

Gas Laws



MDI corporation prototype for vehicle that runs on compressed air.



Explores the relationships between:

Volume, V

Temperature, T

Amount (moles), n

Pressure, P



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 .

Other units of pressure:

Atmosphere: The average pressure of the atmosphere on the surface of the Earth at sea-level (atm)

Torr: Unit of pressure based on the mercury barometer (torr). $1\text{atm} = 760\text{torr} = 101,300\text{Pa}$

Mercury Barometer

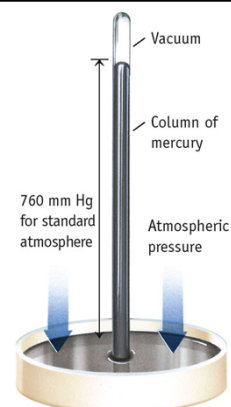
The atmospheric pressure pushes the mercury column up 760mm, before the weight (Force) of the column down per unit area is equal to the upward pressure (Note the vacuum above the Hg column in the tube)

$$1\text{mmHg} = 1\text{torr}$$

Pressure Units Summary:

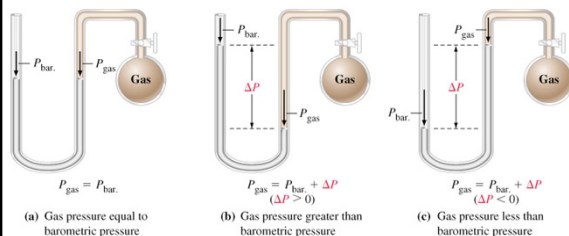
$$1\text{atm} = 760\text{mmHg (torr)} = 101,300\text{Pa} = 101.3\text{kPa}$$

$$\text{(also } 29.92\text{''Hg, } 1.013\text{bar, } 14.7\text{psi)}$$

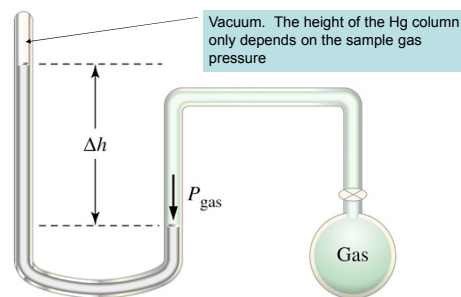


Measuring Sample Gas Pressure

Open-end Manometer (Ma-naw-mah-ter)



Closed-end Manometer



Three Relationships

<p>Boyle's Law $PV = \text{constant}$ (n, T kept constant) Inverse Relationship $P_1V_1 = P_2V_2$</p>	<p>Charles's Law $V/T = \text{constant}$ (n, P kept constant) Direct Relationship $V_1/T_1 = V_2/T_2$</p>	<p>Avogadro's Law $V/n = \text{constant}$ (T, P kept constant) Direct Relationship $V_1/n_1 = V_2/n_2$</p>
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← Boyle's Law Relationship

Combined Gas Law:

$PV/nT = \text{constant}$ (T in Kelvins)

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

Avogadro's Hypothesis:

Equal volumes of gases under the same conditions of temperature and pressure have equal numbers of particles (either molecules or atoms depending on the composition of the gas).

$V \propto n$ at constant P and T

Ideal gas Law:

$PV = nRT$

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

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

Variations on the ideal gas law equation:

$PV = mRT/M$ (m = sample mass, M = molar mass of the gas)

$M = mRT/PV$

$d = MP/RT$ (d = density of the gas in g/L)

Stoichiometric Relationships

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Gas Mixtures and Dalton's Law of Partial Pressures

Dalton's Law of Partial Pressures:

The total pressure exerted by a mixture of gases is equal to the sum of the partial pressures exerted by the separate gases.

Recall that if a gas behaves ideally, the identity of the gas is irrelevant in the ideal gas equation

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$$

$$P_{\text{total}} = n_1RT/V + n_2RT/V + n_3RT/V + \dots \quad \text{where } T \text{ and } V \text{ are constant since the gases are in the same container}$$

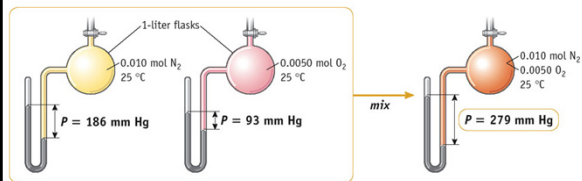
$$P_{\text{total}} = (n_1 + n_2 + n_3)RT/V$$

Also, the ratio of the partial pressure of a gas in a container is equal to its mole fraction.

$$P_1/P_{\text{total}} = n_1/n_{\text{total}}$$

(The volume percentage is also related to the mole percentage)

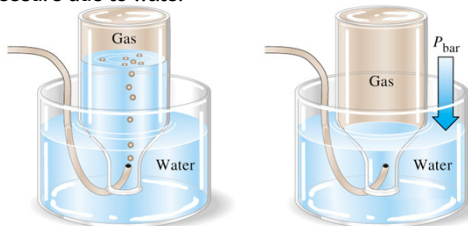
Dalton's Law of Partial Pressures Visualized



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Water Vapor Pressure

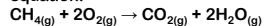
Sometimes gases are collected by water displacement. Since some of the water "vaporizes" at a given temperature, the total pressure inside the container is the sum of the collected sample gas and the vapor pressure due to water



Water vapor pressure is a function of temperature and must be looked up

Example: You have a 22.-L cylinder of helium at a pressure of 150atm and a temperature of 31°C. How many balloons can you fill, each with a volume of 5.0L, on a day when the atmospheric pressure is 755mmHg and the temperature is 22°C?

Methane burns in oxygen to give CO₂ and H₂O, according to the equation:



If 22.4L of gaseous CH₄ is burned, what volume of O₂ is required for complete combustion? What volumes of CO₂ and H₂O are produced? Assume all gases are at the same temperature and pressure.

Answers:

$$1. P_1V_1/T_1 = P_2V_2/T_2 \\ (150\text{atm})(22.\text{L})/(304.15\text{K}) = (755\text{mmHg}/760)(V_2)/(295.15\text{K}) \\ V_2 = 3223\text{L} \\ 3223\text{L}/5.0\text{L} = 644.7 = \mathbf{640\text{balloons}}$$

$$2. 22.4\text{L CH}_4 \\ 22.4\text{L CH}_4 (2 \text{ volumes O}_2 / 1 \text{ volume CH}_4) = \mathbf{44.8\text{L O}_2} \\ 22.4\text{L CH}_4 (2 \text{ volumes H}_2\text{O} / 1 \text{ volume CH}_4) = \mathbf{44.8\text{L H}_2\text{O}} \\ 22.4\text{L CH}_4 (1 \text{ volume of CO}_2 / 1 \text{ volume CH}_4) = \mathbf{22.4\text{L CO}_2}$$

Examples:

The balloon used by Jacques Charles in his historic flight in 1783 was filled with about 1300mol of H₂. If the temperature of the gas was 23°C and its pressure was 750mmHg, what was the volume of the balloon?

A 0.105g sample of a gaseous compound has a pressure of 561mmHg in a volume of 125mL at 23.0°C. What is its molar mass?

Answers:

1. $V = nRT/P$

$V = (1300\text{mol})(.0821\text{Latm/molK})(296.15\text{K})/(750/760)$

$V = 32,029.53\text{L} = 3.2 \times 10^4\text{L}$

2. $M = nRT/PV$

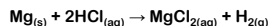
$M = (0.105\text{g})(.0821\text{Latm/molK})(296.15\text{K}) / (561/760)(.125\text{L})$

$M = 27.668 = 27.7\text{g/mol}$

Example: A sample of magnesium metal was placed in a solution of hydrochloric acid producing magnesium chloride and hydrogen gas. The hydrogen was collected by water displacement at 25.0°C and found to have a total pressure of 1.10atm and a volume of 2.00L. If the vapor pressure of water at 25.0°C is 23.76torr, how many grams of magnesium were used in the reaction?

Example: A sample of magnesium metal was placed in a solution of hydrochloric acid producing magnesium chloride and hydrogen gas. The hydrogen was collected by water displacement at 25.0°C and found to have a total pressure of 1.10atm and a volume of 2.00L. If the vapor pressure of water at 25.0°C is 23.76torr, how many grams of magnesium were used in the reaction?

Answer:



Adjusted pressure: $1.10\text{atm} - (23.76\text{torr} / 760\text{torr/atm}) = 1.069\text{atm}$

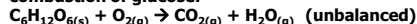
Moles $\text{H}_2 = PV/RT = (1.069\text{atm})(2.00\text{L}) / [(0.0821\text{Latm/molK})(298.15\text{K})]$

$= .0873\text{mol H}_2$

$.0873\text{mol H}_2 (1\text{mol Mg} / 1\text{mol H}_2)(24.30\text{gMg/mol}) = 2.12\text{g Mg}$

Example:

A large portion of metabolic energy arises through the biological combustion of glucose:



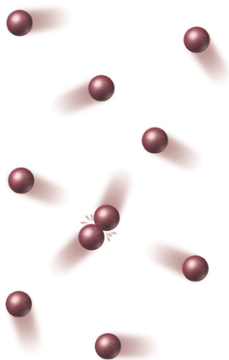
If this reaction is carried out at 35.0°C in a 5.00L rigid container using 18.0g of glucose (180.16g/mol) and 24.00g of $\text{O}_2(g)$:

a) What is the pressure inside the container (in atm) after the reaction has gone to completion? (Assume 100% yield)

b) What is the mole fraction and final partial pressure of the $\text{CO}_2(g)$?

c) What (if anything) will happen to the pressure inside the container if sufficient glucose is injected into the sealed container to react with the remainder of the oxygen? By what percentage will the pressure increase/decrease? Explain.

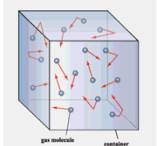
Kinetic molecular theory



- 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

$KE = \frac{1}{2}(\text{mass})(\text{speed})^2 = \frac{1}{2}mu^2$

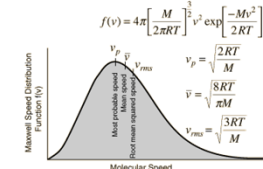
$\overline{KE} = \frac{1}{2}\overline{mu^2}$ ← Mean square speed of all molecules



$\overline{KE} = \frac{3}{2}\left(\frac{R}{N_A}\right)T$

$N_A = M / m$

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



$u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$ ← Root-mean-square (rms) speed

Maxwell's Equation

Optional Derivation

Given: $P = Nmu^2/3V$ (Pressure of a gas in a closed container)
 (N = number of particles; m = mass of atom/molecule; V = volume; The 3 is related to motion in 3-dimensional space)

$$PV = Nmu^2/3 \quad PV = nRT$$

(substituting)
 $nRT = Nmu^2/3$

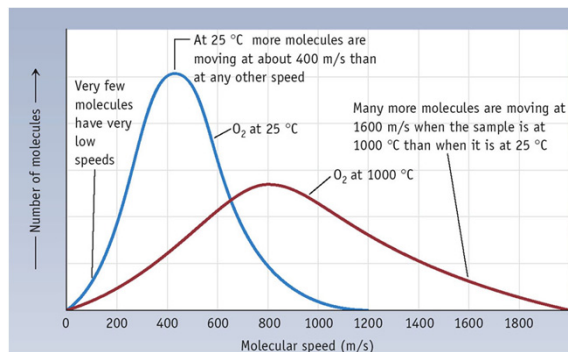
$$E_t = \frac{1}{2} mu^2 \quad mu^2 = 2E_t$$

(substituting)
 $nRT = 2NE_t/3$

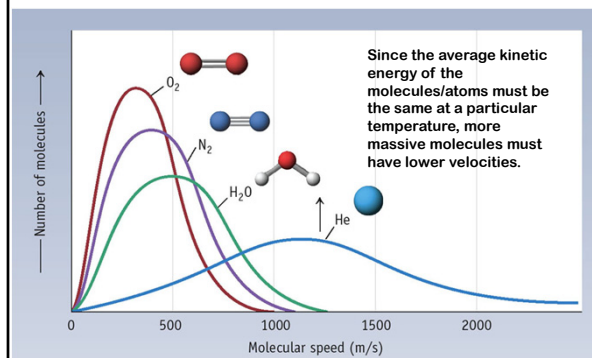
(rearranging)
 $E_t = 3nRT/2N$ N/n is Avogadro's number N_A
 (substituting)

$$E_t = 3RT/2N_A$$

Maxwell Distribution of O₂ Speeds at Different Temperatures



Effect of Molecular Mass on Distribution of speed



According to KMT, gas pressure is caused by gas molecules bombarding the container walls.

$$P = F/A$$

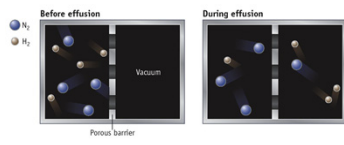
The greater the frequency of collisions (for a given average kinetic energy) the greater the pressure will be (i.e. more collisions per unit time per unit area of the container.)

Graham's Law of Effusion

Diffusion: The mixing of molecules of two or more gases due to their random molecular motions.



Effusion: The movement of gas through a tiny opening in a container into another container where the pressure is very low.



The relative rates of effusion (diffusion) between two gases is inversely proportional to the square roots of their molar masses

Rate: How fast, relative to something else, something is occurring.

Time: How long it takes for something to happen.

Rate is inversely proportional to time (be careful of this distinction)

$$\frac{Rate_{gas1}}{Rate_{gas2}} = \sqrt{\frac{M_{gas2}}{M_{gas1}}}$$

$$\frac{Time_{gas1}}{Time_{gas2}} = \sqrt{\frac{M_{gas1}}{M_{gas2}}}$$

Example:

Calculate the rms speeds of helium atoms and N₂ molecules at 25°C. $u_{rms} = (3RT/M)^{1/2}$; R = 8.314J/molK

Answer:

$$\text{He} = (3(8.314)(298.15K)/.004003\text{kg/mol})^{1/2}$$

$$\text{N}_2 = (3(8.314)(298.15K)/.02802\text{kg/mol})^{1/2}$$

$$\text{He} = 1362.98 = 1400\text{m/s} \quad \text{N}_2 = 515.168 = 520\text{m/s}$$

Example: A gas takes 3.50 times longer to effuse than helium. Determine the molar mass of the gas.

$$\frac{\text{Time}_{\text{gas1}}}{\text{Time}_{\text{gas2}}} = \sqrt{\frac{M_{\text{gas1}}}{M_{\text{gas2}}}} \quad \frac{\text{Rate}_{\text{gas1}}}{\text{Rate}_{\text{gas2}}} = \sqrt{\frac{M_{\text{gas2}}}{M_{\text{gas1}}}}$$

Answer:

$$\text{MM} = 4.003(3.50)^2$$

Molar mass of unknown gas is **49.0g/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

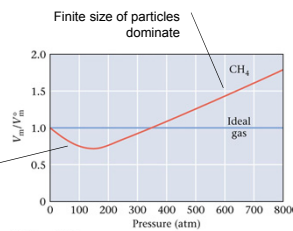
Gases are most ideal at:

Low pressures

High temperatures

$V_m = \text{true volume}$
 $V_m^o = \text{Ideal gas predicted volume}$

Intermolecular attractions dominate



Nonideal Gas Behavior and the van der Waal's Equation

In reality:

The molecules of gases do occupy some of the space of the container (reduces the free volume from ideal)

There are attractive forces between particles (reduces the pressure from ideal)

In general: Higher pressure and lower temperature behave less ideally.

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Observed Pressure Container V

Correction for molecular volume

Correction for intermolecular forces

The constants a and b depend on the gas involved

Van der Waals Constants for Gaseous Molecules

Substance (L/mol)	a (L ² -atm/mol ²)	b
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
H ₂ O	5.46	0.0305
CH ₄	2.25	0.0428
CO ₂	3.59	0.0427

Example:

Calculate the percent deviation from ideal pressure for nitrogen gas if 6.00g of nitrogen are sealed in a 50.0mL container at -200.0°C.
 a = 1.39atmL²/mol²;
 b = 0.0391L/mol for nitrogen.

Answer:

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

$$P = (6.00\text{g}/28.02\text{g/mol})(.0821\text{Latm/molK})(73.15\text{K}) / (.0500\text{L}) = 25.7\text{atm}$$

$$(P + (1.39)(.21413)^2/(.0500)^2)(.0500 - (.21413)(0.0391)) = (.21413)(.0821)(73.15)$$

$$P = 5.40\text{atm}$$

$$P_{\text{actual}}/P_{\text{ideal}} = 5.40/25.7 = .2099$$

\cong **20.99% (79.01% deviation)**