

In the early 1800's after the publication of Dalton's theory and based on numerous experiments of his own and of others, Avogadro proposed the following:

**At the same temperature and pressure, equal volumes of all gases contain the same number of molecules.**

We now know this to be true but at that time this was a revolutionary idea and it took about 50 years before Avogadro's hypothesis was accepted.

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An implication of what is now called Avogadro's Law is that at fixed temperature and pressure the volume of a gas is proportional to the number of moles of the gas.

This can be expressed as

$$V \propto n \quad \text{or} \quad V = a n$$

where n is the number of moles of gas

This implies that if we have two different volumes of gas ( $V_1$  and  $V_2$ ,  $V_2 > V_1$ ) and they are at the same temperature and pressure, the larger volume has more molecules.

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

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

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

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At a given temperature and pressure, one can find the volume that will be occupied by one mole of any gas. It has been shown that at STP the volume is 22.414 L. (Note Table 5.4 on p195 in the text shows that no one common gas has a molar volume of this value.)

The gases we are dealing with are "ideal" as opposed to real. The "P-V-T-n" properties of real gases deviate from those predicted by Boyle's, Charles' and Avogadro's Laws (e.g., they condense to liquids). Some real gases are nearly ideal others show significant deviations from ideality.

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So far we have discussed

Boyle's Law  $V \propto 1/P$  (n, T constant)

Charles Law  $V \propto T$  (n, P constant)

Avogadro's Law  $V \propto n$  (P, T constant)

Combined Gas Law  $PV \propto T$  (n constant)

It requires only a small amount of math to show that

$$V \frac{nT}{P} \quad \text{or} \quad PV = nT$$

which can also be written

$$PV = nRT$$

where R is a constant.

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$$PV = nRT$$

Is called the Ideal Gas Equation since it shows the "P-V-T-n" relations for an ideal gas.

R can be calculated from  $R = \frac{PV}{nT}$  since we know

$V = 22.414$  L when  $P = 1$  atm,  $T = 273.15$  K and  $n = 1$

$$R = \frac{1 \text{ atm} \times 22.414 \text{ L}}{1 \text{ mol} \times 273.15 \text{ K}} = 0.082057 \frac{\text{L} \cdot \text{atm}}{\text{mol K}}$$

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R can have many units since as we have seen there are several units for P and V.

The Gas Constant, as "R" is called, is a term which appears very frequently in chemical equations, definitions, and calculations. Although the R-value we calculated is very useful for gas P, V, n, T calculations, different R values will appear in other areas which we will study later this term. One area called "Thermodynamics" involves energy, temperature, and system changes (such as chemical reactions) for which the R used is

$$R = \frac{101325 \text{ Pa} \times 22.414 \text{ L}}{1 \text{ mol} \times 273.15 \text{ K}} = 8.3144 \frac{\text{J}}{\text{mol K}}$$

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The pascal is a derived unit which is the same as a Newton/m<sup>2</sup>.

The Joule is another derived unit which is the same as a Newton • m.

The liter is a derived unit which is the same as 10<sup>-6</sup> m<sup>3</sup>.

Note that if we multiply Pa • L, it is the same, in terms of units, as

$$\text{Pa} \cdot \text{L} = \frac{\text{N}}{\text{m}^2} \times \text{m}^3 = \text{N} \cdot \text{m} = \text{J}$$

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The Ideal Gas Equation can be written to correspond to

Boyle's Law  $PV = nRT = k$ ; n, T constant

Charles' Law  $\frac{V}{T} = \frac{nR}{P} = k'$ ; n, P are constant

Avogadro's Law  $\frac{V}{n} = \frac{RT}{P} = k''$ ; T, P constant

Gay-Lussac's Law  $\frac{P}{T} = \frac{nR}{V} = k'''$ ; n, V constant

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One more thing about gases, especially ideal gases.

Gases usually exist as the smallest stable particles of a substance, i.e., as molecules or atoms.

Such particles are in constant, rapid motion.

They frequently collide with each other. We assume that the collisions are perfectly elastic and that there are not attractive forces between particles

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What is pressure? We know how to measure it but what is it?

As gas particles move they collide with each other but also with the walls of the container.

When a particle strikes a wall it changes direction and in doing so it exerts a force on the wall. Although the force of one molecule or atom is vanishingly small - with  $N_A$  particles the force becomes easily measurable.

The sum of all these forces make up the pressure.

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Consider now, that we mix two different ideal gases - gas A and gas B. Since there are no attractions the particles behave independently, they just move and collide.

The number of collisions that each gas has with the walls (its pressure) is determined by the number of particles of that gas present. Thus, each gas in a mixture exerts its own pressure independent from other gases.

The total pressure is the sum of the pressures of the individual gases.

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That last sentence “The total pressure is the sum of the pressures of the individual gases.” is important to understanding ideal gases and is called Dalton’s Law of Partial Pressures.

In our atmosphere composed mostly of N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>, and gaseous H<sub>2</sub>O each gas exerts its own pressure. While the percentage of the first four components is nearly constant (CO<sub>2</sub> is slowly increasing) the pressure of water vapor is quite variable from day to day and place to place.

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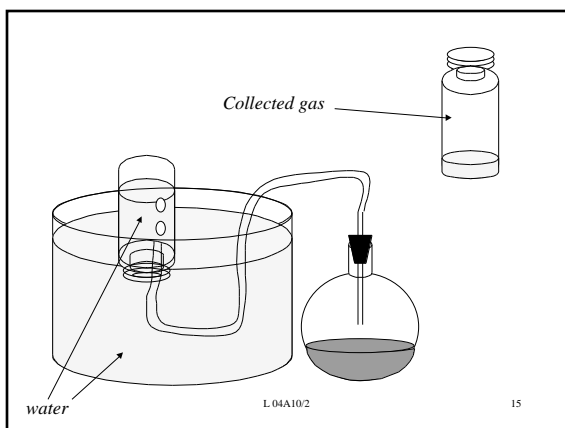
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The amount of water vapor the air can hold is determined by the temperature - warm air holds more water than cold. The maximum pressure of water vapor varies with temperature. The fraction of the maximum water vapor actually present is called the humidity. Given sufficient time for liquid water in contact with the air to evaporate the humidity would be 100% and the pressure of water vapor its maximum.

Often we collect samples of gas over water, which is really a displacement of water.

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In the bottle, the total pressure equals the barometric pressure. What is the pressure of the collected gas?

Since water vapor is present,



$$P_{\text{total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}}$$

$$P_{\text{H}_2\text{O}} = f(T)$$

Temp, °C	P <sub>v</sub> torr
19	26.5
20	17.5
21	18.6
22	19.8
23	21.1
24	22.4
25	23.8
26	25.2
27	26.7
28	28.4

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The Ideal Gas Equation is essential for many gas problems, however, the old gas laws i.e., Boyle’s, Charles’ and the combined equation are more useful for calculating the new state if just one or two parameters, P, V, or T are changed.

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For a given volume of gas, if we know its pressure and temperature we can calculate n, the number of moles of gas.

since  $n = \frac{m}{MW}$  the IGE becomes  $PV = \frac{mRT}{MW}$

$$MW = \frac{mRT}{PV} \quad m = \frac{MW \cdot PV}{RT}$$

We can determine the molecular weight of gaseous substances from mass and P, V, T data.

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### Application of the Ideal Gas Equation

Find mass and/or moles of gas given P, V, and T

A cylinder has a 20 L volume of N<sub>2</sub> at 20 °C the pressure is 70 atm., what mass of N<sub>2</sub> is present?

$$m = \frac{MW \cdot PV}{RT} = \frac{28.0 \frac{\text{g}}{\text{mol}} \cdot 70 \text{ atm} \cdot 20 \text{ L}}{0.08205 \frac{\text{L atm}}{\text{mol K}} \cdot 293 \text{ K}}$$

$$= 1630 \text{ g of N}_2 \text{ or } 1.63 \text{ kg of N}_2$$

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Find molecular weight given P, V, T, and the mass of gas.

A few grams of a pure liquid is added to a 500 mL volumetric flask whose empty weight, with stopper, is 68.3874 g. The flask was placed on a 50 °C water bath and when the liquid has vaporized completely (i.e., no liquid remained) the flask is stoppered, cooled to room temperature, and weighed. The flask filled with the vapor of the liquid weighed 69.7854 g. The barometric pressure was 722 mm Hg. (Assume the pressure of the vapor in the flask is the prevailing atmospheric pressure.)

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$$MW = \frac{mRT}{PV}$$

$$m = 69.7854 - 68.3874 = 1.3980 \text{ g}$$

$$T = 273 + 50 = 323$$

$$P = 722/760 = 0.95 \text{ atm}$$

$$V = 500 \text{ mL} \cdot 1 \text{ L}/1000 \text{ mL} = 0.500 \text{ L}$$

$$MW = \frac{1.3980 \text{ g} \cdot 0.08205 \frac{\text{L atm}}{\text{mol K}} \cdot 323 \text{ K}}{0.950 \text{ atm} \cdot 0.500 \text{ L}} = 78.0 \frac{\text{g}}{\text{mol}}$$

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150 mL of a gas is collected over water. The temperature is 24 °C and the barometric pressure is 745 mm Hg. How many moles of gas have been collected?

$$P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{gas}} \quad P_{\text{H}_2\text{O at } 24^\circ\text{C}} = 22.4 \text{ mm Hg}$$

$$P_{\text{gas}} = 745 - 22.4 = 722.6 \text{ mm Hg}$$

$$722.6 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.951 \text{ atm}$$

$$T = 24 + 273 = 297 \quad 150 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.150 \text{ L}$$

$$n = \frac{PV}{RT} = \frac{0.951 \text{ atm} \times 0.150 \text{ L}}{0.08205 \frac{\text{L atm}}{\text{mol K}} \times 297 \text{ K}} = 0.00585 \text{ mol}$$

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How many molecules are in a 1.00 L container of gaseous oxygen if the pressure is  $2.50 \times 10^9$  torr and the temperature is 1225 K?

V	1	Liters
P	$2.50 \times 10^9$	torr
P	$3.29 \times 10^{-12}$	atm
T	1225	K
R	0.08206	L atm mol <sup>-1</sup> K <sup>-1</sup>
m	$3.27 \times 10^{-14}$	mol
N <sub>A</sub>	$6.02 \times 10^{23}$	molecules/mol
	$1.97 \times 10^{10}$	molecules

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