

CHAPTER 6: Gases (183)

Pressure (184)

Gases exert pressure by pushing against their surroundings. The air in a balloon presses against the walls of the balloon and is counterbalanced by the air pressure on the outside of the balloon.

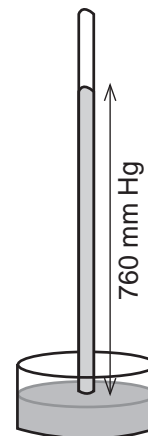


a column of air 1" by 1" weighs 14.7 lbs

$$\text{pressure} = \frac{\text{force}}{\text{unit area}} = 14.7 \text{ lbs/sq. in} = 1 \text{ atm}$$

barometer, invented by Torrecelli, is glass tube filled with mercury inverted into a dish of mercury

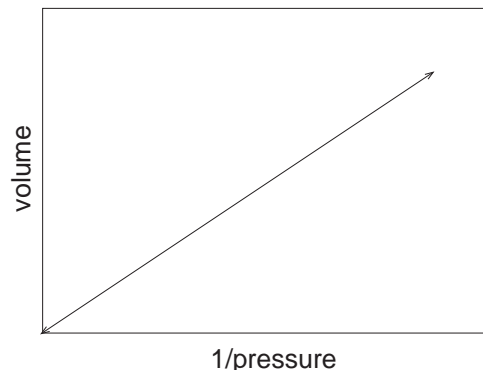
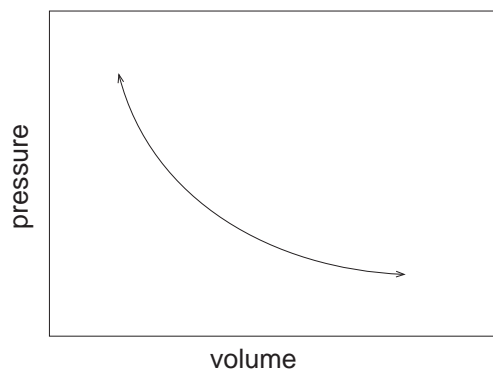
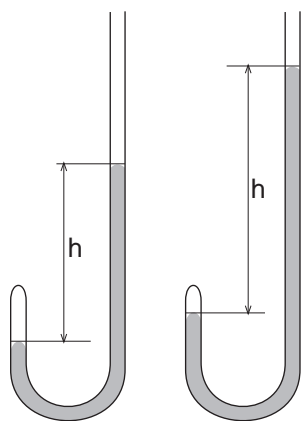
1 atm exerts enough pressure against the Hg in a barometer to push it up 760 mm against a vacuum.



$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101,325 \text{ pascals} \quad 1 \text{ Pa} = 1 \text{ N/m}^2$$

The Gas Laws of Boyle, Charles, and Avogadro (186)

Boyle's Law (187) Robert Boyle (1627 - 1691) investigated the relationship between the volume of a gas and the pressure on it by changing the height of a column of mercury in a J-shaped tube. (see data, table 5.1, pg 187). A plot of P vs. V gives a hyperbola; a plot of V vs. 1/P gives a straight line



$$PV = k \text{ or } P = \frac{k}{V} \text{ or } V = \frac{k}{P} \text{ where } k \text{ is a constant which depends on } T \text{ and amount of gas.}$$

For a fixed amount of gas at a fixed temperature, PV is constant, so

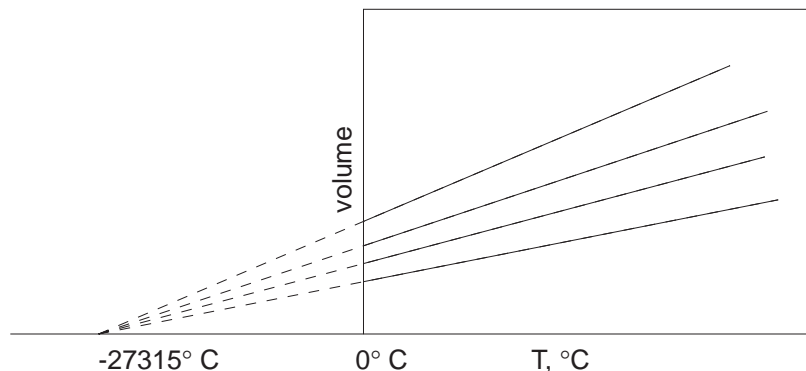
$$P_1V_1 = P_2V_2$$

For a sample of 2.00 L of gas at 1.00 atm pressure, what will be the new volume if the pressure is increased to 2.50 atm?

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{(1.00 \text{ atm})(2.00 \text{ L})}{2.50 \text{ atm}} = 0.800 \text{ L}$$

As pressure increases, there is a deviation from ideal behavior (fig. 5.6, pg 189)

Charles's Law (189) Law of Charles and Gay-Lussac: Jaques Charles, french balloonist, found that volume increases linearly with T.



The slope of the line depends on P and amount of gas, but the X-intercept is constant, -273.15°C . We define the Kelvin scale

$$\text{K} = ^\circ\text{C} + 273.15$$

0 K is absolute zero, the temperature at which all molecular motion stops.

Charles Law: $V = bT$, where T is Kelvin temperature and b is a constant that depends on P and amount of gas.

$$V = bT \text{ or } \frac{V}{T} = b \text{ therefore } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

What happens to the volume of a gas when the temperature doubles from 25°C to 50°C ?

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} = \frac{273 + 50}{273 + 25} = 1.08 \quad \text{the volume increases by 8\%}$$

Avogadro's Law (191) 1811: equal volumes of gases at the same T and P contain the same number of particles

$$V = an \quad \text{where a depends on P and T, and n is number of moles}$$

The Ideal Gas Law (192)

$$V = an \quad \text{Avogadro's Law}$$

$$V = bT \quad \text{Charles' Law}$$

$$V = \frac{k}{P} \quad \text{Boyle's Law}$$

these can be combined to give $V = R \left(\frac{nT}{P} \right)$ where R is the gas law constant = abk

$$R = 0.08206 \text{ L atm/mol K}$$

$$PV = nRT \quad \text{ideal gas law}$$

How many moles of gas are in 250 mL of gas at 765 mm Hg and 28° C?

$$n = \frac{PV}{RT} = \frac{(765 \text{ mm Hg})\left(\frac{1 \text{ atm}}{760 \text{ mm Hg}}\right)(0.250 \text{ L})}{(0.08206 \text{ L atm/mol K})(301 \text{ K})} = 0.0102 \text{ mol}$$

for a constant n, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

A balloon initially at 1.00 atm, 25° C occupies 2.50 L. What will be the volume of the balloon if it rises to an altitude where the pressure is 0.500 atm and the temperature is -15° C?

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{(1.00 \text{ atm})(2.50 \text{ L})(273 - 15 \text{ K})}{(0.500 \text{ atm})(273 + 25 \text{ K})} = 4.33 \text{ L}$$

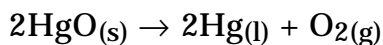
Gas Stoichiometry (197)

What is the volume of 1 mole of gas at 1 atm pressure and 0° C?

$$V = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.08206 \text{ L atm/mol K})(273.2 \text{ K})}{1 \text{ atm}} = 22.42 \text{ L}$$

We define Standard Temperature and Pressure (STP) to be 0° C (273 K) and 1 atm. At STP, 1 mole of a gas has a volume of 22.42 L.

What volume of O₂(g) is formed from the decomposition of 2.000 g HgO at STP?



$$2.000 \text{ g HgO} \times \frac{1 \text{ mol HgO}}{216.59 \text{ g HgO}} = 0.00923 \text{ mol HgO} \times \frac{1 \text{ mol O}_2}{2 \text{ mol HgO}} = 0.00462 \text{ mol O}_2$$

$$V = \frac{nRT}{P} = \frac{(0.00462 \text{ mol})(0.08206 \text{ L atm/mol K})(273.15 \text{ K})}{1 \text{ atm}} = 0.103 \text{ L} = 103 \text{ mL}$$

Molar Mass

$$n = \frac{\text{mass}}{\text{molar mass}} = \frac{m}{\text{molar mass}}$$

$$P = \frac{nRT}{V} = \frac{mRT}{V(\text{molar mass})} = \frac{dRT}{\text{molar mass}} \quad \text{where } d = \text{density (in g/L)} = \frac{m}{V}$$

so $\text{molar mass} = \frac{dRT}{P}$

What is the molar mass of a gas with a density of 3.16 g/L at STP?

$$\text{molar mass} = \frac{(3.16 \text{ g/L})(0.08206 \text{ L atm/mol K})(273 \text{ K})}{1 \text{ atm}} = 70.8 \text{ g/mol}$$

Dalton's Law of Partial Pressures (201) (1803)

The total pressure of a mixture is equal to the sum of the pressures that each gas would exert if were alone.

partial pressure P_x = pressure that a gas x would exert if were alone

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

since $P = \frac{nRT}{V}$,

$$P_{\text{tot}} = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} + \dots \quad \text{or} \quad P_{\text{tot}} = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = n_{\text{tot}} \frac{RT}{V}$$

The fact that the identity of the gas molecules is not important implies that

- the volume of a gas molecule must be insignificant
- the forces between gas molecules must be insignificant

We define the mole fraction $X_1 = \frac{n_1}{n_{\text{tot}}}$

but $n_1 = \frac{P_1V}{RT}$ and $n_{\text{tot}} = \frac{P_{\text{tot}}V}{RT}$, so

$$X_1 = \frac{\frac{P_1V}{RT}}{\frac{P_{\text{tot}}V}{RT}} = \frac{P_1}{P_{\text{tot}}} \quad \text{or}$$

$$P_1 = X_1 P_{\text{tot}}$$

Air is 78.08% N_2 , 20.95% O_2 , 0.934% Ar, and 0.0345% CO_2 (table 5.4, pg 217). Calculate the partial pressures of each gas in a sample of air under 5.0 atm pressure.

$$P(N_2) = (0.7808)(5.0 \text{ atm}) = 3.9 \text{ atm}$$

$$P(O_2) = (0.2095)(5.0 \text{ atm}) = 1.0 \text{ atm}$$

$$P(\text{Ar}) = (0.00934)(5.0 \text{ atm}) = 0.047 \text{ atm}$$

$$P(CO_2) = (0.000345)(5.0 \text{ atm}) = 0.0017 \text{ atm}$$

A common application of Dalton's Law of Partial Pressures is to correct for the presence of water vapor in a sample of gas.

A sample of $KClO_3$ is heated and produces 229 mL gas collected over water at 25° and total pressure of 754 mm Hg. How many moles of O_2 are formed? (see table 10.8, pg 474)

$P(H_2O)$ at 25° C = 23.756 mm Hg; $P(O_2) = P_{\text{tot}} - P(H_2O) = 754 \text{ mmHg} - 24 \text{ mmHg} = 730 \text{ mmHg}$

$$n = \frac{PV}{RT} = \frac{(730 \text{ mm Hg}) \left(\frac{1 \text{ atm}}{760 \text{ mm Hg}} \right) (0.229 \text{ L})}{(0.08206 \text{ L atm/mol K})(298 \text{ K})} = 0.00899 \text{ mol}$$

The Kinetic Molecular Theory of Gases (206)

Postulates of the Kinetic Molecular theory:

- 1 gas molecules are so small compared to the distances between them that they behave as if they had zero volume (point sized particles)
- 2 gas molecules are in constant motion. pressure is the result of collisions with the walls of the container
- 3 gas molecules exert neither attractive nor repulsive forces on each other
- 4 the average kinetic energy of a gas is directly proportional to T in K

The extent to which real molecules deviate from these postulates will direct the amount of deviation from ideal behavior.

From the theory, $P \propto (\text{number of collisions})(\text{average kinetic energy})/(\text{volume of container})$ but the number of collisions $\propto n$ and the kinetic energy $\propto T$, so

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

which is in agreement with the experimentally determined ideal gas law.

The Meaning of Temperature (209) Temperature is a measure of the random kinetic energy of molecules

Root Mean Square Velocity (209) $u_{\text{rms}} = \sqrt{\overline{u^2}}$

where $\overline{u^2}$ is the average of the squares of the individual particle velocities.

Since $\text{KE} = 1/2 mu^2$, $(\text{KE})_{\text{ave}} = N_a(1/2 m \overline{u^2})$ but $(\text{KE})_{\text{ave}} = 3/2(RT)$ so

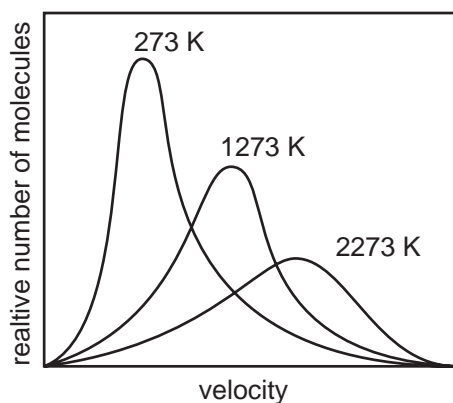
$$N_a(1/2 m \overline{u^2}) = 3/2(RT) \text{ or } \overline{u^2} = \frac{3RT}{N_a m} \text{ so } u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{N_a m}}$$

but m is the mass of one molecule and N_a is Avogadro's number, so $N_a m = M$, the molar

mass, so $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ $R = 8.3145 \text{ J/mol K}$ $1 \text{ J} = 1 \text{ kg m}^2/\text{sec}^2$

Calculate u_{rms} for NH_3 at 25°C

$$u_{\text{rms}} = \sqrt{\frac{3(8.3145 \text{ J/mol K})(298 \text{ K})}{(17.03 \text{ g/mol})(1 \text{ kg}/1000 \text{ kg})}} = 660 \text{ m/sec}$$



Mean free path: distance a molecule travels between collisions. A molecule may travel very fast but not in a straight line.

At a given T, there will be a distribution of molecular velocities around the u_{rms} . As T increases the distribution shifts to the right but at any given T there will be both very fast and very slow molecules.

Effusion and Diffusion (211)

Effusion (212): rate at which a gas passes through an orifice into an evacuated chamber

Graham's Law of Effusion:
$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}}$$

by the kinetic molecular model,

$$\frac{R_1}{R_2} = \frac{u_{\text{rms}} \text{ for gas 1}}{u_{\text{rms}} \text{ for gas 2}} = \frac{\sqrt{\frac{3RT}{M_1}}}{\sqrt{\frac{3RT}{M_2}}} = \sqrt{\frac{M_2}{M_1}}$$

Diffusion (213): rate at which two gases mix. Diffusion obeys the same law as effusion.

How much faster than $^{238}\text{UF}_6$ (235.04) does $^{235}\text{UF}_6$ (238.05) diffuse?

$$\frac{R_{(235)}}{R_{(238)}} = \sqrt{\frac{M_{(238)}}{M_{(235)}}} = \sqrt{\frac{352.05}{349.04}} = 1.004$$

Real Gases (214)

Gases deviate from ideal behavior at high pressure or low temperature, and approach ideal behavior at low P and high T

1873 van der Waals equation corrects for non-ideal behavior

$$P = \frac{nRT}{V}$$

adjust for actual volume of gas molecules

$$P' = \frac{nRT}{V - nb} \quad \text{where } b \text{ is a constant for a given gas}$$

next, adjust for intermolecular attractive forces, which tend to reduce pressure

$$P_{\text{obs}} = (P' - \text{correction factor}) = \left(\frac{nRT}{V - nb} - \text{correction factor}\right)$$

where the correction factor has the form $a\left(\frac{n}{V}\right)^2$, therefore

$$P_{\text{obs}} = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \quad \text{or}$$

$$\left(P_{\text{obs}} + a\left(\frac{n}{V}\right)^2\right) \times \frac{nRT}{V - nb} = nRT$$

see table 5.3, pg 217 for van der Waals constants for various gases