied the same volume on its own.

One of the properties of gases is that they mix with each other. When they do so, they become a solution—a homogeneous mixture. Some of the properties of gas solutions are easy to determine if we know the composition of the gases in the mixture.

In gas mixtures, each component in the gas phase can be treated separately. Each component of the mixture shares the same temperature and volume. (Remember that gases expand to fill the volume of their container and all gases in a mixture do that as well.) However, each gas has its own pressure. The partial pressure of a gas, P_i , is the pressure that an individual gas in a mixture has. Partial pressures are expressed in psi, millimeters of mercury, or atmospheres like any other gas pressure; however, we use the term *pressure* when talking about pure gases and the term *partial pressure* when talking about the individual gas components in a mixture.

Dalton's law of partial pressures states that the total pressure of a gas mixture, P_{tot} , is equal to the sum of the partial pressures of the components, P_i (see Figure 1.5):



The situation is summarized in **Dalton's Law of Partial Pressures**: the total pressure of a mixture of gases is equal to the sum of the partial pressure of all the gases.

Figure 1.5 Dalton's law of partial pressures.

$$P_{\text{tot}} = P_1 + P_2 + P_3 + \dots = \sum_{\text{\# of gases}} P_i \quad (1.8)$$

$$P_{\text{tot}} = P_A + P_B \quad (1.9)$$

Although this may seem to be a trivial law, it reinforces the idea that gases behave independently of each other.

1.7 Molecular Weight of a Gas Mixture

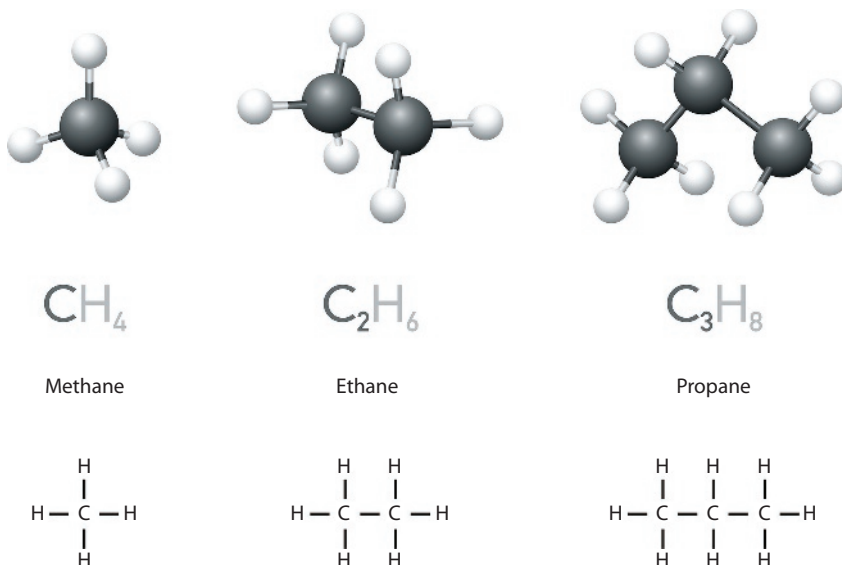
Because most industrial gases are composed of a mixture of gas, it is important to be able to determine the molecular weight of a gas mixture. To accurately calculate the molecular weight of a gas mixture, you need to know the molecular weights and percentage makeup of the mixture's constituent gases. The molecular weight of a gas mixture can affect a compressor's performance in several ways: for example, in dynamic compressors, a gas's molecular weight directly affects the compressor's horsepower consumption and the generated differential pressure.

Molecular weight (M) of a pure substance is the total mass of one of its molecules. It is calculated in practice by summing the atomic weights of the molecules making up the substance's molecular formula. For example, the molecular weight of a hydrogen molecule (chemical formula H_2) is 2 (after rounding

Table 1.1 Composition of methane.

Element	Symbol	Atomic mass	Number of atoms in molecule	Mass percent
Hydrogen	H	1.00794	4	25.132%
Carbon	C	12.0107	1	74.686%

Molecular weight of methane = $4 \times 1.00794 + 12.0107 = 16.04246$

**Figure 1.6** Molecular structure of methane, ethane, and propane.

off) and the molecular weight of methane is 16.04246 g/mol (see Table 1.1 below).

Hydrocarbons, such as methane, are substances composed entirely of carbon and hydrogen atoms. The three-dimensional molecular structures of the three common hydrocarbon molecules can be seen in Figure 1.6. You will notice that the methane molecule is tetrahedral in shape. The molecular structures seen in Figure 1.6 are dependent on the preferred orientation of covalent bonds between their atoms. (A covalent bond is a chemical

Table 1.2 Molecular weights of some common hydrocarbons. Compare the chemical formulas in this table with the molecular structures shown in Figure 1.6.

Gas	Chemical formula	Molecular weight
Methane	CH ₄	16.4
Ethane	C ₂ H ₆	30.07
Propane	C ₃ H ₈	44.09

bond that involves the sharing of electron pairs between atoms.) Table 1.2 lists the chemical formulas and molecular weights of these three common hydrocarbon molecules.

The average molecular weight of a gas mixture is determined by multiplying the molecular weights of each component by its mole fraction (Mole %/ 100) and then adding up all the values. (Note: The mole fraction or molar fraction (x_i) is defined as the quantity of a constituent (expressed in moles), n_i , divided by the total quantity of all constituents in a mixture (also expressed in moles), n_{tot} . In other words, the mole fraction of each constituent is determined as follows:

$$x_i = \frac{n_i}{n_{\text{tot}}} \quad (1.10)$$

To fully understand how to calculate the average molecular weight of a gas mixture, let's go through the following example (Table 1.3):

Note that we need to know the mole fraction and molecular weight of each component gas to determine the proportional molecular weight. The four-gas mixture has an average molecular weight of 14.84.

1.8 Gas Density

The density of a gas can be determined by utilizing a variation of the ideal gas law where density and molar mass replace moles

Table 1.3 Calculating the molecular weight of a gas mixture.

Gas	Mole % or Vol %	Molecular weight	Proportional MW
H ₂	61.4 x	2	1.228
N ₂	19.7 x	28	5.516
CO ₂	17.5 x	44	7.700
CO	1.4 x	28	0.392
Total %	100.0		14.84 is the MW of the total gas mixture

and volume. Where the original ideal gas law uses the formula $PV = nRT$, the density version of the ideal gas law is $PM = dRT$, where M is the molar mass. The molar mass of a gas composed of single atoms is given by the standard atomic weight of the element multiplied by the molar mass constant, $M_u = 1 \times 10^{-3} \text{ kg/mol} = 1 \text{ g/mol}$. For a molecule, the molar mass is the combined mass of all the atoms in a molecule in grams per mole. To calculate the molar mass of a molecule, first obtain the atomic weights from the individual elements in a periodic table. Then count the number of atoms and multiply it by the individual atomic masses. This sum represents the molecular weight of each molecule. Multiplying the molecules molecular weight by the molar mass constant ensures that the calculation is dimensionally correct.

1.9 Density of Mixtures

We learned from the ideal gas law that the density of a gas is directly proportional to its molecular mass (M), which is related to its molecular weight:

$$P \times M_A = \rho \times RT \tag{1.11}$$

where M_A is the molecular weight of the gas, ρ is the density of the gas, and R is the universal gas constant. If we know the density, total pressure and temperature of the gas the molecular weight can be easily determined from this equation.

What happens when we have a gas mixture? We use the density of the gas to determine the composition with the following equation: Density = mass (m) divided by the volume.

$$\rho = m/V \quad (1.12)$$

The density of a mixture of gases A and B is obtained knowing the total mass of the gases, which is the sum of the masses of each.

$$\rho = \frac{m_A + m_B}{V} = \frac{m_A}{V} + \frac{m_B}{V} \quad (1.13)$$

The ideal gas law indicates that the mass of A divided by the total volume is equal to $P_A \times M_A / RT$; therefore, if we replace the right side of the above equation with this relationship for each component we get:

$$\rho = \frac{P_A \times M_A}{R \times T} + \frac{P_B \times M_B}{R \times T} \quad (1.14)$$

Where P_A is the partial pressure of gas A and P_B is the partial pressure of gas B. Therefore, by knowing the partial pressure of each as in the mixture, we can determine the overall density of the mixture.

1.10 Heat of Compression

If you compress a gas adiabatically (without allowing heat to enter or leave) you are doing work on the gas, which increases its internal energy. Here's another way to look at the heat of compression:

compression occurs $\rightarrow$ gas volume decreases $\rightarrow$ the frequency of gas particle collisions increases $\rightarrow$ the gas temperature increases



Figure 1.7 Air fin cooler, which is located on the far right of the skid, provides interstage cooling for the reciprocating compressor (far left).

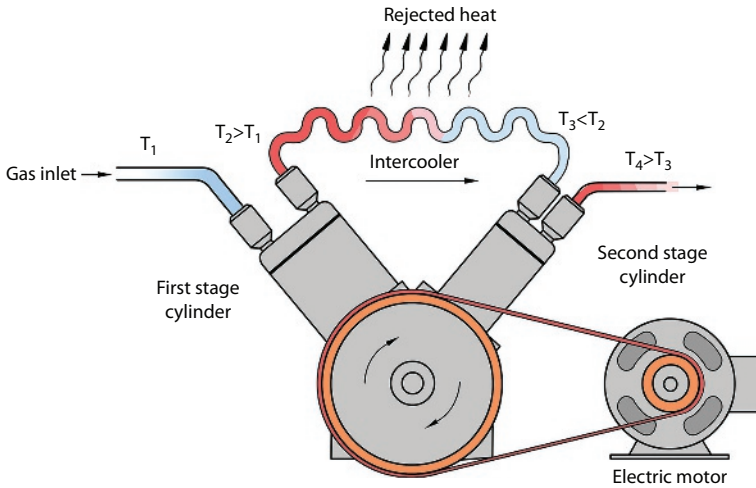


Figure 1.8 Schematic of a two-stage reciprocating compressor with an intercooler between stages. Notice that gas entering the second stage of compression has been cooled ($T_3 < T_2$) with an air-cooled heat exchanger before entering the second stage of compression.

Remember that the temperature is a measure of the internal energy (kinetic energy of the molecules for an ideal gas). Thus, compression tends to increase a gas's temperature.

Another way to explain the heat of compression is by remembering Boyle's Law: temperature increases because temperature and volume of gas are inversely proportional to each other according to gas laws. Therefore, when a gas is compressed rapidly, its volume decreases leading to increase in temperature.

The heat of compression effect is why we often need cooling between compression stages or downstream of the discharge of a compressor. In the processing industry, air fin coolers (Figure 1.7) are the most common means of cooling discharge gas. Air fin coolers, which can either be configured vertically or horizontally, force air across finned tubes filled with hot compressor discharge gas. The air coolers can either be driven off the driver shaft or powered by one or more electric motors. If designed properly, air fin coolers will drop the gas temperature to a manageable level, preferably between 80 to 100 °F, before it enters the next stage of compression (Figure 1.8) or the gas distribution piping.

