

# 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

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

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.

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

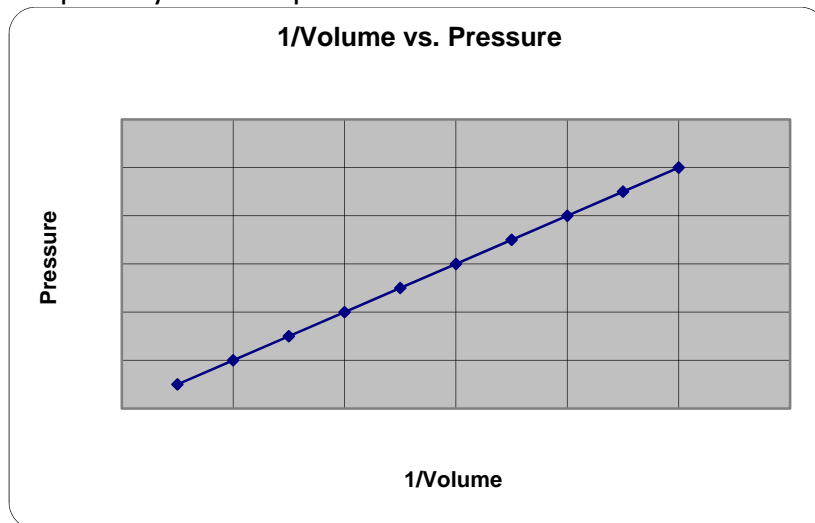
## Laws Describing the Behavior of Gases

### Boyle's Law

Robert Boyle was a "Natural philosopher" who lived in the 1600's. He was one of the first people to do experiments to determine the way nature worked. One of his experiments is summed up in Boyle's law, which relates the pressure of a gas to its volume. Boyle discovered that the pressure a gas exerts is inversely proportional to its volume or that the product of the pressure and the volume of a gas is a constant. The more volume a gas has, the lower its pressure and vice versa. This only applies in the number of moles of gas and the temperature remains constant. This can be stated mathematically as:

$$P \propto \frac{1}{V} \text{ or } PV = \text{constant}$$

Graphically this is represented as:

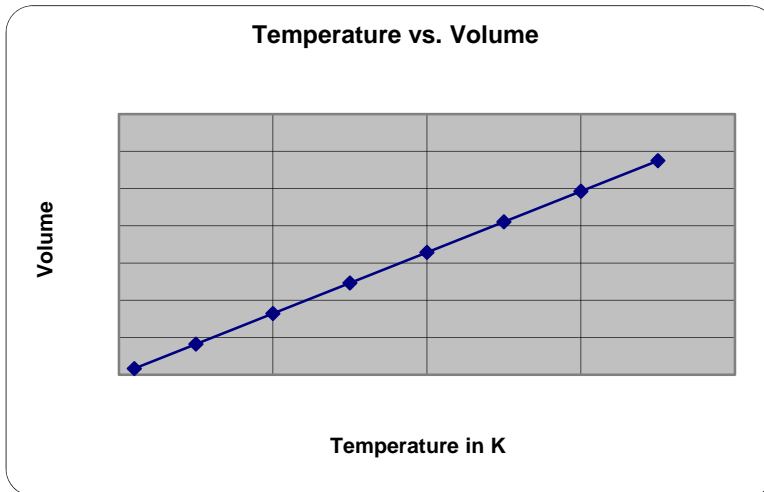


### Charles' Law

Charles looked at the relationship between the volume and the temperature of a gas with the number of mole of gas and the pressure being held constant. He discovered that the temperature of a gas and the volume are directly proportional to one another. This discovery leads to the formation of the absolute or Kelvin temperature scale. If the temperature is measured in Kelvin the proportionality is exact. We can state this mathematically as:

$$T_K \propto V \text{ or } \frac{T_K}{V} = \text{constant}$$

Again we can also show this graphically as:

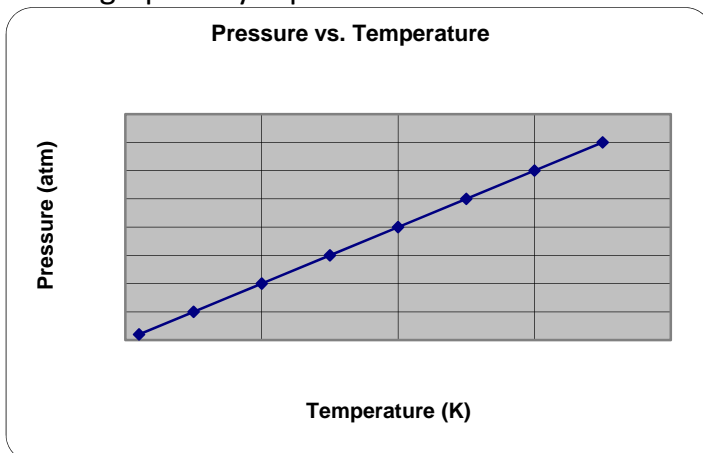


### Gay-Lussac's Law

This gas law deals with the relationship between the pressure and temperature of a gas. We can deduce from the other two gas laws that the pressure is directly proportional to the temperature. Gay-Lussac discovered that it is. We can express this mathematically as

$$T_K \propto P \text{ or } \frac{T_K}{P} = \text{constant}$$

This is graphically represented as:



## Avogadro's Law

Avogadro hypothesized that for two gases at the same temperature and pressure, the number of molecules (or moles) of gas would be the same if the volumes were the same. This is now expressed as Avogadro's Law. Because of the relationships above the pressure is also directly related to the number of moles of gas (if the volume is held constant).

## Ideal Gas Law

To what is the pressure of a gas proportional? In the relationships above we have determined that the pressure is proportional in some way to the following:

1. Volume (inversely)
2. Temperature (directly)
3. Amount of gas (directly)

This can be expressed mathematically as:

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

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:

$$\begin{aligned} R &= 0.08206 \text{ L-atm/mol-K} \\ &= 62.37 \text{ L-mmHg/mol-K} \end{aligned}$$

- = 62.37 L-torr/mol-K
- = 8.314 L-kPa/mol-K
- = 8.314 J/mol-K (used primarily in thermochemistry and electrochemistry)

### **Comparing gases**

When we wish to compare two gases, we must compare them on equal footing. We have a standard to use to do this that is called Standard Temperature and Pressure (STP). STP is defined to be 0.00 °C (273.15 K) and 1.00 atm. This state can be used to compare the amounts of two gases by looking at the volume of each gas. We also find that if we are at STP we can also simplify the calculation of how many moles of gas we have. At STP 1 mole of any gas occupies a volume of 22.414 L. We can use this as a conversion factor in our calculations.

### **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.

## Stoichiometry and gas laws

We can use the data given for a gas (P,V, and T) to calculate the number of moles of gas present. This is the same as using molar mass to calculate the number of moles if we are given grams. The stoichiometric calculation is the same. We either convert:

grams A → moles A → moles B → desired unit for B

or

PVT A → moles A → moles B → desired unit for B

The overall calculation is the same. Calculating the theoretical yield and the limiting reactant is the same. The only difference is whether we use the molar mass or the ideal gas law.