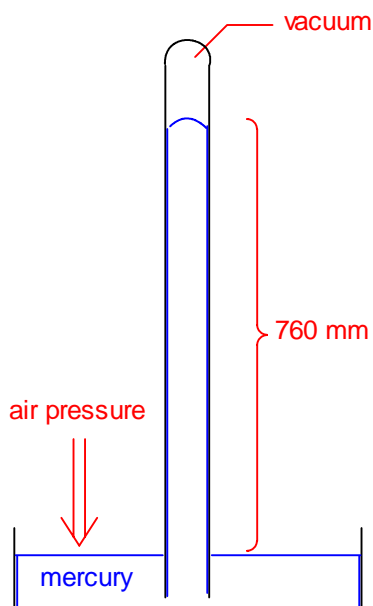


Gas Laws

Some chemical reactions take place in the gas phase and others produce products that are gases. We need a way to measure the quantity of compounds in a given volume of gas and relate that to moles. We also need to have some familiarity about the way the volume, pressure and temperature of a gas are related. Knowledge of some of the basic behavior of gases is very important in the prevention of some very serious health risks in sports such as scuba diving and white-water rafting.

We previously learned that one mole of a gas occupies 22.4 liters at standard temperature and pressure. Remember that standard temperature is equal to 273 K and standard pressure is equal to 1 atmosphere or 760 mm of Hg.

- Atmospheric pressure is caused by the weight of the molecules in the atmosphere. This is equal to 14.7 pounds per square inch at sea level or the pressure needed to support a column of mercury 760 mm high.



- There are three temperature scales but only Celsius and Kelvin are used in science. Since you are familiar with Fahrenheit, the following equation will let you convert Celsius to Fahrenheit.

$$^{\circ}F = \frac{9}{5} \times ^{\circ}C + 32$$

- Convert 20°C into °F. You can actually come to an approximation of this in your head since 9/5 is about 2. Multiply the degrees Celsius

by 2 and add 32. The answer in this case would be 72°F. The equation can be solved to give an answer of 68°F.

The Celsius or centigrade scale is very convenient in that water freezes at 0°C and boils at 100°C at sea level. The problem with using Celsius in calculations is that temperatures less than 0°C would have negative numbers. In order to avoid this problem, scientists use the Kelvin scale for calculations involving temperature. Degrees Kelvin or absolute are always positive numbers. At zero degrees Kelvin, all molecular motion stops. Celsius is converted to Kelvin by the following equation.

$$K = ^\circ\text{C} + 273.15 \quad \text{The degree sign is not shown for K.}$$

- Convert 25°C to K

$$K = 25 + 273.15 = 298.15$$

The Ideal Gas Law

Since one mole of a gas occupies 22.4 L at standard temperature (273 K) and pressure (1 atm), it is possible to arrive at a mathematical expression to relate moles, pressure, temperature and volume.

This expression is called the ideal gas law. This law contains an additional term “R” which is called the universal gas constant. In this expression “n” equals the number of moles of a gas, the volume “V” must be expressed in liters, the pressure “P” must be expressed in atmospheres and the temperature must be expressed in degrees Kelvin.

$$\frac{PV}{T} = nR$$

This constant can be calculated by using the above values in this law. The gas law, solved for R, becomes...

$$\frac{PV}{nT} = R$$

When the values of 22.4 liters and 273 degrees Kelvin are applied, the value of R is found to be...

$$\frac{1\text{atm} \times 22.4\text{L}}{1\text{mol} \times 273\text{K}} = R = 0.0821 \frac{\text{atmL}}{\text{molK}}$$

The pressure is given in atmospheres, the volume in liters and the temperature in degrees Kelvin. Remember, when looking at the following illustrations, that room temperature equals about 300 K.

Now we can say that the pressure times the volume, divided by the temperature equals a constant.

$$\frac{\text{pressure} \times \text{volume}}{\text{temperature}} = K$$

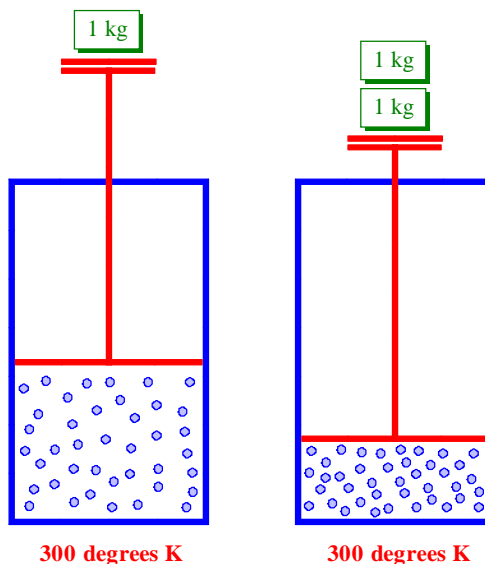
Using the PV/T Relationship

Since PV/T equals a constant, we can understand how any of these variables change with respect to each other.

Pressure and Volume (Boyle's law)

If the temperature remains constant, then the relationship changes to $P \times V = \text{constant}$. If either the pressure or volume is changed, the other must change in the opposite direction.

Therefore, if you increase the pressure, the volume must decrease. This makes sense if you think of a bicycle pump. When you push down on the plunger, the volume inside the pump is decreased and you can feel more pressure the further you push down on the plunger.



This relationship is an example of an inverse proportion. An inverse proportion is a mathematical expression where if one quantity of a pair increases, the other quantity of the pair must decrease in a proportional manner.

$$P_1 \times V_1 = P_2 \times V_2$$

- If a gas at 760 mm Hg occupies one liter, what volume would it occupy at 380 mm Hg?

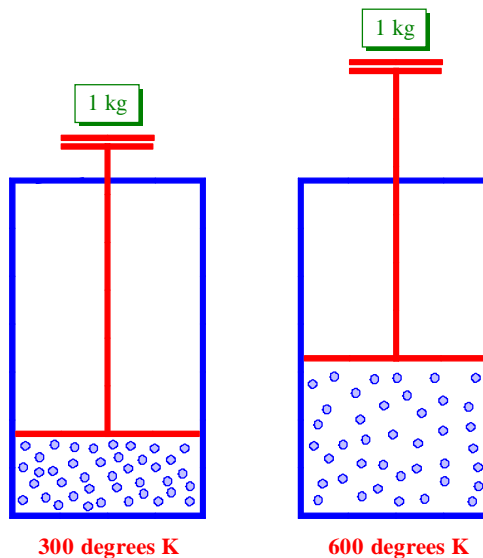
$$1 \text{ L} \times 760 \text{ mm} = V \times 380 \text{ mm}$$

$$V = 2 \text{ L}$$

This relationship has great importance to divers because the density of water is so much greater than the density of air. If a diver descends without scuba gear, the amount of gas contained in their body cavities decreases as they descend. This crushing effect is not experienced by scuba divers since their regulators deliver air at the same pressure as the surroundings. At a depth of 30 meters, the air pressure in their lungs is equivalent to 4 atmospheres. If a scuba diver makes an emergency ascent, the diver must breathe out forcefully to prevent their lungs from expanding painfully. If the lungs experience severe distortion, some of the alveoli can rupture and air can enter the bloodstream. This could cause a blockage that might cause loss of consciousness, a heart attack or brain damage.

Volume and Temperature (Charles' law)

If the pressure remains constant, then the relationship changes to $V/T = \text{constant}$. If either the volume or the temperature is changed, the other must also change exactly the same way. This also makes sense. If you heat up a gas the volume will increase since the molecules are moving faster.



Try blowing up a balloon on a cold day and carefully measure the circumference with a piece of string. Now bring the balloon indoors and let it warm up to room temperature. If you now measure the circumference, you will see that the balloon has increased in size.

This relationship is an example of a direct proportion. A direct proportion is a mathematical expression where if one quantity of a pair increases, the other quantity of the pair must also increase in the same proportions. If one quantity of a pair decreases, the other quantity of the pair must also decrease.

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

- The temperature scale used must be Kelvin.
- If a gas at 300 K occupies 1 liter, how many liters will it occupy at 373 K?

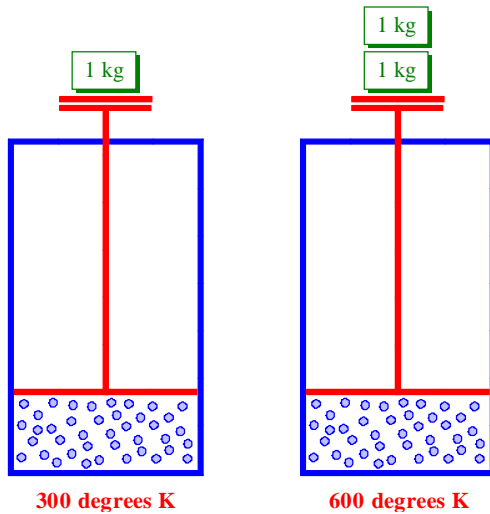
$$\frac{1L}{300K} = \frac{V}{373K}$$

$$V = 1.24 L$$

This law answers the question...would a raft pumped up on a sandy beach in the sun be adequately inflated once it is placed in a river? The answer is "no" and this can be really important to someone who floats rivers.

Pressure and Temperature

If the volume remains constant, then the relationship changes to $P/T = \text{constant}$. If either the pressure or the temperature is changed, the other must also change exactly the same way.



This relationship also makes sense. If you measure the air pressure in the tires of your car and then take a drive on a hot day, you will be amazed at how much the pressure has increased. Tire manufacturers recommend pressures of inflation to account for this increase in pressure.

Would a tire pumped up on a cold morning be safe on a hot afternoon drive? The answer here is "maybe". Tires have a high margin of safety with regard to high pressure, but this can be a bad gamble.

This relationship is also an example of a direct proportion.

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

- If a gas has a pressure of 760 mm at 311 K, what will the pressure of the gas be at 283 K?

$$\frac{760\text{mm}}{311\text{K}} = \frac{P_2}{283\text{K}}$$

$$P_2 = 691 \text{ mm}$$

Combination Pressure Volume Temperature Law

This law merely combines the previous three laws into one mathematical expression.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

- How many liters would 20 liters of a gas at STP occupy at 20 atm at temperature of 38°C?

$$\frac{760\text{mm} \times 20\text{L}}{273\text{K}} = \frac{15,200\text{mm} \times V_2}{311\text{K}}$$

$$V_2 = 1.1 \text{ L}$$

Solubility of a Gas and Pressure

The relationship of solubility to pressure is given by Henry's law. Henry's law states that the amount of gas that will dissolve in a liquid at a given temperature varies directly with the pressure above the liquid.

When you open a can of soda, the dissolved carbon dioxide bubbles out of the solution because the pressure of the container has been lowered.

This law also explains why during a dive, gases entering the lungs from the scuba gear are absorbed to a greater extent in the diver's blood. This does not create problems during the dive, but if the diver ascends rapidly to the surface, the excess dissolved gases can form bubbles in the blood.

The bubbles can cause localized pain, difficulty of breathing, paralysis, unconsciousness and even death. Divers must carefully follow ascent rates prepared by the Navy for ascents from depths greater than 10 meters. By remaining at fixed interval depths for a period of time, the diver allows dissolved nitrogen to slowly escape without creating large bubbles in the blood. Deep dives require several intervals for decompression.

Increased nitrogen concentration in the blood can also cause nitrogen narcosis (rapture of the deep) when divers dive below 30 meters. Divers experience intoxicating symptoms such as happiness, overconfidence and impaired memory.

Another complication of Henry's law to diving is the problem with impure air. If a harmful contaminant such as carbon monoxide is present in the compressed air, it will have a greater effect on a deep dive. If a diver is at 40 meters, the

pressure is equivalent to 5 atmospheres. If the concentration of a contaminant is 1% at atmospheric pressure, that contaminant will be delivered at a concentration of 5% at 40 meters.

Solubility of a Gas and Temperature

Temperature also plays a role in the solubility of a gas in a liquid. As the temperature is increased the solubility of a dissolved gas is actually decreased. You see this every day as bubbles form when a cold glass of water is allowed to warm to room temperature.

A diver must not take a hot shower or bath immediately after a deep dive because an increase of body temperature will cause a faster release of dissolved gases.

Calculations Using the Ideal Gas Law

- When calcium carbonate is heated, it decomposes to form calcium oxide and carbon dioxide. After a sample of calcium carbonate was heated and the carbon dioxide was collected in a one-liter flask, the carbon dioxide had a pressure of 1.5 atm at 27°C. How many moles of carbon dioxide were formed from this sample?

$$P = 1.5 \text{ atm}$$

$$T = 300 \text{ K}$$

$$V = 1 \text{ L}$$

$$\frac{PV}{RT} = n$$

$$\frac{1.5\text{atm} \times 1\text{L}}{0.0821\text{atmL} / \text{molK} \times 300\text{K}} = n$$

$$n = 6 \times 10^{-2} \text{ moles of carbon dioxide}$$

Mixtures of Gases and Partial Pressures

Dalton observed that the total pressure of a mixture of gases was equal to the sum of the pressures that each gas would exert if it were present alone. This is called **Dalton's law of partial pressures**.

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots$$

Since $p_1 = n_1 \frac{RT}{V}$, then $P_{\text{total}} = (n_1 + n_2 + n_3 + \dots)RT/V$.

- A mixture of 8 g of oxygen and 7 g of nitrogen are placed in a 1 liter container at 273 K. What is the partial pressure of each gas and the total pressure in the container?

First calculate the moles of each gas...

$$n_{\text{oxygen}} = 8g O_2 \times \frac{1\text{mol } O_2}{32g O_2} = 0.25\text{mole } O_2$$

$$n_{\text{nitrogen}} = 7g N_2 \times \frac{1\text{mol } N_2}{28g N_2} = 0.25\text{mole } N_2$$

Next we can calculate the individual partial pressures...

$$p_{\text{oxygen}} = \frac{n_{\text{oxygen}} RT}{V} = \frac{0.25\text{mol} \times 0.0821 \frac{\text{atmL}}{\text{molK}} \times 273\text{K}}{1\text{L}} = 5.6\text{atm}$$

$$p_{\text{nitrogen}} = \frac{n_{\text{nitrogen}} RT}{V} = \frac{0.25\text{mol} \times 0.0821 \frac{\text{atmL}}{\text{molK}} \times 273\text{K}}{1\text{L}} = 5.6\text{atm}$$

Finally we can calculate the total pressure...

$$P_{\text{total}} = p_{\text{oxygen}} + p_{\text{nitrogen}} = 11.2 \text{ atm}$$

Kinetic-Molecular Theory

The theory that explains the behavior of gases with respect to temperature, pressure and volume is the kinetic-molecular theory.

- a. Gases consist of large numbers of molecules or atoms that are in continuous random motion.
- b. The volume of the molecules of the gas is negligible to the volume occupied by the gas.
- c. Attractive and repulsive forces between gas molecules are negligible.
- d. Energy is transferred between molecules of a gas during collisions, but the average kinetic energy remains constant because the collisions are perfectly elastic.
- e. The average kinetic energy of the molecules is proportional to the absolute temperature since the molecular motion increases with temperature. The average kinetic energy is only dependent on temperature...not pressure or volume.

- If a gas is compressed at constant temperature, what effect does this change have on the average speed of the gas molecules and the average kinetic energy?

It has no effect on the average speed because the average speed of the molecules depends on temperature not volume. Likewise, it has no effect on the average kinetic energy. The pressure will increase because the number of collisions with the container wall is increased due to the smaller volume.

- How is the average speed of gas molecules changed when the temperature is increased?

The average speed of the gas molecules is increased.

- How is the average speed of gas molecules changed when the volume of the container is increased and the temperature remains constant?

The average speed of the gas molecules remains the same.

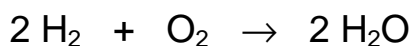
Problems

1. A sample of oxygen with a volume of 525 mL and a pressure of 750 mm has to be given a volume of 475 mL. What pressure is needed if the temperature is kept constant?
2. What is the new pressure on a sample of helium that has an initial volume of 1.5 L and a pressure of 745 mm if the volume becomes 2.1 L at the same temperature?
3. A balloon contains hydrogen gas with a volume of 1.05 L at 20°C and 755 mm. What would be the volume of the hydrogen at a higher altitude where the pressure of the gas in the balloon decreases to 500 mm? Assume the temperature remains the same.

4. A bacteria culture isolated from sewage produced 34.5 mL of methane gas (CH₄) at 30°C and 749 mm. What is the volume of methane at STP? How many moles of methane were produced?

5. How many liters will 10 g of dry ice (carbon dioxide) occupy at 1 atm and 23°C?

6. If 20 liters of hydrogen at STP react with 10 liters of oxygen at STP, how many grams of water will be formed?



7. When the atmospheric pressure is increased on a balloon, the volume of the balloon will...

(a) increase. (b) decrease. (c) stay the same.

8. When the temperature of a gas is increased in a balloon, the volume of the balloon will...

(a) increase. (b) decrease. (c) stay the same.

9. When the volume of a gas is decreased, the pressure of the gas will...

(a) increase. (b) decrease. (c) stay the same.

10. A flashbulb contains 2.4×10^{-4} mol of oxygen at a pressure of 1.9 atm. What is the volume of the flashbulb in cubic centimeters if the temperature is 300 K? Remember that a cubic centimeter is equal to a mL.

11. What is the total pressure, in atmospheres, of a 3.0 L container that contains 20 moles of nitrogen gas and 10 moles of oxygen gas at 300 K?

12. If the temperature of a solution of a gas is increased, how will the solubility of the gas change?

13. If the pressure on a solution of a gas is decreased, how will the solubility of the gas change?

Answers

1. $750\text{ mm} \times 525\text{ mL} = P \times 475\text{ mL}$ $P = 829\text{ mm}$
2. $745\text{ mm} \times 1.5\text{ L} = P \times 2.1\text{ L}$ $P = 532\text{ mm}$
3. $755\text{ mm} \times 1.05\text{ L} = 500\text{ mm} \times V$ $V = 1.59\text{ L}$
- 4.

$$\frac{749\text{mm} \times 34.5\text{mL}}{303\text{K}} = \frac{760\text{mm} \times V}{273\text{K}} \quad V = 30.6 \quad \text{mL}$$

$$30.6\text{mL} \times \frac{\text{L}}{1000\text{mL}} \times \frac{\text{mol}}{22.4\text{L}} = 1.4 \times 10^{-3} \text{ mol}$$

5.

$$10\text{g CO}_2 \times \frac{\text{mole CO}_2}{44\text{g CO}_2} \times \frac{22.4\text{L}}{\text{mole}} = 5.1\text{L CO}_2 \text{ at STP}$$

$$\frac{5.1\text{L}}{273\text{K}} = \frac{V}{296\text{K}} \quad V = 5.5 \text{ L}$$

6.

$$20\text{L H}_2 \times \frac{\text{mole H}_2}{22.4\text{L}} \times \frac{2\text{mole H}_2\text{O}}{2\text{mole H}_2} \times \frac{18\text{g H}_2\text{O}}{\text{mole H}_2\text{O}} = 16\text{g H}_2\text{O}$$

$$10\text{L O}_2 \times \frac{\text{mole O}_2}{22.4\text{L}} \times \frac{2\text{mole H}_2\text{O}}{1\text{mole O}_2} \times \frac{18\text{g H}_2\text{O}}{\text{mole H}_2\text{O}} = 16\text{g H}_2\text{O}$$

both calculations give the same answer of 16 g H₂O

7. b

8. a

9. a

$$10. \quad V = \frac{nRT}{P} \quad V = \frac{2.4 \times 10^{-4} \text{ mol} \times 0.0821 \text{ Latm/molK} \times 300\text{K}}{1.9\text{atm}} \quad V = 3.1 \times 10^{-3} \text{ L}$$

$$3 \times 10^{-3} \text{ L} \times \frac{1000\text{mL}}{\text{L}} = 3\text{mL} = 3\text{cm}^3$$

$$11. \quad P_{\text{total}} = p_{\text{nitrogen}} + p_{\text{oxygen}} = (n_{\text{nitrogen}} + n_{\text{oxygen}})RT/V$$

$$P_{\text{total}} = (20 \text{ mol} + 10 \text{ mol})(0.0821 \text{ Latm/degmol})300 \text{ K}/3 \text{ L}$$

$$P_{\text{total}} = 250 \text{ atm}$$

12. It will decrease.

13. It will decrease.