

Gas Laws



So far we have looked at:

1. How to determine the number of particles (moles) in a given amount of mass (using molar mass)
2. How to determine the number of particles (moles) in a given amount of solution (using molarity)

Now we will explore (among other things) how to determine the number of particles (moles) in a given amount of a gas.

Pressure

Pressure is defined as force per unit area:

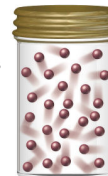
$$P = F/A$$

In physics, the unit of pressure is the Pascal (Pa) and is equal to 1N/m^2 .

In a sealed container containing a gas, pressure is caused by the particles (atoms or molecules) bouncing off the sides of its walls.



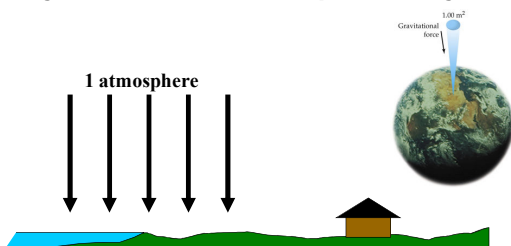
Lower pressure



Higher pressure

The Atmosphere

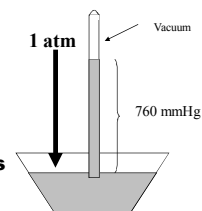
At sea-level, on an "average" day, there is said to be 1 atmosphere (1 atm) of pressure pressing down on the Earth. A day that is only .96 atm would be a low-pressure day.



The Atmosphere

If a tube of mercury (Hg) is inverted into a dish of mercury, the mercury will run out of the tube until the pressure (force per unit area) at the bottom of the tube is equal to the atmospheric pressure trying to push it back up.

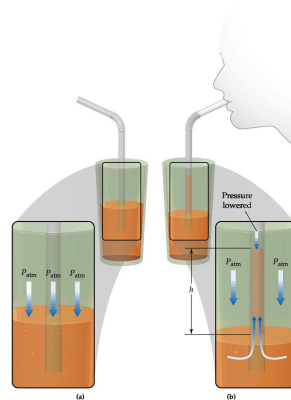
A 1 atm day requires a column of mercury 760mm high to counteract atmospheric pressure. **760mmHg** is also known as **760torr** in honor of the chemist Evangelista Torricelli. This instrument is commonly known as a mercury barometer.

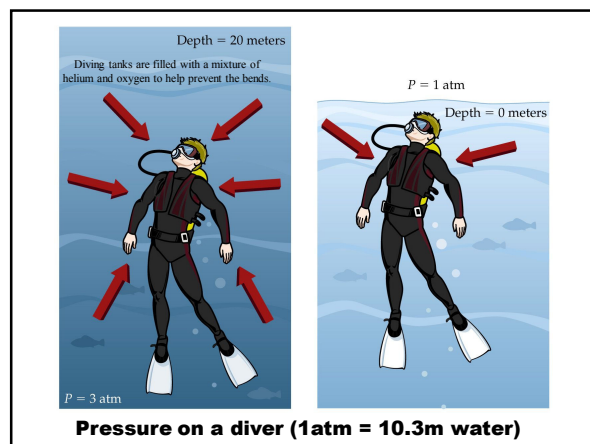
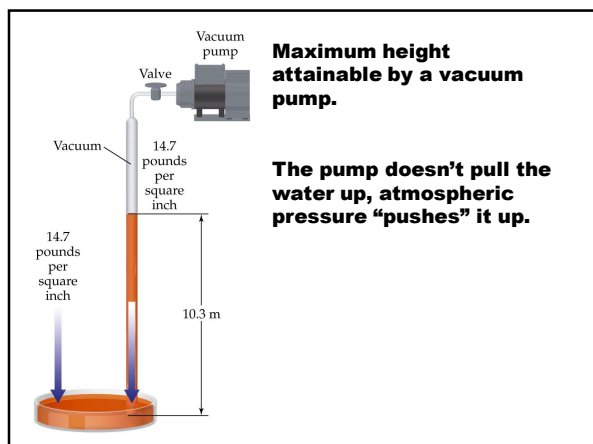


The tube of mercury 760mm high has the same pressure down as a tube of "air" that stretches clear to the "top" of the atmosphere.

Does the diameter of the barometer tube make any difference???

How drinking through a straw works.



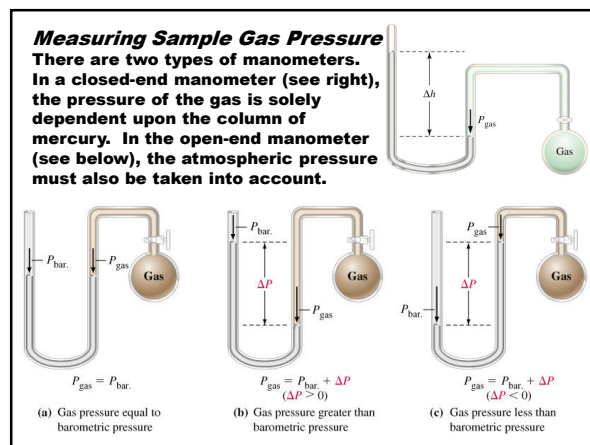


The Atmosphere
 In Pascals (Pa), 1 atmosphere is equal to 101,300Pa or 101.3kPa.

To summarize these relationships:

1atm = 760mmHg (torr) = 101,300Pa = 101.3kPa (also 29.92"Hg, 1.013bar, 14.7psi)

Measuring Pressure
 A common instrument for measuring the pressure of a gas in the laboratory is the manometer. The manometer works on the same principle as the barometer. A column of mercury determines the pressure of the gas.



Measuring Pressure
 The mercury column in a closed-end manometer will always be higher on the side of the u-shaped tube furthest from the sample gas.

The mercury in an open-end manometer will be higher on the side closest to the sample if the gas is at less than atmospheric pressure and higher on the side open to the atmosphere if the sample gas is greater than atmospheric pressure.

The open-end manometer must always be calibrated to the current atmospheric pressure.

Measuring Pressure
On Your Own:

1. What is the pressure (in torr) of a gas enclosed in an open-end manometer in which the mercury in the arm attached to the gas is 5.7cm higher than in the one open to the atmosphere. The atmospheric pressure is 1.05atm.
2. A lead cube with edges 25.0cm in length rests on a flat surface. The density of lead is 11.34g/cm³. Calculate the pressure in pascals exerted by the cube on the surface.
3. An oil with a density of .950g/mL is used for a barometer. How high will the oil column be (in meters) on a 1 atm day? (The density of mercury is 13.6g/mL.)

Answers:

1. $1.05 \text{ atm} (760 \text{ torr}/1 \text{ atm}) = 798 \text{ torr}$. $5.7 \text{ cm} = 57 \text{ mm}$

The pressure of the gas is $798 \text{ torr} - 57 \text{ torr} = 741 \text{ torr}$

2. Surface area of cube = $(25.0 \text{ cm})^2 = 625 \text{ cm}^2$
 Volume of cube = $(25.0 \text{ cm})^3 = 15,625 \text{ cm}^3$. The mass is $15,625 \text{ cm}^3 (11.34 \text{ g/cm}^3) = 177,187.5 \text{ g}$
 Pressure = $(177.1875 \text{ kg})(9.8 \text{ m/s}^2)/(.0625 \text{ m}^2) = 2.8 \times 10^4 \text{ Pa}$

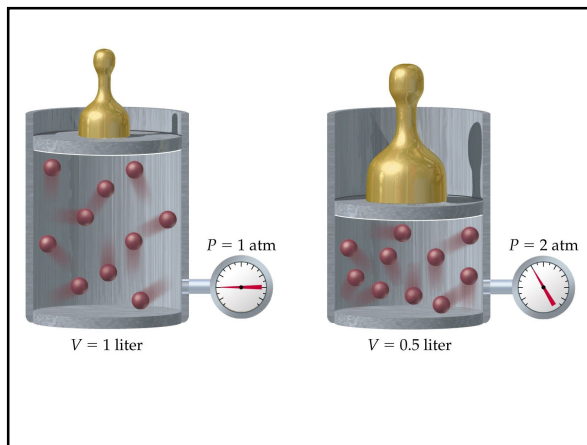
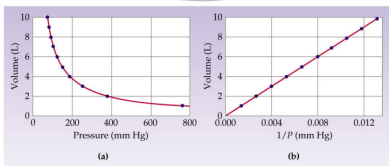
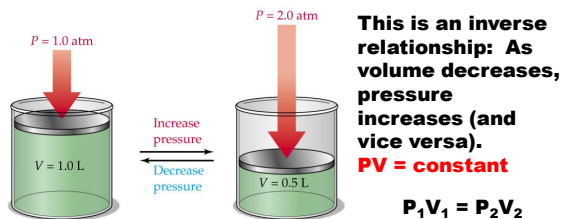
3. The density times the column height must be equal. Therefore, $(13.6 \text{ g/mL})(760 \text{ mm}) = (.950 \text{ g/mL})(h)$
 $h = (13.6 \text{ g/mL})(760 \text{ mm}) / (.950 \text{ g/mL}) = 10,880 \text{ mm} = 10.9 \text{ m}$

Description of Gases

There are four factors that describe the condition of a gas.

1. Pressure (P)
2. Volume (V)
3. Temperature (T) (in Kelvin)
4. Moles of particles (atoms or molecules)(n)

Boyle's Law: P vs. V (T and n kept constant)



Boyle's Law: P vs. V (T and n constant)

Boyle's law deals with the relationship between pressure and volume. Consider a gas of pressure P_1 contained within a volume V_1 . If the volume is reduced to V_2 , the pressure will increase to P_2 due to the decrease in distance the gas particles have to travel to come in contact with the container wall. As the volume decreases, the pressure increases. This is an inverse relationship. $PV = \text{constant}$.



A useful relationship to remember is:

$P_1V_1 = P_2V_2$, where the subscript 1 indicates initial conditions and the 2, the final conditions.

On Your Own:

1. A gas, initially at $.85 \text{ atm}$, has the volume of its container reduced from 4.0 L to 2.5 L . Calculate the final pressure of the gas in torr.
2. By how many cubic centimeters should a container be reduced if it is desired to increase the pressure of a gas from $700. \text{ torr}$ to $850. \text{ torr}$. The initial size of the container is 2.0 m^3 .
3. Calculate the percent increase in the volume of a container whose gas pressure decreases from 3.0 atm to 1.5 atm .

Answers:

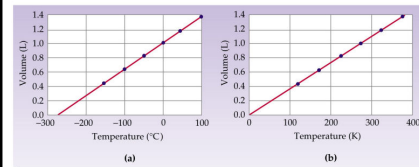
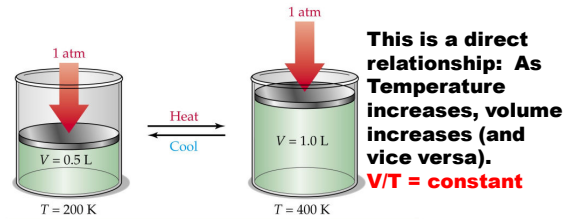
1. $P_2 = P_1V_1/V_2 = (.85\text{atm})(4.0\text{L})/(2.5\text{L}) = 1.36\text{atm}$
 $1.36\text{atm} (760\text{torr}/1\text{atm}) = 1,033.6 = 1.0 \times 10^3 \text{ torr}$

2. $V_2 = P_1V_1/P_2 = (700.\text{torr})(2.0\text{m}^3)/(850.\text{torr}) = 1.647\text{m}^3$

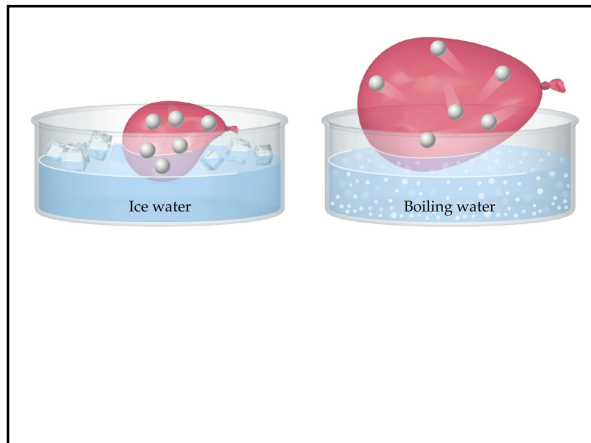
This is a difference of $2.0\text{m}^3 - 1.647\text{m}^3 = .353\text{m}^3$
 $.353\text{m}^3 (1 \times 10^6 \text{cm}^3/1\text{m}^3) = 3.5 \times 10^5 \text{cm}^3$

3. $V_2/V_1 = P_1/P_2 = (3.0\text{atm})/(1.5\text{atm}) = 2$. This corresponds to a 100% increase in the volume.

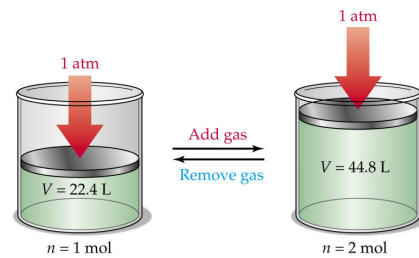
Charles' Law: T vs. V (P and n kept constant)



$V_1/T_1 = V_2/T_2$



Avogadro's Law: n vs. V (P and T kept constant)



This is a direct relationship: As the number of moles increases, volume increases (and vice versa).

$V/n = \text{constant}$

$V_1/n_1 = V_2/n_2$

Examples:

1. Calculate:

a. The new pressure in a closed container if a 5.0L volume of gas at 2.5atm has its volume increased to 7.5L.

b. The new volume of gas (at constant T and P) if 2.0mol of He in a 3.0L container has another 3.0mol of He placed into the container.

Answers:

a. $(5.0\text{L})(2.5\text{atm}) = (7.5\text{L})(P_2)$

$P_2 = 1.7\text{atm}$

b. $3.0\text{L}/2.0\text{mol} = V_2/5.0\text{mol}$

$V_2 = 7.5\text{L}$

Combined Gas Law:
PV/nT = constant (T in Kelvins)

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Ideal gas Law:

$$PV = nRT$$

$$R = .0821 \text{ L atm/mol K}$$

Standard Molar Volume: At *standard temperature and pressure* (STP = 1atm and 273.15K) 1 mole of any ideal gas has a volume of 22.4L

Variations on the ideal gas law equation:

$$PV = mRT/M \quad (m = \text{sample mass, } M = \text{molar mass of the gas})$$

$$M = mRT/PV$$

$$d = MP/RT \quad (d = \text{density of the gas in g/L})$$

2. When a rigid hollow sphere containing 680 L of helium gas is heated from 300.K to 600.K, the pressure of the gas increases to 18atm. How many moles of helium does the sphere contain?

3. A child has a lung capacity of 2.2 L. How many grams of air do her lungs hold at a pressure of 1.0 atm and a normal body temperature of 37°C? Assume a "formula mass" of 29g/mol for air.

2. Answer:

$$n = PV/RT = (18\text{atm})(680\text{L})/ (.0821)(600.\text{K})$$

$$n = 248.48 = 250\text{moles}$$

3. Answer:

$$m = MPV/RT = (29\text{g/mol})(1.0\text{atm})(2.2\text{L})/ (.0821\text{Latm/molK})(310.15\text{K}) = 2.5\text{g}$$

4. A gas with a volume of 300.mL at 150.°C is heated until its volume is 600.mL. What is the new temperature of the gas if the pressure is unaltered?

5. Calculate the number of liters occupied, at STP.

- a. 0.350 mol O₂
- b. 63.5g He

6. Determine the molar mass of a gas for which a 2.5g sample of that gas occupies a volume of 3.0L at STP.

4. Answer:

$$300\text{mL}/423.15\text{K} = 600\text{mL}/T_2$$

$$T_2 = 846\text{K} = 573^\circ\text{C}$$

5. Answers:

$$\text{a. } 0.350\text{mol} (22.4\text{L/mol}) = 7.84\text{L}$$

$$\text{b. } (63.5\text{g})(1\text{mol}/4.003\text{g})(22.4\text{L}/1\text{mol}) = 355\text{L}$$

6. Answer:

$$M = (2.5\text{g})(.0821)(273.15\text{K})/(3.0\text{L})(1.0\text{atm}) = 19\text{g/mol}$$

or

$$(2.5\text{g})/(3.0\text{L}/22.4\text{L/mol}) = 19\text{g/mol}$$

Example

A compound is found to contain 30.45% nitrogen and 69.55% oxygen by mass.

a. Determine the empirical formula for the compound.

b. If a 4.10g sample of the gas occupies 1.00L at STP conditions, what is the molecular formula of the gas?

Answer

a. Assume 100.g sample

$$30.45\text{g N} / 14.01\text{g/mol} = 2.173\text{mol N}$$

$$69.55\text{g O} / 16.00\text{g/mol} = 4.347\text{mol O}$$

$$N_{2.173/2.173}O_{4.347/2.173} = \text{NO}_2 \text{ (empirical formula)}$$

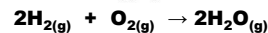
$$\text{Empirical formula mass} = 46.01\text{g/mol}$$

b. $M = mRT/PV$

$$M = (4.10\text{g})(.0821\text{Latm/molK})(273.15\text{K})/(1.00\text{atm})(1.00\text{L})$$

$$= 91.94\text{g/mol}$$

Molecular formula is N_2O_4

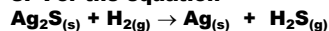
Gay-Lussac's/Avogadro's Law of Combining Volumes

Equal volumes of any gases at the same temperature and pressure contain the same number of moles of gas.

The coefficients of a balanced equation can be used to calculate relative volumes.

7. Find the density of fluorine gas (g/L) at 700.torr and 50.0°C.

8. For the equation

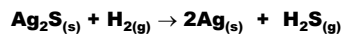


How many Liters of H_2S can be produced from 15.0g of Ag_2S and 1.00L of $\text{H}_{2(\text{g})}$ if the reaction occurs at STP?

7. Answer:

$$d = MP/RT$$

$$= (38.00\text{g/mol})(700/760) / (.0821)(50+273.15) = 1.32\text{g/L}$$

8. Answer:

$$\text{mol Ag}_2\text{S} = 15.0\text{g} (1\text{mol}/247.8\text{g}) = .0605\text{mol}$$

$$\text{mol H}_2 = (1.00\text{L})(1\text{mol} / 22.4\text{L}) = .0446\text{mol}$$

Hydrogen gas limits

$$.0446\text{mol H}_2 (1\text{mol H}_2\text{S} / 1\text{mol H}_2) = .0446\text{mol H}_2\text{S}$$

$$V = .0446\text{mol} (22.4\text{L/mol}) = 1.0\text{L}$$

Dalton's Law of partial pressure: The total pressure inside of a closed container is equal to the sum of the individual pressures of the gases it contains.

Consider three gases in a sealed container with a volume, V and temperature, T.

The pressures for each of the gases are:
 $P_1 = n_1RT/V$ $P_2 = n_2RT/V$ $P_3 = n_3RT/V$

Since R, T and V are the same for all the gases, we can combine like terms to get:

$$P_{\text{Total}} = P_1 + P_2 + P_3 = (n_1 + n_2 + n_3)RT/V$$

Example:

A 1,500.mL sealed container at 30.0°C contains 10.0g of He, 7.00g of N₂ and 30.0g of O₂. Determine the total pressure (in atm) inside the container.

Answer:

$$n_{\text{He}} = 10.0\text{g} / 4.003\text{g/mol} = 2.50\text{mol}$$

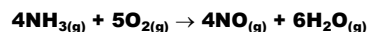
$$n_{\text{N}_2} = 7.00\text{g} / 28.02\text{g/mol} = .250\text{mol}$$

$$n_{\text{O}_2} = 30.0\text{g} / 32.00\text{g/mol} = .938\text{mol}$$

$$n_{\text{Tl}} = 2.50 + .250 + .938 = 3.69\text{mol}$$

$$P_{\text{Tl}} = (3.69\text{mol})(.0821\text{Latm/molK})(303.15\text{K})/(1.500\text{L}) = 61.150\text{atm} = \mathbf{61.2\text{atm}}$$

Question



If 2.00L of NH₃ and 3.00L of O₂ (each initially at 1.00atm and 300.K) are combined and reacted in a 4.00L container (assume no change in temperature)

a) What is the pressure in the container after the reaction takes place?

b) What is the pressure due to the NO gas?

Answer:

$$\text{a. } n_{\text{NH}_3} = PV/RT = (1.00\text{atm})(2.00\text{L})/(.0821\text{Latm/molK})(300.\text{K}) = .0812\text{mol NH}_3$$

$$n_{\text{O}_2} = (1.00\text{atm})(3.00\text{L})/(.0821\text{Latm/molK})(300.\text{K}) = .1218\text{mol O}_2$$

Since NH₃ and O₂ combine in a 4:5 ratio, NH₃ limits
 O₂ Used = .0812mol NH₃ (5mol O₂ / 4mol NH₃) = .1015mol O₂ Used
 O₂ leftover = .1218mol - .1015mol = .0203mol left

$$P = nRT/V$$

$$\text{mol NO} = .0812\text{mol NH}_3 (1\text{mol NO}/1\text{mol NH}_3) = .0812\text{mol NO}$$

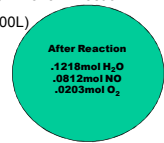
$$\text{mol H}_2\text{O} = .0812\text{mol NH}_3 (6\text{mol H}_2\text{O}/4\text{mol NH}_3) = .1218\text{mol H}_2\text{O}$$

$$\text{Total moles after reaction} = n_{\text{O}_2} + n_{\text{NO}} + n_{\text{H}_2\text{O}} = .0203\text{mol} + .0812 + .1218\text{mol} = .2233\text{mol}$$

$$P_{\text{t}} = (.2233\text{mol})(.0821\text{Latm/molK})(300.\text{K})/(4.00\text{L}) = 1.375 = \mathbf{1.38\text{atm}}$$

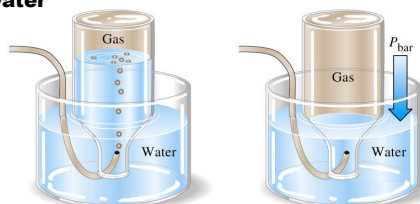
$$\text{b. } P_{\text{NO}} = (.0812\text{mol})(.0821\text{Latm/molK})(300.\text{K})/(4.00\text{L}) = .500\text{atm}$$

$$\text{or } P_{\text{NO}} = [(.0812)/(.2233)](1.375\text{atm}) = .500\text{atm}$$



Vapor Pressure:

Sometimes gases are collected by water displacement. Since some of the water "vaporizes" at a given temperature, the total pressure inside the container is the sum of the collected sample gas and the vapor pressure due to water



Water vapor pressure is a function of temperature and must be looked up (see appendix 1 page 634)

Example:

In a reaction between solid zinc metal and aqueous hydrochloric acid to produce aqueous zinc chloride and hydrogen gas, if the hydrogen gas evolved is collected over water at 25.0°C and the total pressure inside the 1.00L gas collection jar is 760.torr after the reaction is complete, a) How many moles of hydrogen gas are collected? b) How many grams of zinc were reacted?

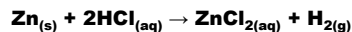


Note: Vapor pressure of water is 23.76torr at 25°C

Answer:

At 25.0°C the vapor pressure of water is 23.76torr. The pressure due to the hydrogen is 760.torr – 23.76torr = 736.24torr = .969atm

The moles of H₂ = PV/RT = (.969atm)(1.00L)/(.0821)(298.15K) = **.0396mol**



The mole ratio of Zn to H₂ is 1:1

The moles of Zn used is .0396mol

Grams of Zn used is .0396mol (65.39g/mol) = **2.59g Zn**

Mole fraction: Mole fraction is the ratio of the moles of a particular gas to that of the total moles of the gases inside an enclosed container

$$\text{mole fraction} = n_1 / (n_1 + n_2 + n_3 + \dots)$$

For a sealed container of volume, V and temperature, T, containing multiple gases; the partial pressure due to one of the gases is equal to the total pressure in the container times the mole fraction of that gas.

$$P_1 = P_{\text{total}} [n_1 / (n_1 + n_2 + n_3 + \dots)]$$

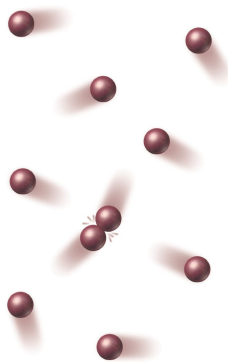
Example:

An oxygen/helium gas sample, collected over water at 23°C, exerts a total pressure of 758torr. Calculate the mole fraction of water vapor in the sample (VP_{water} = 21.07torr.)

Answer:

At 23°C, the vapor pressure of water is 21.07mmHg (from appendix 1, p634). The fraction of the pressure due to water is directly related to the mole fraction of the water. The mole fraction of the H₂O vapor is 21.07/758 = **.0278** (or 2.78% as a percentage)

Kinetic molecular theory



- 1 Collection of particles in constant motion
- 2 No attractions or repulsions between particles; collisions like billiard ball collisions
- 3 A lot of space between the particles compared to the size of the particles themselves
- 4 The speed that the particles move increases with increasing temperature

It can be shown using the equations from physics that the pressure exerted by a gas in a container of volume V is:

$$P = \frac{Nmu^2}{3V}$$

Where N is the number of molecules, m is the mass of a molecule and u is the average (root mean squared) speed.

N/V is the concentration of gas molecules

Using the kinetic energy equation $E_t = \frac{1}{2} mu^2$

And substituting:

$$E_t = \frac{3RT}{2N_A}$$

$$R = 8.314\text{J/molK}$$

At a given temperature, molecules of different gases must all have the same average kinetic energy of translational motion.

The average translational kinetic energy of a gas molecule is directly proportional to the Kelvin temperature, T.

Optional Derivation

$P = Nmu^2/3V$
 $PV = Nmu^2/3$
 (substituting)
 $nRT = Nmu^2/3$

$E_t = \frac{1}{2} mu^2$
 (substituting)
 $nRT = 2NE_t/3$

(rearranging)
 $E_t = 3nRT/2N$
 (substituting)

$E_t = 3RT/2N_A$

$PV = nRT$
 n/n is Avogadro's number N_A

The average speed, u , of the molecule is:

Directly proportional to the square root of the absolute temperature (T)

Inversely proportional to the square root of the molar mass (MM)

At 25 °C more molecules are moving at about 400 m/s than at any other speed.

At 1000 °C many, many more molecules are moving at 1600 m/s than at 25 °C.

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Graham's Law of Effusion:

Effusion: The process by which gas escapes from a container through a tiny hole.

Diffusion: The process by which one substance mixes with one or more other substances as a result of the random motion of molecules (e.g. as in the time it takes to smell someone's perfume from across the room)

The rate of effusion of a gas is inversely proportional to the square root of the molar mass of the substance

Remember: Rate is inversely proportional to time.

$$\frac{Rate_1}{Rate_2} = \left(\frac{MM_2}{MM_1}\right)^{1/2} \quad \frac{Time_1}{Time_2} = \left(\frac{MM_1}{MM_2}\right)^{1/2}$$

Example:

If He gas effuses 1.5 times faster than an unknown gas, what is the molar mass of the unknown?

Answer:

$$1.5/1 = (MM / 4.00g/mol)^{1/2}$$

$$2.25 = MM / 4.00g/mol$$

$$MM = 9.0g/mol$$

Real Gases

In general, the closer a gas is to the liquid state, the more it will deviate from the ideal gas law

Attractive forces between gas particles

The finite volume of gas particles

Gases are most ideal at:

Low pressures

High temperatures

V_m = true volume
 V_m^o = Ideal gas predicted volume

Finite size of particles dominate

Intermolecular attractions dominate

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The van der Waals Correction

$$(P + an^2/V^2)(V-nb) = nRT$$

a and b are constants unique to a gas (determined experimentally) that account for the size of the particles and their intermolecular attractions.

Example:

Calculate the percent deviation from ideal pressure for nitrogen gas if 6.00g of nitrogen are sealed in a 2.00L container at 30.0°C.

a = 1.39atmL²/mol²;

b = 0.0391L/mol for nitrogen.

$$(P + an^2/V^2)(V-nb) = nRT$$

Answer:

$$PV = nRT \quad P = nRT/V$$

$$P = (6.00\text{g}/28.02\text{g/mol})(.0821\text{Latm/molK})(303.15\text{K}) / (2.00) = 2.6647\text{atm}$$

$$(P + (1.39)(.21413)^2/(2.00)^2)(2.00 - (.21413)(0.0391)) = (.21413)(.0821)(303.15)$$

$$(P + .015933)(1.9916) = 5.329399$$

$$P = 2.659968\text{atm}$$

$$P_{\text{actual}}/P_{\text{ideal}} = 2.659968/2.6647 = .9982$$

$$\approx 99.8\%$$