

Chapter 9 - Gases

This chapter covers the physical properties of gases, the mathematical equations that describe their behavior, and the theory that explains both.

9.1 Gas Pressure

Pressure is the force exerted by one "object" on another and depends on the area upon which the force acts. To illustrate this concept imagine holding a brick in your hand. Now imagine the same brick on top of nail. In the latter case, the same force (weight) is present, but now it is acting on a much smaller area, so the pressure is greater at the tip of the nail.

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

Just as gravity pulls you and all the objects in this room downward, it pulls the gas molecules in the atmosphere toward the Earth. Atmospheric pressure equals the weight of a column of air extending from the ground to space divided by the area of the base of the column. (ca. 14.7 lb/in² or about the equivalent of stacking 1 $\frac{3}{4}$ gallons of water on a 1 square inch block at sea level) Table 9.1 (p. 460) lists a variety of pressure units. Interestingly, all of them are used in practice. In chemistry, we primarily will encounter torr and atmospheres.

Barometers measure atmospheric pressure and consist of a glass tube, sealed at one end, filled with mercury, and then placed in a pool of mercury, sealed end up. The mercury level will then drop until the downward pressure of the mercury equals the downward force of the air on the open pool of mercury. Thus, the height of the mercury column measures the outside pressure. Standard atmospheric pressure at sea level is defined as 760 mmHg = 760 torr = 1 atm. A barometer using water would have to be over 30 feet tall to work properly. This explains why mercury barometers are still common despite employing a hazardous material. The pressure on your shoulders equals this 30 foot high water column.

You can see this effect yourself. Fill a sink about six inches deep with water and submerge the tallest glass you can find so that it is filled with water. While completely under water begin to lift the glass out of the sink by the closed end. You will find that you can raise the glass until the rim reaches the surface and the glass will remain filled with water. A longer tube can be used in a bathtub or swimming pool with the same results.

Finally, a manometer is a device that measures the pressure of a gas in a sealed container.

9.2 Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

Much about gases can be described using 4 physical properties, pressure (P), volume (V), temperature (T), and the number of moles (n).

Volume and Temperature: Charles' Law

What happens to a balloon if it's warmed? If it's cooled? Again, experience tells you heating expands a gas and cooling contracts it. Charles' law states that the volume of a fixed quantity of gas at constant pressure is directly proportional to temperature.

$$V \propto T \quad \text{or} \quad \frac{V}{T} = k_2 \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Now consider a graphical plot of volume vs. temperature for any gas. What happens as we cool the gas? The volume decreases for a while, but the gas eventually liquefies. Before then, the plot is linear according to Charles' law. If we extrapolate the line before liquefaction of any gas to $V = 0$, the point of intersection is always the same: $-273.15 \text{ }^\circ\text{C}$. This temperature is called absolute zero and is the lowest possible temperature. The Kelvin scale was developed from this and since it is an absolute scale no degree sign is used. For all gas law calculations, use the Kelvin temperature scale.

Volume and Pressure: Boyle's Law

Imagine a cylinder sealed at one end with a movable piston balanced halfway down on the other end. What happens if you place a weight on the piston? A second weight? What happens if you then

remove the weights? As you know, adding weights will push the piston down and removing them will cause the piston to move up. Thus, there is an *inverse* relationship between pressure and volume. Boyle's law states that the volume of a fixed quantity of gas is inversely proportional to its pressure at constant temperature.

$$V \propto \frac{1}{P} \quad \text{or} \quad PV = k_1 \quad \text{or} \quad P_1V_1 = P_2V_2$$

Note: A common mistake is to substitute the word "indirectly" for "inversely" when discussing the proportionality in Boyle's law. These words are not synonyms.

Moles of Gas and Volume: Avogadro's Law

What happens to a balloon if we put more gas in? Again, as you know, the balloon expands. This yields Avogadro's law. The volume of a gas is directly proportional to the number of moles of gas present. Not surprisingly, doubling the amount of gas doubles the space it occupies.

$$V \propto n \quad \text{or} \quad \frac{V}{n} = k_3 \quad \text{or} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

The stoichiometries of many reactions had long been known by Avogadro's time. Observations by Gay-Lussac showed that for reactions of gases, the ratio of gas volumes mirrored reaction stoichiometries. From this, Avogadro proposed that equal volumes of gases contain equal numbers of molecules at the same pressure and temperature.

It is useful to have a set of standard conditions for reference purposes. For gases, standard temperature and pressure (STP) are defined as 0 °C and 1 atm. At STP, an ideal gas occupies 22.414 L. While no gas is truly ideal, most behave close to ideally at STP and some, like helium and argon do so over very wide temperature ranges. [*Note that standard temperature for a gas, is different from standard temperature for thermochemistry, which we encountered in Chapter 5.*]

Pressure and Temperature: Amontons' (Guy-Lussac's) Law

I've placed this law last because it isn't as intuitive as the others. Earlier, with Charles' Law,

we saw that warming a balloon results in its expansion. What if that balloon was placed in a box and couldn't expand? In that case, the pressure inside the balloon would increase.

$$P \propto T \quad \text{or} \quad \frac{P}{T} = k_4 \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

The Ideal Gas Law

The gas laws in the previous section look very similar:

$$V \propto \frac{1}{P} \quad V \propto T \quad V \propto n \quad P \propto T$$

They may be combined to yield a new proportionality: $V \propto \frac{nT}{P}$. To convert this to an equality, we need to use a proportionality constant called the ideal gas constant, R.

$$PV = nRT$$

This is called the ideal gas equation, where an ideal gas is one whose component molecules do not interact. R has a value of 0.0821 L·atm/mol·K or 8.314 J/mol·K.

The proportionalities used to produce the ideal-gas equation can also be used to produce an equation sometimes called the combined gas law.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This equation turns out to be quite useful. If any of the conditions remains constant from beginning to end, the equation simplifies to the known gas laws:

$$\text{Boyle's law: } P_1 V_1 = P_2 V_2 \quad \text{Charles' law: } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Example: A 1.00 L balloon at STP is heated to 25 °C with the pressure dropping to 0.947 atm.

What is its new volume?

$$\frac{(1.00 \text{ atm})(1.00 \text{ L})}{273 \text{ K}} = \frac{(0.947 \text{ atm})V_2}{298 \text{ K}} \Rightarrow V_2 = 1.15 \text{ L}$$

9.3 Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Gas Density and Molecular Mass

Density is sometimes an important tool used in identifying a gas or in determining its molecular weight. Because gases take up so much space relative to the size of their component molecules, we typically report gas densities in units of g/L. A relatively simple change in the ideal-gas equation allows its use in gas density calculations. We begin by rearranging it to

$$\frac{n}{V} = \frac{P}{RT}$$

Then multiply each side by the molecular weight of the gas

$$\frac{n(\text{MW})}{V} = \frac{P(\text{MW})}{RT}$$

Now mass = (moles)(molecular weight), so

$$d = \frac{P(\text{MW})}{RT} \quad \text{or} \quad \text{MW} = \frac{dRT}{P}$$

This equation allows chemists to determine the molecular weight of an unknown gas, which provides a clue as to its identity. Gas densities account for why hot air balloons float, much like how air bubbles rise to the surface of a pool of water. Imagine a standard hot air balloon filled with cold air. As the air inside the balloon warms, it expands (Charles' law), but the balloon walls can't expand. The only way to deal with the warming is for some of the air to leave the balloon through the hole at the bottom. Because some of the air leaves the balloon the contents weigh less than an equal volume of cold air. Since air is a fluid, any object weighing less than an equal volume of air will rise (float). This is how a hot air balloon works. The very low density of air accounts their large size.

The Pressure of a Mixture of Gases (Dalton's Law of Partial Pressures)

By rearranging the ideal-gas equation, we can show that the pressure of a gas is directly proportional to the number of moles at constant temperature and volume.

$$P = n \left(\frac{RT}{V} \right) \Rightarrow P \propto n$$

Because this relation is valid for any gas, it also holds for gas mixtures. The pressure exerted by each gas of a mixture is called a partial pressure. The total pressure of a system equals the sum of the partial pressures of the component gases.

$$P_T = P_1 + P_2 + P_3 + \dots = \sum P_n$$

$$P_T = \left(\frac{RT}{V} \right) (n_1 + n_2 + n_3 + \dots) = \left(\frac{RT}{V} \right) \sum n_n$$

Percentage composition provides another way to describe gas mixtures. The mole fraction, χ , of a compound is the number of moles of the compound divided by the number of moles in the mixture.

$$\text{mol fraction of compound A} = \chi_A = \frac{\text{mol}_A}{\text{total moles}}$$

$$\text{Now } \frac{P_A}{P_T} = \frac{\left(\frac{RT}{V} \right) n_A}{\left(\frac{RT}{V} \right) n_T} \longrightarrow \frac{P_A}{P_T} = \frac{n_A}{n_T} = \chi_A$$

$$\text{Thus } P_A = \chi_A P_T$$

Basically, this equation shows that if 80% of a gas mixture is carbon dioxide, the partial pressure of CO_2 is 80% of the total pressure.

Collecting a Gas Over Water

Sometimes we collect a gas resulting from a reaction. (You may do this in CHM 217.) Figure 9.21 (p. 486) shows an apparatus for doing so. As the gas forms, it flows through a tube, bubbles into a flask containing water, and displaces some of the water. The volume of water displaced equals the volume of gas. The gas in the flask is a mixture of the product gas and water vapor. The volume of the latter must be subtracted from the total. Since pressure is proportional to volume, this can be accomplished by the following equation.

$$P_{\text{Total}} = P_{\text{product}} + P_{\text{H}_2\text{O}}$$

Chemical Stoichiometry and Gases

There is something about the reaction between gases that does not apply to solids or liquids. Avogadro's law or the ideal gas equation shows us that the number of moles is directly proportional the volume of a gas. Thus, for a reaction involving only gasses as reactants, the stoichiometry of the reaction converts directly from moles to volume. Stated a little differently, if you have the reaction $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$, then two liters of hydrogen will react with one liter of oxygen to yield water. If the product is also a gas, then the volume of the gas will be proportional to its stoichiometric coefficient. Thus, if the water produced was a gas, there would be two liters generated from 2 liters of hydrogen and 1 liter of oxygen.

9.4 Effusion and Diffusion of Gases

In many ways, the most important property of gases is the mobility of their component molecules. Gas molecules generally travel at hundreds of miles an hour (e.g. At room temperature, a typical oxygen molecule travels at about 1100 mph!) and the large spaces between them allow rapid redistribution. When gases are allowed to mix at the same pressure, the process is called diffusion. Diffusion occurs when you smell dinner being cooked or someone opens a bottle of a fragrance. This raises the question "Why, if molecules travel hundreds of miles an hour, does it take minutes or more for an odor to cross a room?" We'll come back to this question shortly.

Effusion is a related process. Effusion is the movement of a gas from a place of high pressure to a place of low pressure (usually a vacuum) through a small hole. As you would guess, effusion depends on both the velocity of the gas and the size of the hole. Faster molecules have more opportunities to strike the hole in a given period of time and a larger hole provides a larger target. If the effusion rates of two gases measured in the same device are compared, the hole size cancels out and can be ignored. The relationship, Graham's law of effusion, results.

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{MW_2}{MW_1}}$$

This law allows for an effective method for gas separation. It has a major historical application. Only one isotope of uranium undergoes fission (Chapter 21, Section 4 describes fission). During World War II, the US needed a sizable amount of uranium-235 to build the first two atomic bombs (a test bomb and "Little Boy," the one actually used on Hiroshima). It separated the isotopes by converting uranium metal to UF_6 . This compound has a high vapor pressure, which allowed its easy conversion to the gas phase. After many hundreds of cycles, pure $^{235}\text{UF}_6$ was prepared and converted back to the metal. The gas centrifuges you may have heard about in Iran's nuclear program are used for this purpose. Graham's law also works for diffusion.

So why does it take so long for an odor to cross the room? Because there are many molecules of air blocking the path. Odor molecules will take a zigzag path across the room making about 10 billion collisions per second and travel an average distance of 0.06 micrometers between collisions. For reference, the period at the end of this sentence is more than 100 micrometers in diameter.

9.5 The Kinetic-Molecular Theory

Near the beginning of the chapter you were asked what happened to a volume of a gas when the pressure, temperature, and number of moles changed. You answered in terms of your experience, but why do these things happen the way they do?

In the mid-1800s, Rudolf Clausius proposed a theory to account for the observed properties of gases. At the time, they were postulates, but have since been demonstrated as correct.

- 1) Gases consist of large numbers of molecules of widely spaced molecules. Because of this, the total volume of the molecules is negligible when compared to the total volume of the container. (i.e. We can ignore the volume of the molecules.)
- 2) The gas molecules are in continuous, random, straight-line motion.

- 3) The pressure inside a container arises from the collisions the gas molecules have with the container walls.
- 4) Attractive and repulsive forces between molecules are not important. Energy can be transferred between molecules during collisions, but the average kinetic energy is constant at constant temperature. (i.e. The collisions are elastic.)
- 5) The average kinetic energy is proportional to absolute temperature.

How do these postulates account for the observed properties of gases? Postulate 5 tells us that the energy of molecules increases with temperature. The energy increase manifests as increased molecular velocity. Thus, an increase in temperature causes molecules to move faster.

Postulates 4 and 5 concern average kinetic energy; thus, the gas molecules travel at a range of velocities. The kinetic energy of a gas molecule is given by:

$$KE = \frac{1}{2} m u_{\text{rms}}^2$$

Velocity is measured as root-mean-square velocity, u , where

$$u_{\text{rms}} = \sqrt{\frac{3RT}{MW}}$$

Average velocity is about 92% of rms velocity. The need to use root-mean-square velocity instead of average velocity arises from the algebra used to derive the formula. [Optional: The kinetic energy for a single particle is $\frac{1}{2}mv^2$. When this is averaged over all molecules, one takes the average of (velocity)² (rather than the square of the average of the velocities) and this gives rise to the root-mean-square term.] Since all gas molecules have the same kinetic energy, heavier gas molecules must travel at lower speeds than lighter molecules.

Do you recall the definition of pressure? It is force per unit area. The question here is "How does a gas exert force?" Imagine the gas in a balloon at the atomic scale. Gas molecules travel around and occasionally hit the wall of the balloon. When they do, they exert a force that pushes the walls outward. Using this description, let's look at the two-component gas laws.

Boyle's Law: $V \propto 1/P$ @ constant temperature. If the volume increases (the walls move outward) the molecules must travel longer distances to strike the container walls. Since the velocity doesn't change, the rate of collisions with the wall decreases and the pressure drops.

Avogadro's Law: $V \propto n$ @ constant pressure & temperature. If the number of molecules increases, the rate of collisions with the walls increases. If pressure is constant, the walls must move out to decrease the collision rate to the original value. Thus, volume increases.

Charles' Law: $V \propto T$ @ constant pressure. If the temperature increases, so does the kinetic energy and velocity of the gas molecules, but here the external pressure is constant, so the walls move outward to increase the distance the molecules must travel so that collision rates with the walls drop until the original pressure is reached. Thus, volume increases.

Amonton's Law: $P \propto n$ @ constant volume & temperature. The reasoning here is closely related to that for Charles' law. For Amonton's law, the molecules are striking the walls harder, just like in the Charles' law situation, but now the walls are locked in place so the while the force of impact increases, the net impact isn't reduced by decreasing the rate of molecules hitting the wall. The result is a higher total force and, so, a higher pressure.

9.6 Non-Ideal Gas Behavior (i.e. 'the behavior of real gases')

In reality, all gases deviate from ideality under some conditions. You've already seen one example: when gases cool sufficiently, they liquefy. The gas is certainly not behaving ideally just before it condenses. What is happening during the process of condensation?

The molecules have attractions for each other (see Chap. 10) but at "high" temperatures the molecules are traveling so rapidly the forces don't matter. Imagine throwing a refrigerator magnet past a piece of iron at 1000 mph. It certainly wouldn't stop and stick. The same is true of molecules. But as the temperature drops, those intermolecular forces become more important and first alter the flight paths of gas molecules and eventually cause them to "stick" to each other and form liquids or solids.

Likewise, we assumed that the volumes of molecules were unimportant. At low pressures this is true, but as pressure goes up the free space in the container is reduced (there are more molecules in the same space) and molecules come into contact with each other more frequently. This also causes the attractions between molecules to become more important.

The van der Waals Equation

You aren't responsible for remembering this equation,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

but you need to know its basis. The van der Waals equation takes the influence of molecular size and attractions into account by altering the factors in the ideal gas equation. For example, a term is subtracted from the measured (ideal) volume to account for the volumes molecules displace. That is, the actual volume for the molecules to move about in is smaller than ideal because the molecules themselves take up some of the space. A second term is added to the ideal pressure to account for molecular attractions. Because molecules are attracted to one another, they make contact with the container walls less frequently and less forcefully. The result is the pressure is lower than expected for real gases. This may not be obvious by thinking about it, but here is how it is obtained mathematically (rearranging the ideal gas equation, then putting in correction factors:

$$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

Rearranging this equation, you get the formula at the beginning of this section.

Vapors

An important class of gases that your book doesn't mention is vapors, which are gases of substances that normally occur as liquids or solids at ambient temperature. Vapors almost always exist around solids and liquids of the same substance, although the liquid/solid may be absent if it has completely evaporated. For example, we normally find gasoline vapor around gasoline stations. Vapors differ from 'normal' gases in that they will typically be in contact with the liquid/solid phase. This causes them to behave somewhat differently from 'normal' gases when outside conditions change. For example, it is easier to force a vapor from the gas phase to the liquid/solid phase when pressure increases.

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