

Chapter 5

Gases...

Pressure and its measurement.

Units of pressure.

SI

Pressure is force divided by area. Force is mass times acceleration. This means that the SI unit of pressure is

$$P = F/A = \text{kg} \times (\text{m}/\text{s}^2) / \text{m}^2 = \text{kg}/\text{m} \cdot \text{s}^2$$

This unit is known as a Pascal (Pa), named after Blaise Pascal, a French physicist. This is a very small amount of pressure (a penny on a table exerts a pressure of 93 Pa on the table). As a result we do not use it in chemistry on a regular basis.

Other units.

Atmosphere (atm). This is a unit of pressure equal to the pressure of the Earth's atmosphere at sea level and 0°C.

mmHg. This is a unit of pressure based on the barometer.

Torr. A unit of pressure equivalent to mmHg. Named after Evangelista Torricelli, inventor of the barometer.

Pounds per square inch (psi). The English system unit of pressure.

Bar. A unit of pressure used in meteorology.

Unit conversions.

$$\begin{aligned} 1 \text{ atm} &= 760 \text{ mmHg} \\ &= 760 \text{ torr} \\ &= 14.7 \text{ psi} \\ &= 101325 \text{ Pa} \\ &= 1.01325 \text{ bar} \end{aligned}$$

Ideal Gas Law.

To what is the pressure of a gas proportional?

1. Volume
2. Temperature
3. Amount of gas

$$P \propto \frac{nT}{V}$$

To make this expression equal we need a constant of proportionality. This constant is given the symbol R and is called the ideal gas constant. We get:

$$P = R \frac{nT}{V}$$

Rearranging this gives the standard form of the ideal gas law:

$$PV = nRT$$

The ideal gas constant has the value 0.08206 L-atm/mol-K. Note that the unit of temperature in this constant is kelvin. When working with gas laws, the temperature must always be in kelvin.

Other values for the ideal gas constant:

$$\begin{aligned} R &= 0.08206 \text{ L-atm/mol-K} \\ &= 62.37 \text{ L-mmHg/mol-K} \\ &= 62.37 \text{ L-torr/mol-K} \\ &= 8.314 \text{ L-kPa/mol-K} \\ &= 8.314 \text{ J/mol-K (used primarily in thermochemistry and} \\ &\quad \text{electrochemistry)} \end{aligned}$$

Other gas laws derived from the IGL.

Imagine changing the state of a gas (changing one of the variables). Let's imagine that we are changing the volume of a gas while keeping the amount of gas and the temperature constant. We can rearrange the IGL keeping variables on one side and constants on the other side.

$PV=nRT$ This is going to be true regardless of the change in volume.

$$P_1 V_1 = nRT = P_2 V_2 \quad \text{or} \quad P_1 V_1 = P_2 V_2$$

This last equation is known as Boyle's Law. Named after Robert Boyle, the 17th century natural philosopher (scientist).

The thing to remember about these individual gas laws is that they are the same as the Ideal Gas Law. It is just a matter of what is being held constant.

Molar mass and gases

We can multiply both sides of the Ideal Gas Law by mass and divide both sides by the volume and the number of moles. When we do this we get the following:

$$MP = dRT$$

This expression gives us the relationship between the molar mass of a gas and the density of that gas. The higher the molar mass is, the more dense the gas. We can use gas density measurements to obtain the molar mass of volatile compounds. This is essentially what you did in the molar mass lab. (See the problems from that lab for practice.)

Dalton's Law of Partial Pressures

When we have a mixture of gases, the gases act independently of one another in the container. They do not interfere with each other.

If we consider that the number of moles of a gas is directly proportional to the pressure of that gas (at a given volume and temperature) then we can derive an expression for the pressure of a gas in terms of the individual gases present.

$$n_t = n_1 + n_2 + \dots + n_n$$

gives

$$P_t = P_1 + P_2 + \dots + P_n$$

Where the individual P_i 's are the **Partial pressures**. The last expression is the mathematical form of Dalton's Law of Partial Pressures, which states that the total pressure in a container is the sum of the individual partial pressures of all the gases present.

From the definition of mole fraction,

$$X_i = \frac{n_i}{n_T}$$

we can find an expression for each of the partial pressures based on their mole fractions.

$$X_i = \frac{n_i}{n_T} = \frac{P_i}{P_T}$$

$$P_i = X_i P_T$$

In words, this means that the partial pressure is equal to the total pressure times the mole fraction of the gas.

Vapor pressure

For volatile substances, especially water; the partial pressure of the substance is called the **vapor pressure**. The vapor pressure of water is tabulated in your textbook and Laboratory Handbook. The reason we have tables of the vapor pressure of water is because product gases are often collected by bubbling them through water. The gas then picks up water vapor and the gas collected is a combination of the product gas and water vapor. In order to get the pressure of the gas we are interested in we must subtract out the vapor pressure of water and any pressure due to the difference in the height of the column of water in the collection vessel and the height of the water outside of the vessel.

Kinetic Molecular Theory

A model we use to describe the behavior of gases is called the **Kinetic Molecular Theory**. This theory can be used to derive the Ideal Gas Law, which shows that the theory has some elements of validity. The Kinetic Molecular Theory has five postulates or assumptions to it:

- Gases are comprised of infinitesimal particles. The particles are so small that they do not alter the volume of the container by their presence.
- The gas particles move randomly in straight lines until they hit something.
- The gas particles have no forces between them unless they are in a collision. This means that there are no attractions or repulsions between the gas particles. The only time they affect one another is when they hit one another.
- The gas particles undergo elastic collisions. This means that the total energy of the collision is conserved. No energy is lost or gained, but it can be transferred between two gas particles in a collision.
- The average kinetic energy of the gas particles is proportional to the Kelvin temperature.

Using these postulates and the basic laws of physics we can derive the ideal gas law. We can also derive an expression for an average speed of the molecules. This is called root-mean-squared speed, u_{rms} . This is what we get if we take the speed of all the gas particles and square them. We then take the average of the squares of the speeds. Then we take the square root of the average. This is a bit of an unwieldy way to do it for a large collection of gas particles. Fortunately, we can use statistical methods and the Kinetic Molecular Theory to come up with an expression for this. We get

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

where R is the ideal gas constant in $\text{J mol}^{-1} \text{K}^{-1}$ ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), T is the Kelvin temperature and M is the molar mass in kg mol^{-1} . The unit for u_{rms} in this equation is m s^{-1} . If we plug the correct values for various gases into this equation it will tell us what the “average” speed of those molecules is. These speeds range from a few hundred to a couple of thousand meters per second.

Effusion and Diffusion

Diffusion is the movement of one fluid (gas or liquid) through another. **Effusion** is the movement of a gas through a small hole into a vacuum. Kinetic Molecular Theory can describe both. If we consider the above result for the “average” speed of a gas particle and that the rate at which the particle moves is proportional to the speed. We can show that the rate of effusion (or diffusion) is proportional to the inverse of the square root of the molar mass

$$\text{Rate} \propto \frac{1}{\sqrt{M}}$$

Often what we are interested in is the ratio of the rates of effusion. Graham’s Law gives this as

$$\frac{\text{rate}_1}{\text{rate}_2} = \sqrt{\frac{M_2}{M_1}}$$

This is another method that can be used to find the molar mass of a gas.