Chapter 8: Gases

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Properties of Gases

Gases differ from solids and liquids in the following ways:
1) A sample of gas assumes both the shape and volume of the container.
2) Gases are compressible.
3) The densities of gases are much smaller than those of liquids and solids and are highly variable depending on temperature and pressure.
4) Gases form homogeneous mixtures (solutions) with one another in any proportion.

Pressure is defined as the force applied per unit area: $\text{pressure} = \frac{\text{force}}{\text{area}}$

The SI unit of force is the **newton (N)**, where: $1\ \text{N} = \frac{1\ \text{kg} \cdot \text{m}}{\text{s}^2}$

The SI unit of pressure is the **pascal (Pa)**, defined as 1 newton per square meter. $1\ \text{Pa} = \frac{1\ \text{N}}{\text{m}^2}$

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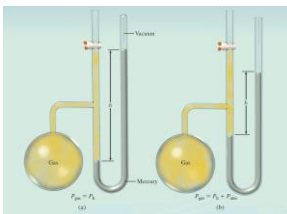
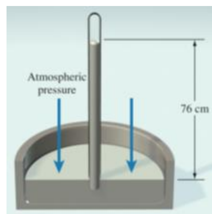
Properties of Gases

Units of Pressure Commonly Used in Chemistry		
Unit	**Origin**	**Definition**
Standard Atmosphere (atm)	pressure at sea level	1 atm = 101,325 Pa
mmHg	barometer measurement	1mmHg = 133.322 Pa
torr	Named after Torricelli (inventor of barometer)	1 torr = 133.322 Pa
bar	Same order of magnitude as atm but a decimal multiple of Pa	1 bar = 1 x 10^5 Pa

A barometer is an instrument that is used to measure atmospheric pressure. A manometer is a device used to measure pressures other than atmospheric pressure.



manometer



barometer

1 atm* = 101,325 Pa
= 760 mm Hg*
= 760 torr*
= 1.01325 bar
= 14.7 psi

* Represents an exact number

Practice

- Convert 1218 mm Hg to atm

$$\left(\frac{1218\ \text{mmHg}}{}\right)\left(\frac{1\ \text{atm}}{760\ \text{mmHg}}\right) = 1.60\ \text{atm}$$

- Convert 0.325 atm to torr

$$\left(\frac{0.325\ \text{atm}}{}\right)\left(\frac{760\ \text{torr}}{1\ \text{atm}}\right) = 247\ \text{torr}$$

- How many atm would be 1442 torr?

$$\left(\frac{1442\ \text{torr}}{}\right)\left(\frac{1\ \text{atm}}{760\ \text{torr}}\right) = 1.90\ \text{atm}$$

Gay–Lussac's Law (Amanton's law): The Pressure–Temperature Relationship

Pressure of a gas at a constant volume is directly proportional to the temperature.

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

A gas has a pressure of 0.12 atm at 421°C. What is the pressure at 273 K?:

Convert Temperature to Kelvin = 421 + 273.15 = 694.15 K

Use Gay–Lussac's Law to solve for P_2:

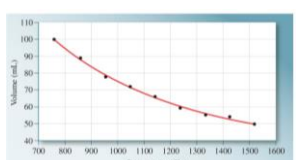
$$P_2 = \frac{(P_1)(T_2)}{(T_1)} = \frac{(0.12\ \text{atm})(273\ \text{K})}{(694.15\ \text{K})} = 0.047\ \text{atm}$$

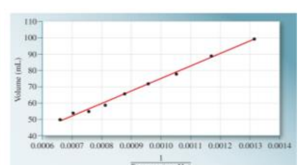
Boyle's Law: The Pressure–Volume Relationship

Boyle's law states that the pressure of a fixed amount of gas at a constant temperature is inversely proportional to the volume of the gas.

$$P_1V_1 = P_2V_2$$

at constant temperature





Calculate the volume of a sample of gas at 5.75 atm if it occupies 5.14 L at 2.49 atm. (Assume constant temperature.)

Use Boyle's law to solve for V_2: $V_2 = \frac{(P_1)(V_1)}{(P_2)} = \frac{(2.49\ \text{atm})(5.14\ \text{L})}{(5.75\ \text{atm})} = 2.26\ \text{L}$

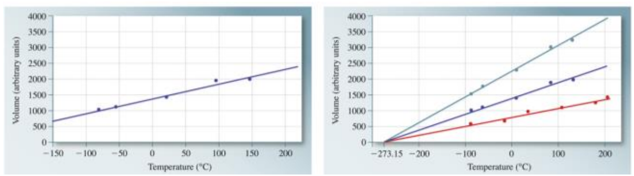
If a skin diver takes a breath at the surface, filling his lungs with 5.82 L of air, what volume will the air in his lungs occupy when he dives to a depth where the pressure of 1.92 atm? (Assume constant temperature and that the pressure at the surface is exactly 1 atm.)

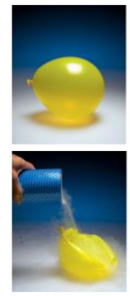
$$V_2 = \frac{(P_1)(V_1)}{(P_2)} = \frac{(1.00\ \text{atm})(5.82\ \text{L})}{(1.92\ \text{atm})} = 3.03\ \text{L}$$

Charles' Law: The Temperature–Volume Relationship

Charles's Law states that the volume of a gas maintained at constant pressure is directly proportional to the absolute temperature of the gas.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$ at constant pressure





Higher temp.

Lower temp.

A sample of gas originally occupies 29.1 L at 0.0°C. What is its new volume when it is heated to 15.0°C? (Assume constant pressure.)

$$V_2 = \frac{(T_2)(V_1)}{(T_1)} = \frac{(288.15\ \text{K})(29.1\ \text{L})}{(273.15\ \text{K})} = 30.7\ \text{L}$$

A sample of argon gas that originally occupied 14.6 L at 25°C was heated to 50.0°C at constant pressure. What is its new volume?

$$V_2 = \frac{(T_2)(V_1)}{(T_1)} = \frac{(323.15\ \text{K})(14.6\ \text{L})}{(298.15\ \text{K})} = 15.8\ \text{L}$$

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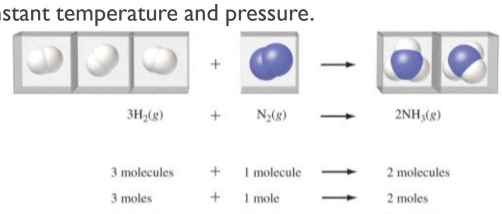
Avogadro's Law: The Amount–Volume Relationship

Avogadro's law states that the volume of a sample of gas is directly proportional to the number of moles in the sample at constant temperature and pressure.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

at constant temperature and pressure



What volume in liters of water vapor will be produced when 34 L of H_2 and 17 L of O_2 react according to the equation below at constant temperature and pressure:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Because volume is proportional to the number of moles, the balanced equation determines in what volume ratio the reactants combine and the ratio of product volume to reactant volume. The amounts of reactants given are stoichiometric amounts. 34 L of H_2O will form.

If we combine 3.0 L of NO and 1.5 L of O_2, and they react according to the balanced equation $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, what volume of NO_2 will be produced? (Assume that the reactants and products are all at the same temperature and pressure.)

3.0 L of NO_2 will form.

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The Combined Gas Law: The Pressure–Temperature–Amount–Volume Relationship

The **combined gas law** can be used to solve problems where any or all of the variable's changes.

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

If a child releases a 6.25 L helium balloon in the parking lot of an amusement park where the temperature is 28.50 °C and the air pressure is 757.2 mmHg, what will the volume of the balloon be when it has risen to an altitude where the temperature is –34.35 °C and the air pressure is 366.4 mmHg?

$$V_2 = \frac{P_1T_2V_1}{P_2T_1} = \frac{(757.2\ \text{mmHg})(238.80\ \text{K})(6.25\ \text{L})}{(366.4\ \text{mmHg})(301.65\ \text{K})} = 10.2\ \text{L}$$

A sample of gas occupies 754 mL at 22°C and a pressure of 165 mm Hg. What is its volume if the temperature is raised to 42°C and the pressure is raised to 265 mm Hg?

$$V_2 = \frac{P_1T_2V_1}{P_2T_1} = \frac{(0.217\ \text{atm})(315.15\ \text{K})(0.754\ \text{L})}{(0.349\ \text{atm})(295.15\ \text{K})} = 0.50\ \text{L}$$

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The Ideal Gas Equation

The **ideal gas equation** (below) describes the relationship among the four variables Pressure (P), Volume (V), moles (n), and Temperature (T). **R** is the proportionality constant, called the gas constant and its value and units depend on the units in which P and V are expressed.

PV = nRT

An **ideal gas** is a hypothetical sample of gas whose pressure-volume-temperature behavior is predicted accurately by the ideal gas equation.

Fun Fact: If you solve the ideal gas equation for R, then you have one side of the equation for the combined gas law. Additionally, from the combined gas law you get all other gas law relationships.

Various Equivalent Expression of the Gas Constant, R	
Numerical Value	**Unit**
0.08206	$\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$ ← $PV = nRT$
8.314	$\frac{\text{J}}{\text{mol}\cdot\text{K}}$ ← $u_{rms} = \sqrt{\frac{3RT}{M}}$
0.08314	$\frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}}$
1.987	$\frac{\text{cal}}{\text{mol}\cdot\text{K}}$

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The Ideal Gas Equation

Standard Temperature and Pressure (STP) are a special set of conditions where:
Pressure is 1 atm
Temperature is 0 °C (273.15 K)

Calculate the volume of a mole of ideal gas at 0 °C and 1 atm.

$$V = \frac{nRT}{P} = \frac{(1\ \text{mol})\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(273.15\ \text{K})}{(1\ \text{atm})} = 22.41\ \text{L}$$

Calculate the volume of a mole of ideal gas at room temperature (25 °C) and 1 atm.

$$V = \frac{nRT}{P} = \frac{(1\ \text{mol})\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.15\ \text{K})}{(1\ \text{atm})} = 24.5\ \text{L}$$

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Practice

$$PV = nRT$$

What is the pressure exerted by 1.55 g of Xe gas at 20 °C in a 560 mL flask?

$$P = \frac{nRT}{V} = \frac{(0.0118\ \text{mol Xe})\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{mol K}}\right)(293.15\ \text{K})}{0.560\ \text{L}} = 0.507\ \text{atm}$$

A 1.00 g sample of water vaporizes completely inside a 10.0 L container. What is the pressure of the water vapor at a temperature of 150 °C?

$$\left(\frac{1.00\ \text{g}\ H_2O}{}\right)\left(\frac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O}\right) = 0.055\ \text{mol}\ H_2O$$

$$P = \frac{nRT}{V} = \frac{(0.055\ \text{mol}\ H_2O)\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{mol K}}\right)(423.15\ \text{K})}{10.0\ \text{L}} = 0.193\ \text{atm}$$

28.15 mol of a gas is in a 1799 L container at 0 °C. What is the pressure?

$$P = \frac{nRT}{V} = \frac{(28.15\ \text{mol})\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{mol K}}\right)(273.15\ \text{K})}{1799\ \text{L}} = 0.351\ \text{atm}$$

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Applications of the Ideal Gas Equation

Using algebraic manipulation, it is possible to solve for variables other than those that appear explicitly in the ideal gas equation (like density).

MM is the Molar Mass(in g mol^{-1})

d is the density (in g L^{-1})

$$PV = nRT$$

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

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

$$d = \frac{(P)(MM)}{(R)(T)}$$

Carbon dioxide is effective in fire extinguishers partly because its density is greater than that of air, so CO_2 can smother the flames by depriving them of oxygen. (Air has a density of approximately 1.2 g L^{-1} at room temperature and 1 atm.) Calculate the density of CO_2 at room temperature (25°C) and 1.0 atm.

$$d = \frac{(P)(MM)}{(R)(T)} = \frac{(1\ \text{atm})\left(\frac{44.01\ \text{g}}{\text{mol}}\right)}{\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.15\ \text{K})} = 1.80\ \text{g L}^{-1}$$

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Practice

What is the molar mass of a gas that has a density of 5.75 g L^{-1} at STP?

$$MM = \frac{\text{dRT}}{\text{P}} = \frac{\left(\frac{5.75\ \text{g}}{\text{L}}\right)\left(\frac{0.08206\ \text{L atm}}{\text{mol K}}\right)(273.15\ \text{K})}{1\ \text{atm}} = \frac{128.9\ \text{g}}{\text{mol}}$$

Ammonia is placed in a container at 550 °C and 245 atm. What is the density?

$$d = \frac{(P)(MM)}{(R)(T)} = \frac{(245\ \text{atm})\left(\frac{17.04\ \text{g}}{\text{mol}}\right)}{\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(823.15\ \text{K})} = \frac{61.81\ \text{g}}{\text{L}}$$

At 741 torr and 44 °C, 7.10 g of a gas occupies a volume of 5.40 L. What is the molar mass of the gas?

$$PV = nRT$$

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

$$n = \frac{(0.975\ \text{atm})(5.40\ \text{L})}{\left(\frac{0.08206\ \text{L atm}}{\text{mol K}}\right)(317.15\ \text{K})}$$

$$n = 0.202\ \text{mol gas}$$

$$MM = \frac{grams}{mol}$$

$$MM = \frac{7.10\ g\ gas}{0.202\ mol\ gas}$$

$$MM = \frac{35.15\ g}{mol}$$

What is the molar mass (in g mol^{-1} to one decimal place) of a gas which has a density of 1.30 g L^{-1} measured at 27 °C and 0.400 atm?

$$MM = \frac{\text{dRT}}{\text{P}} = \frac{\left(\frac{1.30\ \text{g}}{\text{L}}\right)\left(\frac{0.08206\ \text{L atm}}{\text{mol K}}\right)(300.15\ \text{K})}{0.400\ \text{atm}} = \frac{80.05\ \text{g}}{\text{mol}}$$

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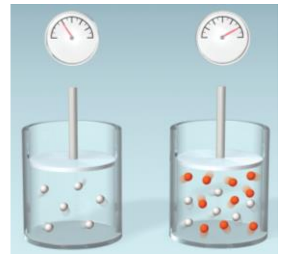
Gas Mixtures: Dalton's Law of Partial Pressures



$P_{total} = \Sigma P_i$

When two or more gases are placed in a container, each gas behaves as though it occupies the container alone. Find the pressure of each gas and then sum all pressures for total pressure of the system.

1.00 mole of N_2 in a 5.00 L container at 0°C exerts a pressure of 4.48 atm.

$$P_{i(N_2)} = \frac{nRT}{V} = \frac{(1\ \text{mol})\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(273.15\ \text{K})}{(5.00\ \text{L})} = 4.48\ \text{atm}$$

An additional 1.00 mole of O_2 is added to the same container. It exerts an additional 4.48 atm of pressure.

$$P_{i(O_2)} = \frac{nRT}{V} = \frac{(1\ \text{mol})\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(273.15\ \text{K})}{(5.00\ \text{L})} = 4.48\ \text{atm}$$

The total pressure of the mixture is the sum of the **partial pressures (P_i)**:

$$P_{total} = P_{i(N_2)} + P_{i(O_2)} = 4.48\ \text{atm} + 4.48\ \text{atm} = 8.96\ \text{atm}$$

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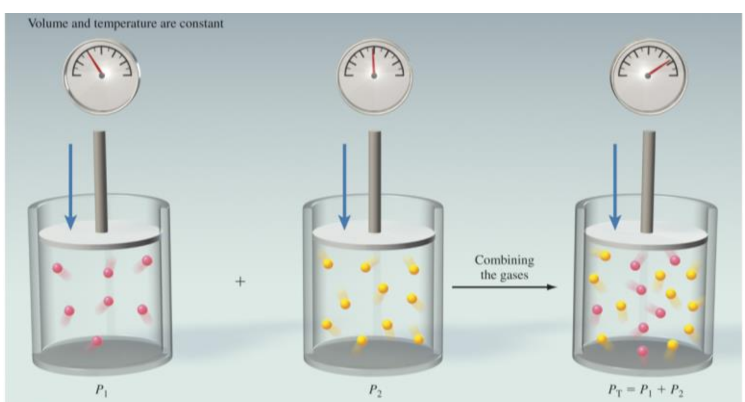
Gas Mixtures: Dalton's Law of Partial Pressures

Each component of a gas mixture exerts a pressure independent of the other components. The total pressure is the sum of the partial pressures.



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Practice

A 1.00–L vessel contains 0.215 mole of N_2 gas and 0.0118 mole of H_2 gas at 25.5°C. Determine the partial pressure of each component and the total pressure in the vessel.

$$P_{i(N_2)} = \frac{nRT}{V} = \frac{(0.215\text{ mol})\left(\frac{0.08206\text{ L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.65\text{ K})}{(1.00\text{ L})} = 5.27\text{ atm}$$

$$P_{i(H_2)} = \frac{nRT}{V} = \frac{(0.0118\text{ mol})\left(\frac{0.08206\text{ L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.65\text{ K})}{(1.00\text{ L})} = 0.289\text{ atm}$$

$$P_{total} = P_{i(N_2)} + P_{i(H_2)} = 5.27\text{ atm} + 0.289\text{ atm} = 5.56\text{ atm}$$

What is the total pressure exerted by a mixture of 1.50 g H_2 and 5.00 g N_2 in a 5.00 L vessel at 25 °C?

$$\left(\frac{1.50\text{ g }H_2}{}\right)\left(\frac{1\text{ mol}}{2.02\text{ g}}\right) = 0.7426\text{ mol }H_2$$

$$P_{i(H_2)} = \frac{nRT}{V} = \frac{(0.215\text{ mol})\left(\frac{0.08206\text{ L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.15\text{ K})}{(5.00\text{ L})} = 3.63\text{ atm}$$

$$\left(\frac{5.00\text{ g }N_2}{}\right)\left(\frac{1\text{ mol}}{18.02\text{ g}}\right) = 0.1784\text{ mol }N_2$$

$$P_{i(N_2)} = \frac{nRT}{V} = \frac{(0.1784\text{ mol})\left(\frac{0.08206\text{ L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.15\text{ K})}{(5.00\text{ L})} = 0.8730\text{ atm}$$

$$P_{total} = P_{i(H_2)} + P_{i(N_2)} = 3.63\text{ atm} + 0.8730\text{ atm} = 4.50\text{ atm}$$

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Mole Fractions

The relative amounts of the components in a gas mixture can be specified using *mole fractions*.

$$\chi_i = \frac{n_i}{n_{total}}$$

There are three things to remember about mole fractions:

1) The mole fraction of a mixture component is always less than 1.
2) The sum of mole fractions for all components of a mixture is always 1.
3) Mole fractions are dimensionless.

$$\chi_i = \frac{P_i}{P_{total}}$$

$$(\chi_i)(P_{total}) = P_i$$

$$(\chi_i)(n_{total}) = n_i$$

n and P are proportional to each other at a specified Temperature and Volume

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Practice

In 1999, the FDA approved the use of nitric oxide (NO) to treat and prevent lung disease, which occurs commonly in premature infants. The nitric oxide used in this therapy is supplied to hospitals in the form of a N_2/NO mixture. Calculate the mole fraction of NO in a 10.00-L gas cylinder at room temperature (25°C) that contains 6.022 mol N_2 and in which the total pressure is 14.75 atm.

$$n_{\text{Total}} = \frac{P_{\text{Total}}V}{RT} = \frac{(14.75\ \text{atm})(10.0\ \text{L})}{\left(\frac{0.08206\ \text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.15\ \text{K})} = 6.029\ \text{mol gas total}$$

$$n_{\text{NO}} + n_{N_2} = n_{\text{Total}} \longrightarrow n_{\text{NO}} = n_{\text{Total}} - n_{N_2}$$

$$= 6.029 - 6.022$$

$$= 0.007\ \text{mol NO}$$

$$\chi_{\text{i}} = \frac{n_{\text{i}}}{n_{\text{total}}}$$

$$\chi_{\text{i}} = \frac{0.007\ \text{mol NO}}{6.029\ \text{Total mol}}$$

$$\chi_{\text{i}} = 0.001$$

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Reactions with Gaseous Reactants and Products: Calculating the Required Volume of a Gaseous Reactant

$2\ CO(g) + O_2(g) \longrightarrow 2\ CO_2(g)$

The ratio of carbon monoxide to oxygen is 2:1 in moles or volume (all gas phase)

$2\ Na(s) + Cl_2(g) \longrightarrow 2\ NaCl(s)$ (use the ideal gas equation for 1 gas reactant)

grams Na $\xrightarrow{\text{Molar Mass}}$ *moles Na* $\xrightarrow{\text{mol:mol}}$ *moles Cl_2* $\xrightarrow{PV = nRT}$ *liters Cl_2*

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Practice

Sodium peroxide (Na_2O_2) is used to remove carbon dioxide from (and add oxygen to) the air supply in spacecrafts. It works by reacting with CO_2 in the air to produce sodium carbonate (Na_2CO_3) and O_2.

$$2Na_2O_2(s) + 2CO_2(g) \longrightarrow 2Na_2CO_3(s) + O_2(g)$$

What volume (in liters) of CO_2 (at STP) will react with a kilogram of Na_2O_2?

$$\left(\frac{1000\text{ g}}{}\right)\left(\frac{1\text{ mol }Na_2O_2}{77.98\text{ g }Na_2O_2}\right)\left(\frac{2\text{ mol }CO_2}{2\text{ mol }Na_2O_2}\right) = 12.82\text{ mol }CO_2$$

$$V_{CO_2} = \frac{nRT}{P} = \frac{(12.82\text{ mol }CO_2)\left(\frac{0.08206\text{ L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(273.15\text{ K})}{(1\text{ atm})} = 287.4\text{ L }CO_2$$

What volume of oxygen at 45 °C and 2 atm pressure is needed to react with nitrogen gas to form 0.35 moles of N_2O_4?

$$2O_2(g) + N_2(g) \longrightarrow N_2O_4(g)$$

$$\left(\frac{0.35\text{ mol }N_2O_4}{}\right)\left(\frac{2\text{ mol }O_2}{1\text{ mol }N_2O_4}\right) = 0.7\text{ mol }O_2$$

$$V_{O_2} = \frac{nRT}{P} = \frac{(0.7\text{ mol }O_2)\left(\frac{0.08206\text{ L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(318.15\text{ K})}{(2\text{ atm})} = 9.138\text{ L }O_2$$

If 2.7 g of Al metal is reacted with excess HCl, how many liters of H_2 gas are produced at 25 °C and 1.00 atm pressure?

$$2Al(s) + 6HCl(aq) \longrightarrow 3H_2(g) + 2AlCl_3$$

$$\left(\frac{2.7\text{ g}}{}\right)\left(\frac{1\text{ mol }Al}{26.98\text{ g }Al}\right)\left(\frac{3\text{ mol }H_2}{2\text{ mol }Al}\right) = 0.15\text{ mol }H_2$$

$$V_{H_2} = \frac{nRT}{P} = \frac{(0.15\text{ mol }H_2)\left(\frac{0.08206\text{ L}\cdot\text{atm}}{\text{K}\cdot\text{mol}}\right)(298.15\text{ K})}{(1.00\text{ atm})} = 3.67\text{ L }H_2$$

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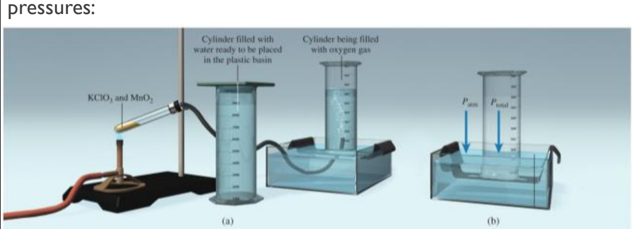
Using Partial Pressures to Solve Problems

The volume of gas produced by a chemical reaction can be measured using an apparatus like the one shown below. When gas is collected over water in this manner, the total pressure is the sum of two partial pressures:



$$P_{total} = P_{collected\ gas} + P_{H_2O}$$

The vapor pressure of water is known at various temps.

Vapor Pressure of Water as a Function of Temperature					
T(°C)	P(torr)	T(°C)	P(torr)	T(°C)	P(torr)
0	4.6	35	42.2	70	233.7
5	6.5	40	55.3	75	289.1
10	9.2	45	71.9	80	355.1
15	12.8	50	92.5	85	433.6
20	17.5	55	118.0	90	525.8
25	23.8	60	149.4	95	633.9
30	31.8	65	187.5	100	760.0

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Practice

Calcium metal reacts with water to produce hydrogen gas:

$$Ca(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Determine the mass of H_2 produced at 25 °C and 0.967 atm when 525 mL of the gas is collected over water.

$$P_{H_2O} + P_{H_2} = P_{\text{Total}}$$

$$P_{H_2} = P_{\text{Total}} - P_{H_2O}$$
$$= 0.967 \text{ atm} - 0.0313 \text{ atm}$$
$$= 0.9357 \text{ atm}$$

$$n_{\text{H}_2} = \frac{P_{\text{H}_2}V}{RT} = \frac{(0.9357 \text{ atm})(0.525 \text{ L})}{\left(\frac{0.08206 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}}\right)(298.15 \text{ K})}$$

$$n_{\text{H}_2} = 2.01 \text{ x } 10^{-2} \text{ mol H}_2$$

$$\left(\frac{2.01 \text{ x } 10^{-2} \text{ mol H}_2}{}\right)\left(\frac{2.016 \text{ g H}_2}{1 \text{ mol H}_2}\right) = 0.0405 \text{ g H}_2$$

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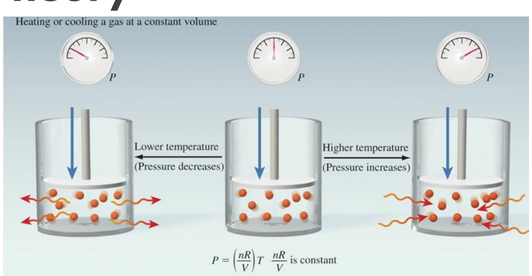
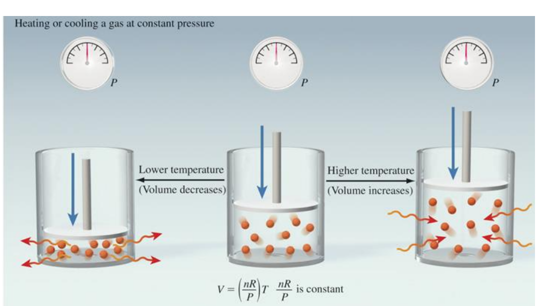
The Gas Laws and the Kinetic Molecular Theory



Cooling at constant volume: pressure decreases

Heating at constant volume: pressure increases



Cooling at constant pressure: volume decreases

Heating at constant pressure: volume increases

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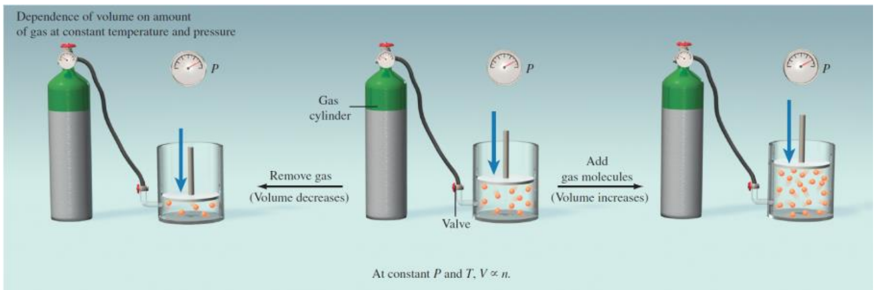
The Gas Laws and the Kinetic Molecular Theory

The presence of additional molecules causes an increase in pressure.



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The Kinetic Molecular Theory

The **kinetic molecular theory** explains how the molecular nature of gases gives rise to their macroscopic properties.

The basic assumptions of the kinetic molecular theory are as follows:

1) A gas is composed of particles that are separated by large distances. The volume occupied by individual molecules is negligible.

Gases are compressible because molecules in the gas phase are separated by large distances.

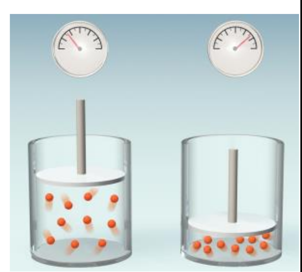
2) Gas molecules are constantly in random motion, moving in straight paths, colliding with perfectly elastic collisions.

Pressure is the result of the collisions of gas molecules with the walls of their container.

3) Gas molecules do not exert attractive or repulsive forces on one another.

4) The average kinetic energy of a gas molecules in a sample is proportional to the absolute temperature: $\bar{E}_k \propto T$

Heating a sample of gas increases its average kinetic energy. Gas molecules must move faster at higher T. Faster molecules collide more frequently and at a greater speed. Pressure increases as collision frequency increases.



Decreasing volume increases the frequency of collisions. Pressure increases as collision frequency increases.

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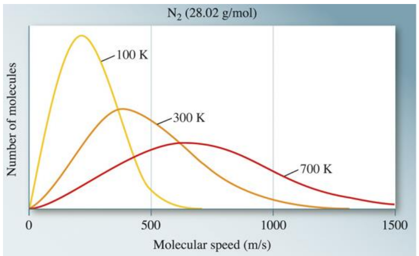
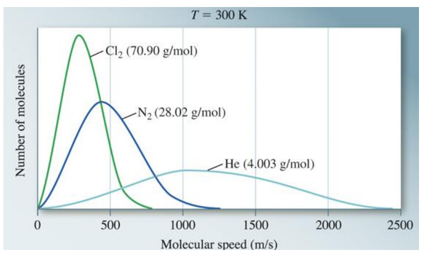
The Kinetic Molecular Theory and Molecular Speed

The root–mean–square (rms) speed (u_{rms}) is the speed of a molecule with the average kinetic energy in a gas sample. Where, u_{rms} is the average molecular speed (m/s), R = gas constant (8.314 J/mol K), T = Temperature (K), M = Formula weight (g/mol)





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

1 J = 1 kgm^2/s^2 = 1000 g m^2/s^2

u_{rms} is directly proportional to temperature (makes sense based on assumption 4 also)

u_{rms} is inversely proportional to the square root of *MM*.

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The Kinetic Molecular Theory

When two gases are at the same temperature, it is possible to compare the the u_{rms} values of the different gases.

$$\frac{u_{rms}(1)}{u_{rms}(2)} = \sqrt{\frac{M_2}{M_1}}$$

Determine how much faster a helium atom moves, on average, than a carbon dioxide molecule at the same temperature.

$$\frac{u_{rms}(He)}{u_{rms}(CO_2)} = \sqrt{\frac{\frac{44.02\ \text{g}}{1\ \text{mol}}}{\frac{4.003\ \text{g}}{1\ \text{mol}}}} = 3.316$$

On average, He atoms move 3.316 times as fast as CO_2 molecules at the same temperature.

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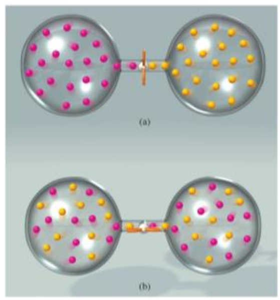
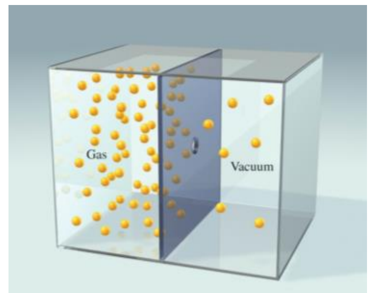
Diffusion and Effusion

Diffusion is the mixing of gases as the result of random motion and frequent collisions.

Effusion is the escape of gas molecules from a container to a region of vacuum.





Graham's law states that the rate of diffusion or effusion of a gas is inversely proportional to the square root of its molar mass.

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

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Practice

Determine the molar mass and identity of a diatomic gas that moves 4.67 times as fast as CO_2.

$$\frac{u_{\mathrm{rms}}(1)}{u_{\mathrm{rms}}(2)} = \sqrt{\frac{M_2}{M_1}}$$

$$u_{\mathrm{rms}}(\text{unknown gas}) = (4.67)(u_{\mathrm{rms}}(\mathrm{CO_2}))$$

$$\frac{u_{\mathrm{rms}}(\text{unknown gas})}{u_{\mathrm{rms}}(\mathrm{CO_2})} = 4.67$$

$$\frac{u_{\mathrm{rms}}(1)}{u_{\mathrm{rms}}(2)} = 4.67 = \sqrt{\frac{M_2}{M_1}} \longrightarrow \frac{u_{\mathrm{rms}}(1)}{u_{\mathrm{rms}}(2)} = 4.67 = \sqrt{\frac{44.02\ \mathrm{g/mol}}{\mathrm{M(unknown)}}} \longrightarrow M = 2.018\ \mathrm{g/mol}$$

The gas must be H_2.

How much faster will hydrogen gas effuse than oxygen gas?

$$\frac{u_{\mathrm{rms}}(\mathrm{H_2})}{u_{\mathrm{rms}}(\mathrm{O_2})} = \sqrt{\frac{32.00\ \mathrm{g/mol}}{2.02\ \mathrm{g/mol}}} = 3.98 \text{ times as fast}$$

Place these gases in order of increasing average molecular speed at 25 °C :

Kr, CH_4, N_2, CH_2Cl_2

CH_2Cl_2 < Kr < N_2 < CH_4

Higher Molar Mass leads to a slower gas

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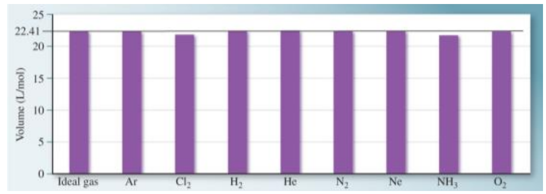
Real Gases: Factors that cause deviation from Ideal Behavior

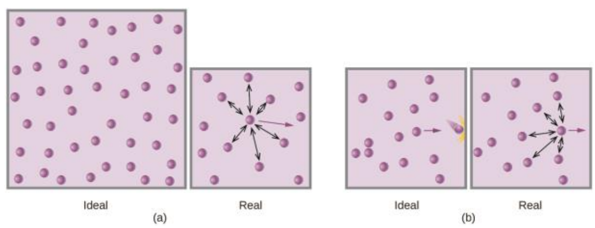
At high pressure molecules are close together and individual volume becomes significant (PV=nRT)

At low temperatures molecules are moving slower and any intermolecular forces become significant (u=$\sqrt{\frac{3RT}{M}}$)



Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces.

These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas.



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The van der Waals Equation

The **van der Waals equation** is useful for gases that do not behave ideally.

experimentally measured pressure

container volume

$$\underbrace{\left(P + \frac{an^2}{V^2}\right)}_{\text{corrected pressure}} \underbrace{(V - nb)}_{\text{corrected volume}} = nRT$$

a = molecular attraction (low pressure)
b = volume of molecules (high pressure/small volume)

Van der Waals Constants of Some Common Gases					
Gas	a$\left(\frac{\text{atm}\cdot\text{L}}{\text{mol}^2}\right)$	b$\left(\frac{\text{L}}{\text{mol}}\right)$	**Gas**	a$\left(\frac{\text{atm}\cdot\text{L}}{\text{mol}^2}\right)$	b$\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237	**O_2**	1.36	0.0318
Ne	0.211	0.0171	**Cl_2**	6.49	0.0562
Ar	1.34	0.0322	**CH_4**	2.25	0.0428
H_2	0.244	0.0266	**CCl_4**	20.4	0.138
N_2	1.39	0.0391	**H_2O**	5.46	0.0305

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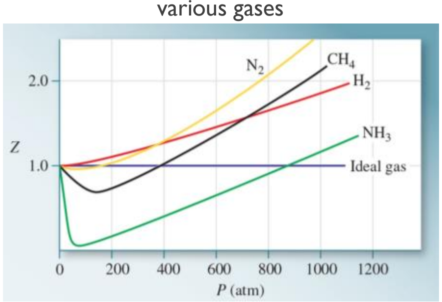
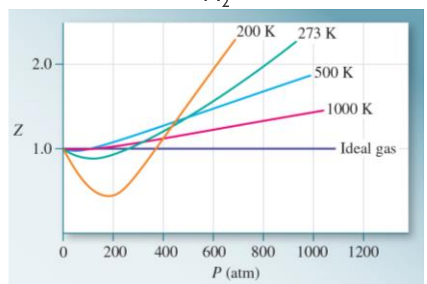
The van der Waals Constants

Compressibility as a Function of Pressure

various gases



N$_2$



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