

GASES

A Gas

- ☐ Uniformly fills any container.
- ☐ Mixes completely with any other gas
- ☐ Exerts pressure on its surroundings.

Pressure

- Force exerted per unit area of surface by molecules in motion.

$$P = \text{Force/unit area}$$

- 1 atmosphere = 14.7 psi
- 1 atmosphere = 760 mm Hg (see Fig. 5.2)
- 1 atmosphere = 101,325 Pascals
- 1 Pascal = 1 kg/m·s²

Figure 5.2: A torricellian barometer. The tube, completely filled with mercury, is inverted in a dish of mercury.

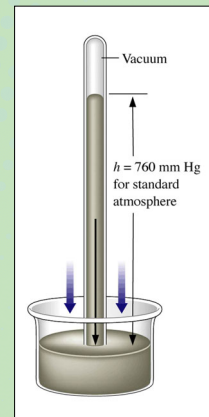


Figure 5.3:
Atmospheric pressure from air

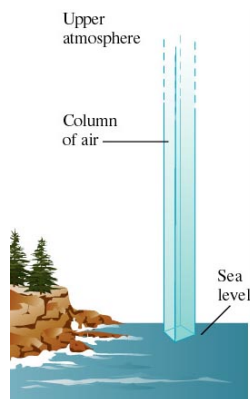
mass.

$$P = gdh$$

To compare the height of Hg and H₂O columns at 1 atm pressure: Both = 1 atm, so

$$gd_{\text{water}}h_{\text{water}} = gd_{\text{Hg}}h_{\text{Hg}}, \text{ or}$$

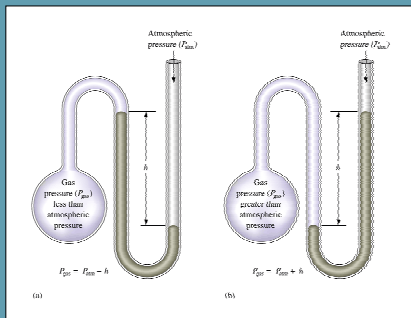
$$(h_{\text{water}}/h_{\text{Hg}}) = (d_{\text{Hg}}/d_{\text{water}})$$



Pressure

- ☐ is equal to force/unit area
- ☐ SI units = Newton/meter² = 1 Pascal (Pa)
- ☐ 1 standard atmosphere = 101,325 Pa
- ☐ 1 standard atmosphere = 1 atm =
760 mm Hg = 760 torr

Figure 5.3: A simple manometer.



Boyle's Law*

Pressure \times Volume = Constant ($T = \text{constant}$)

$$P_1 V_1 = P_2 V_2 \quad (T = \text{constant})$$

$$V \propto 1/P \quad (T = \text{constant})$$

(*Holds *precisely* only at very low pressures.)

As pressure increases, the volume of SO_2 decreases.

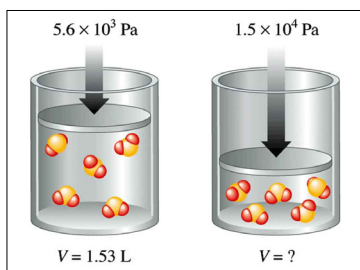


TABLE 5.1 Actual Data from Boyle's Experiment

Volume (in ³)	Pressure (in Hg)	Pressure \times Volume (in Hg \times in ³)
117.5	12.0	14.1×10^2
87.2	16.0	14.0×10^2
70.7	20.0	14.1×10^2
58.8	24.0	14.1×10^2
44.2	32.0	14.1×10^2
35.3	40.0	14.1×10^2
29.1	48.0	14.0×10^2

Figure 5.4: A J-tube similar to the one used by Boyle.

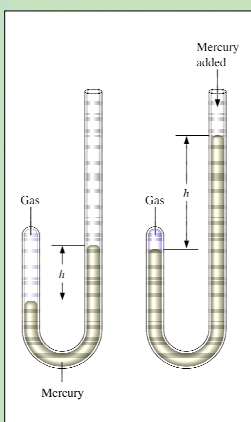
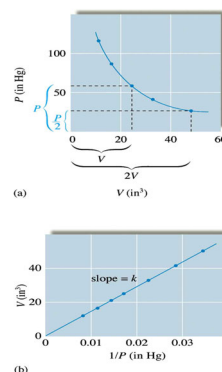


Figure 5.5: Plotting Boyle's data from Table 5.1. (a) A plot of P versus V shows that the volume doubles as the pressure is halved. (b) A plot of V versus $1/P$ gives a straight line. The slope of this line equals the value of the constant k .

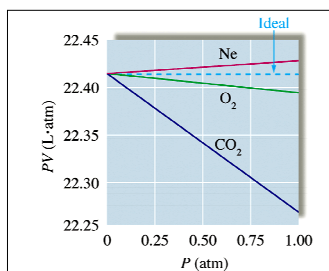


A gas that strictly obeys Boyle's Law is called an ideal gas.

Table 5.3
Pressure–Volume Data for 1.000 g O₂ at 0°C

	<i>P</i> (atm)	<i>V</i> (L)	<i>PV</i>
Increasing pressure ↓	0.2500	2.801	0.7002
	0.5000	1.400	0.7000
	0.7500	0.9333	0.7000
	1.000	0.6998	0.6998
	2.000	0.3495	0.6990
↑ Increasing volume	3.000	0.2328	0.6984
	4.000	0.1744	0.6976
	5.000	0.1394	0.6970

Figure 5.6: A plot of *PV* versus *P* for several gases at pressures below 1 atm.



A Problem to Consider

- A sample of chlorine gas has a volume of 1.8 L at 1.0 atm. If the pressure increases to 4.0 atm (at constant temperature), what would be the new volume?

using $P_f \times V_f = P_i \times V_i$

$$V_f = \frac{P_i \times V_i}{P_f} = \frac{(1.0 \text{ atm}) \times (1.8 \text{ L})}{(4.0 \text{ atm})}$$

$$V_f = 0.45 \text{ L}$$

Charles's Law

The volume of a gas is directly proportional to temperature, and extrapolates to zero at zero Kelvin.

$$V = bT \quad (P = \text{constant})$$

b = a proportionality constant

Figure 5.7: Effect of temperature on a volume of gas. (A)

Photo courtesy of James Scherer.

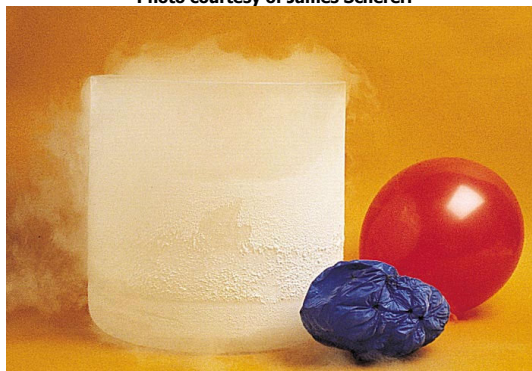
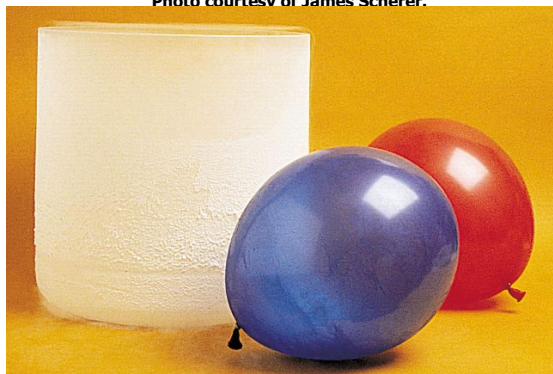


Figure 5.7: Effect of temperature on a volume of gas. (B)

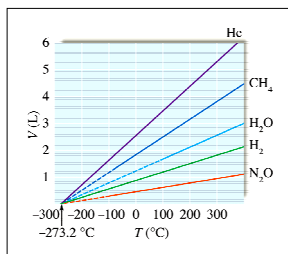
Photo courtesy of James Scherer.



Charles's Law

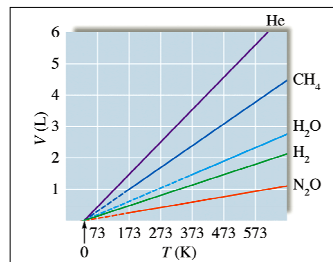
$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (P = \text{constant})$$

Figure 5.8: Plots of V versus T ($^{\circ}\text{C}$) for several gases.



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Figure 5.9: Plots of V versus T as in Fig. 5.8 except here the Kelvin scale is used for temperature.



A Problem to Consider

- A sample of methane gas that has a volume of 3.8 L at 5.0 $^{\circ}\text{C}$ is heated to 86.0 $^{\circ}\text{C}$ at constant pressure. Calculate its new volume.

using $\frac{V_f}{T_f} = \frac{V_i}{T_i}$

$$V_f = \frac{V_i \times T_f}{T_i} = \frac{(3.8\text{L})(359\text{K})}{(278\text{K})}$$

$$V_f = 4.9 \text{ L}$$

The Empirical Gas Laws

- Gay-Lussac's Law:** *The pressure exerted by a gas at constant volume is directly proportional to its absolute temperature.*

$$P \propto T_{\text{abs}} \quad (\text{constant moles and } V)$$

or

$$\frac{P_f}{T_f} = \frac{P_i}{T_i} \quad \text{At constant } n$$

A Problem to Consider

- An aerosol can has a pressure of 1.4 atm at 25 °C. What pressure would it attain at 1200 °C, assuming the volume remained constant?

using $\frac{P_f}{T_f} = \frac{P_i}{T_i}$

$$P_f = \frac{P_i \times T_f}{T_i} = \frac{(1.4 \text{ atm})(1473 \text{ K})}{(298 \text{ K})}$$
$$P_f = 6.9 \text{ atm}$$

CONCEPT CHECK 5.2

To conduct some experiments, a 10.0-L flask equipped with a movable plunger, as illustrated here, is filled with enough H₂ gas to come to a pressure of 20 atm.



- In the first experiment, we decrease the temperature in the flask by 10°C and then increase the volume. Predict how the pressure in the flask changes during each of these events and, if possible, how the final pressure compares to your starting pressure.
- Once again we start with the pressure in the flask at 20 atm. The flask is then heated 10°C followed by a volume decrease. Predict how the pressure in the flask changes during each of these events and, if possible, how the final pressure compares to your starting pressure.

- A. Pressure will decrease and will be lower than P_i
B. Pressure will increase and will be higher than P_i

Avogadro's Law

For a gas at constant temperature and pressure, the volume is directly proportional to the number of moles of gas (at low pressures).

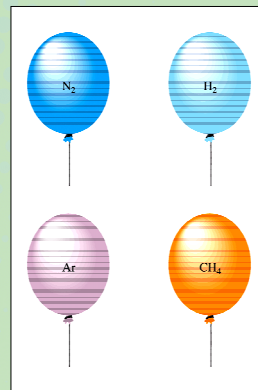
$$V = an$$

a = proportionality constant

V = volume of the gas

n = number of moles of gas

Figure 5.10:
These balloons each hold 1.0L of gas at 25°C and 1 atm. Each balloon contains 0.041 mol of gas, or 2.5 x 10²² molecules.



The Empirical Gas Laws

- Avogadro's Law:** *Equal volumes of any two gases at the same temperature and pressure contain the same number of molecules.*
 - The volume of one mole of gas is called the **molar gas volume**, V_m . (See figure 5.10)
 - Volumes of gases are often compared at standard temperature and pressure (STP), chosen to be 0 °C and 1 atm pressure.

Standard Temperature and Pressure

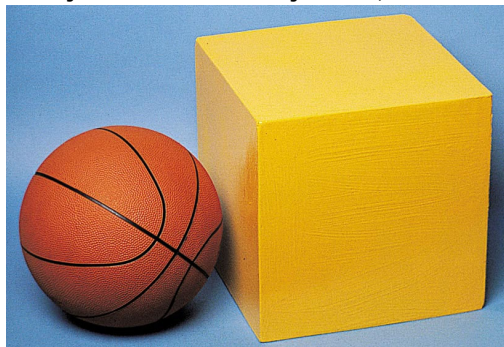
“STP”

$P = 1$ atmosphere

$T = 0^\circ\text{C}$

The molar volume of an ideal gas is 22.414 liters at STP

Figure 5.10: The molar volume of a gas. Photo courtesy of James Scherer.



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Table 5.4
Molar Volumes of Several Gases

Gas	Molar Volume (L) at 0.0°C, 1.00 atm
He	22.40
H ₂	22.43
O ₂	22.39
CO ₂	22.29
NH ₃	22.09
Ideal gas*	22.41

*An ideal gas follows the empirical gas laws.

The Ideal Gas Law

- This implies that there must exist a proportionality constant governing these relationships.
 - Combining the three proportionalities, we can obtain the following relationship.

$$V = "R" \left(\frac{nT_{\text{abs}}}{P} \right)$$

where "R" is the proportionality constant referred to as the **ideal gas constant**.

The Ideal Gas Law

- The numerical value of **R** can be derived using Avogadro's law, which states that one mole of any gas at STP will occupy 22.4 liters.

$$\begin{aligned} R &= \frac{VP}{nT} \\ R &= \frac{(22.4 \text{ L})(1.00 \text{ atm})}{(1.00 \text{ mol})(273 \text{ K})} \\ &= 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \end{aligned}$$

Ideal Gas Law

- 📖 An **equation of state** for a gas.
- 📖 "state" is the condition of the gas at a given time.

$$PV = nRT$$

Ideal Gas Law

$$PV = nRT$$

R = proportionality constant
= 0.08206 L atm K⁻¹ mol⁻¹

P = pressure in atm

V = volume in liters

n = moles

T = temperature in Kelvins

Holds closely at $P < 1$ atm

A Problem to Consider

- An experiment calls for 3.50 moles of chlorine, Cl_2 . What volume would this be if the gas volume is measured at 34 °C and 2.45 atm?

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

then $V = \frac{(3.50 \text{ mol})(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(307 \text{ K})}{2.45 \text{ atm}}$

then $V = 36.0 \text{ L}$

Molecular Weight Determination

- In Chapter 3 we showed the relationship between moles and mass.

$$\text{moles} = \frac{\text{mass}}{\text{molecular mass}}$$

or

$$n = \frac{m}{M_m}$$

Molecular Weight Determination

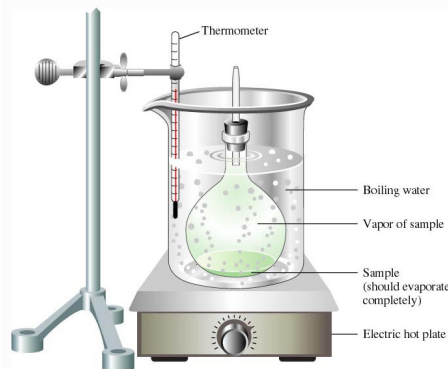
- If we substitute this in the ideal gas equation, we obtain

$$PV = \left(\frac{\text{mass}}{M_m}\right)RT$$

If we solve this equation for the molecular mass, we obtain

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

Figure 5.15: Finding the vapor density of a substance.



A Problem to Consider

- A 15.5 gram sample of an unknown gas occupied a volume of 5.75 L at 25 °C and a pressure of 1.08 atm. Calculate its molecular mass.

Since $M_m = \frac{mRT}{PV}$

then $M_m = \frac{(15.5 \text{ g})(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(298 \text{ K})}{(1.08 \text{ atm})(5.75 \text{ L})}$

$M_m = 61.0 \text{ g/mol}$

Gas Density Determination

- If we look again at our derivation of the molecular mass equation,

$$PV = \left(\frac{m}{M_m}\right)RT$$

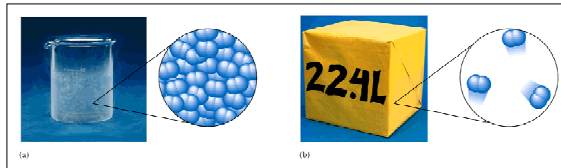
we can solve for m/V , which represents the gas density.

$$\frac{m}{V} = D = \frac{PM_m}{RT}$$

Figure 5.14: (a) One mole of $N_2(l)$ has a volume of approximately 35 mL and density of 0.81 g/mL.

b) One mole of $N_2(g)$ has a volume of 22.4 L (STP) and a density of 1.2×10^{-3} g/mL.

Thus the ratio of the volumes of gaseous N_2 and liquid N_2 is $22.4/0.035 = 640$ and the spacing of the molecules is 9 times farther apart in $N_2(g)$.



A Problem to Consider

- Calculate the density of ozone, O_3 ($M_m = 48.0$ g/mol), at $50^\circ C$ and 1.75 atm of pressure.

Since $D = \frac{PM_m}{RT}$

then $D = \frac{(1.75 \text{ atm})(48.0 \text{ g/mol})}{(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(323 \text{ K})}$

$D = 3.17 \text{ g/L}$

CONCEPT CHECK 5.3

Three 3.0-L flasks, each at a pressure of 878 mmHg, are in a room. The flasks contain He, Ar, and Xe, respectively.

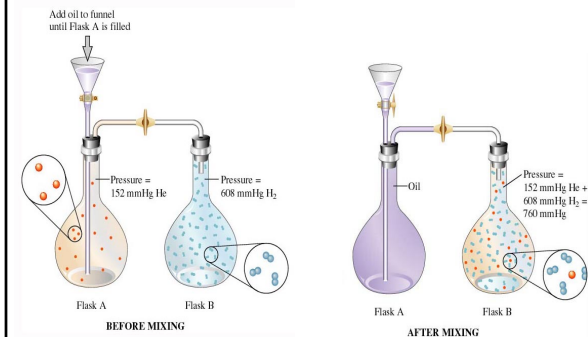
- Which of the flasks contains the most atoms of gas?
 - Which of the flasks has the greatest density of gas?
 - If the He flask was heated and the Ar flask cooled, which of the three flasks would be at the highest pressure?
 - If the temperature of the He was lowered while the Xe was raised, which of the three flasks would have the greatest number of moles of gas?
- A. All have the same number of atoms
 B. The flask with Xe because its M_m is greatest, so mass/V is the largest
 C. The He flask - $(PV/T) = \text{constant}$ If T increases, so must P
 D. All have the same number of moles - we can't create or destroy mass!

Dalton's Law of Partial Pressures

For a mixture of gases in a container,

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

Figure 5.17: An illustration of Dalton's law of partial pressures.



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Collecting Gases "Over Water"

- A useful application of partial pressures arises when you collect gases **over water**.
- As gas bubbles through the water, the gas becomes saturated with water vapor.
- The partial pressure of the water in this "mixture" depends only on the temperature.

Figure 5.18: Collection of gas over water.

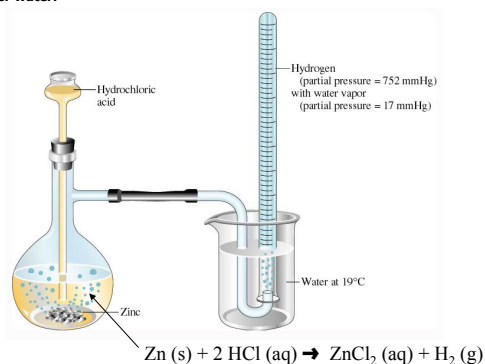


Table 5.6
Vapor Pressure of Water at Various Temperatures

Temperature (°C)	Pressure (mmHg)	Temperature (°C)	Pressure (mmHg)
0	4.6	27	26.7
5	6.5	28	28.3
10	9.2	29	30.0
11		9.8	30.318
12	10.5	35	42.2
13	11.2	40	55.3
14	12.0	45	71.9
15	12.8	50	92.5
16	13.6	55	118.0
17	14.5	60	149.4
18	15.5	65	187.5
19	16.5	70	233.7
20	17.5	75	289.1
21	18.7	80	355.1
22	19.8	85	433.6
23	21.1	90	525.8
24	22.4	95	633.9
25	23.8	100	760.0
26	25.2	105	906.1

A Problem to Consider

- Suppose a 156 mL sample of H₂ gas was collected over water at 19 °C and 769 mm Hg. What is the mass of H₂ collected?
 - First, we must find the partial pressure of the dry H₂.

$$P_{\text{H}_2} = P_{\text{tot}} - P_{\text{H}_2\text{O}}$$

A Problem to Consider

- Suppose a 156 mL sample of H₂ gas was collected over water at 19.5 °C and 769 mm Hg. What is the mass of H₂ collected?
 - Table 5.6 lists the vapor pressure of water at 19 °C as 17.0 mm Hg.

$$P_{\text{H}_2} = 769 \text{ mm Hg} - 17.0 \text{ mm Hg}$$

$$P_{\text{H}_2} = 752 \text{ mm Hg}$$

A Problem to Consider

- Now we can use the ideal gas equation, along with the partial pressure of the hydrogen, to determine its mass.

$$P_{\text{H}_2} = 752 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.989 \text{ atm}$$

$$V = 156 \text{ mL} = 0.156 \text{ L}$$

$$T = (19 + 273) = 292 \text{ K}$$

$$n = ?$$

A Problem to Consider

- From the ideal gas law, $PV = nRT$, you have

$$n = \frac{PV}{RT} = \frac{(0.989 \text{ atm})(0.156 \text{ L})}{(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(292 \text{ K})}$$

$$n = 0.00644 \text{ mol}$$

- Next, convert moles of H₂ to grams of H₂.

$$0.00644 \text{ mol H}_2 \times \frac{2.02 \text{ g H}_2}{1 \text{ mol H}_2} = 0.0130 \text{ g H}_2$$

Figure 5.12:
The partial pressure of each gas in a mixture of gases in a container depends on the number of moles of that gas.

$$P_{\text{total}} = P_A + P_B$$

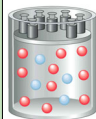
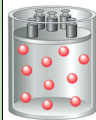
Since $P = (nRT/V)$
we can substitute this into
Dalton's Law.

$$n_{\text{total}}(RT/V) = n_A (RT/V) + n_B (RT/V)$$

Dividing by (RT/V) :

$$n_{\text{total}} = n_A + n_B \text{ or } 1 = (n_A/n_{\text{total}}) + (n_B/n_{\text{total}})$$

Finally, multiplying by P_{total} :
 $P_{\text{total}} = (n_A/n_{\text{total}})P_{\text{total}} + (n_B/n_{\text{total}})P_{\text{total}}$



Partial Pressures of Gas Mixtures

- The composition of a gas mixture is often described in terms of its mole fraction.
- The *mole fraction*, χ , of a component gas is the fraction of moles of that component in the total moles of gas mixture.

$$\chi_A = \text{Mole fraction of A} = \frac{n_A}{n_{\text{tot}}} = \frac{P_A}{P_{\text{tot}}}$$

Partial Pressures of Gas Mixtures

- The partial pressure of a component gas, "A", is then defined as

$$P_A = \chi_A \times P_{\text{tot}}$$

- Applying this concept to the ideal gas equation, we find that each gas can be treated independently.

$$P_A V = n_A RT$$

CONCEPT CHECK 5.4

A flask equipped with a valve contains 3.0 mol of H_2 gas. You introduce 3.0 mol of Ar gas into the flask via the valve and then seal the flask.

- What happens to the pressure of just the H_2 gas in the flask after the introduction of the Ar? If it changes, by what factor does it do so?
- How do the pressures of the Ar and the H_2 in the flask compare?
- How does the total pressure in the flask relate to the pressures of the two gases?

- No change to pressure of hydrogen gas
- They are the same (same V, T & P)
- $P_{\text{total}} = P_{\text{H}_2} + P_{\text{Ar}} = 2 P_{\text{H}_2}$

A Problem to Consider

- Given a mixture of gases in the atmosphere at 760 torr, what is the partial pressure of N_2 ($\chi = 0.7808$) at 25 °C?

$$\text{since } P_{\text{N}_2} = \chi_{\text{N}_2} \times P_{\text{tot}}$$

$$\text{then } P_{\text{N}_2} = (0.7808) \times (760 \text{ torr})$$

$$P_{\text{N}_2} = 593 \text{ torr}$$

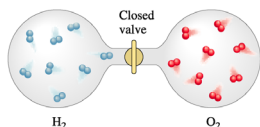
TABLE 5.4
Atmospheric Composition
Near Sea Level (Dry Air)*

Component	Mole Fraction
N_2	0.78084
O_2	0.20948
Ar	0.00934
CO_2	0.000345
Ne	0.00001818
He	0.00000524
CH_4	0.00000168
Kr	0.00000114
H_2	0.0000005
NO	0.0000005
Xe	0.00000087

*The atmosphere contains various amounts of water vapor depending on conditions.

- A. O_2
- B. H_2
- C. Each has the same number of molecules
- D. No change
- E. Mole fraction = $1/4$
so $P_{H_2} = 0.25$ of total P

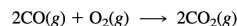
5.27 Consider the following setup, which shows identical containers connected by a tube with a valve that is presently closed. The container on the left has 1.0 mol of H_2 gas; the container on the right has 1.0 mol of O_2 .



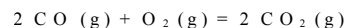
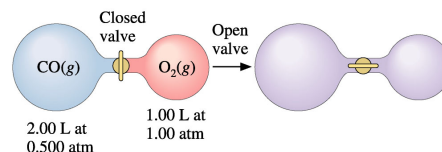
Note: Acceptable answers to some of these questions might be "both" or "neither one."

- Which container has the greatest density of gas?
- Which container has molecules that are moving at a faster average molecular speed?
- Which container has more molecules?
- If the valve is opened, will the pressure in each of the containers change? If it does, how will it change (increase, decrease, or no change)?
- 2.0 mol of Ar is added to the system with the valve open. What fraction of the total pressure will be due to the H_2 ?

5.123 Carbon monoxide, CO, and oxygen, O_2 , react according to



Assuming that the reaction takes place and goes to completion, determine what substances remain and what their partial pressures are after the valve is opened in the apparatus represented in the accompanying figure. Also assume that the temperature is fixed at 300 K.



$$n_{CO} = PV/RT = (0.500)(2.00)/(0.0821)(300) = 0.0406 \text{ mol}$$

$$n_{O_2} = PV/RT = (1.00)(1.00)/(0.0821)(300) = 0.0406 \text{ mol}$$

CO is the limiting reactant

0.0406 mol CO require 0.0203 mole O_2 so that $(0.0406 \text{ mol} - 0.0203 \text{ mol}) = 0.0203 \text{ mol} O_2$ remain.

$$P_{O_2} = nRT/V = \frac{(0.0203)(0.0821)(300)}{3.0 \text{ L}} = 0.167 \text{ atm}$$

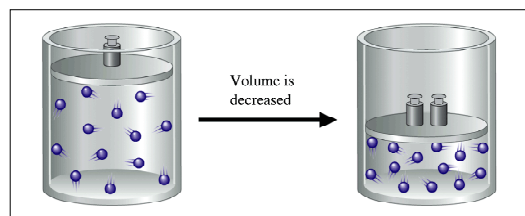
$$P_{CO_2} = nRT/V = \frac{(0.0406)(0.0821)(300)}{3.0 \text{ L}} = 0.334 \text{ atm}$$

$$P_{total} = (0.167 + 0.334) \text{ atm} = 0.501 \text{ atm}$$

Kinetic Molecular Theory

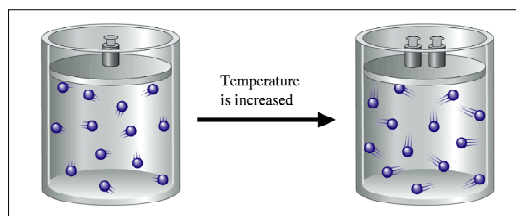
- Volume of individual particles is \approx zero.
- Collisions of particles with container walls cause pressure exerted by gas.
- Particles exert no forces on each other.
- Average kinetic energy \propto Kelvin temperature of a gas.

Figure 5.15: The effects of decreasing the volume of a sample of gas at constant temperature and number of moles.



Boyle's Law
 $V \propto 1/P$

Figure 5.16: The effects of increasing the temperature of a sample of gas at constant volume and number of moles.



Gay-Lussac's Law
 $(P_f/T_f) = (P_i/T_i)$

Figure 5.17: The effects of increasing the temperature of a sample of gas at constant pressure and number of moles.

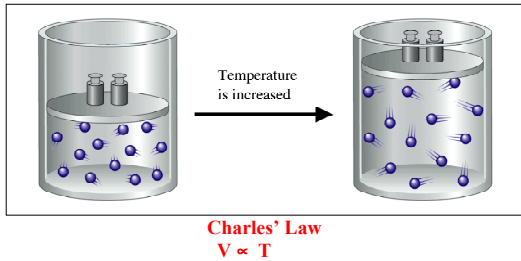


Figure 5.18: The effects of increasing the number of moles of gas particles at constant temperature and pressure.

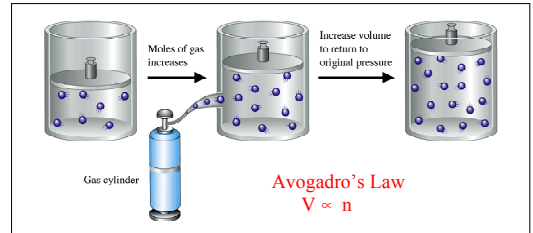


Figure 5.20: A plot of the relative number of O_2 molecules that have a given velocity at STP.

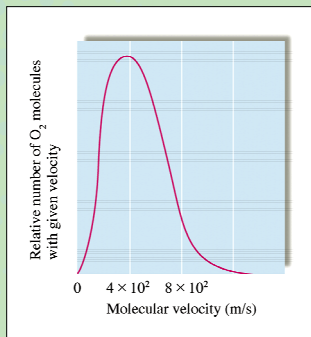


Figure 5.21: A plot of the relative number of N_2 molecules that have a given velocity at three temperatures.

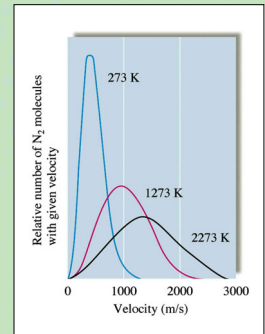
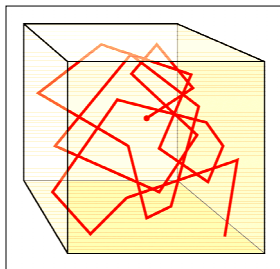


Figure 5.19: Path of one particle in a gas. Any given particle will continuously change its course as a result of collisions with other particles, as well as with the walls of the container.



The Meaning of Temperature

$$(KE)_{avg} = \frac{3}{2} RT$$

Kelvin temperature is an index of the random motions of gas particles (higher T means greater motion.)

Diffusion: describes the mixing of gases. The **rate** of diffusion is the rate of gas mixing.

Effusion: describes the passage of gas into an **evacuated** chamber.

Figure 5.22: The effusion of a gas into an evacuated chamber.

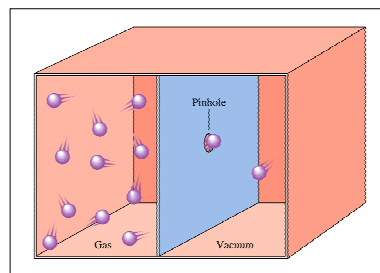


Figure 5.23: Relative molecular speed distribution of H_2 and UF_6 .

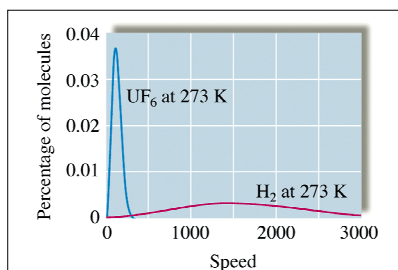
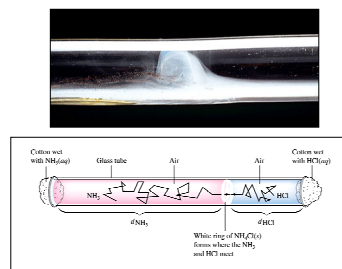
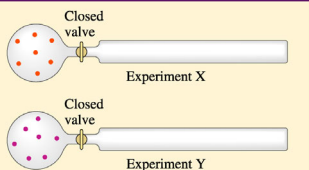


Figure 5.24: (top) When $HCl(g)$ and $NH_3(g)$ meet in the tube, a white ring of $NH_4Cl(s)$ forms. (bottom) A demonstration of the relative diffusion rates of NH_3 and HCl molecules through air.



CONCEPT CHECK 5.5

Consider the experimental apparatus shown. In this setup, each round flask contains a gas and the long tube contains no gas (that is, it is a vacuum).



- A. We use 1.0 mol of He for experiment X and 1.0 mol of Ar for experiment Y. If both valves are opened at the same time, which gas would you expect to reach the end of the long tube first?
 Ans: He - it has a lower molar mass
- B. If you wanted the Ar to reach the end of the tube at the same time as the He, what experimental condition could you change to make this happen?
 Ans: Heat the Ar

Molecular Speeds; Diffusion and Effusion

- According to **Graham's law**, the rate of effusion or diffusion is inversely proportional to the square root of its molecular mass. (See Figure 5.22)

$$\frac{\text{Rate of effusion of gas "A"}}{\text{Rate of effusion of gas "B"}} = \sqrt{\frac{M_m \text{ of Gas B}}{M_m \text{ of gas A}}}$$

A Problem to Consider

- How much faster would H₂ gas effuse through an opening than methane, CH₄?

$$\frac{\text{Rate of H}_2}{\text{Rate of CH}_4} = \sqrt{\frac{M_m(\text{CH}_4)}{M_m(\text{H}_2)}}$$

$$\frac{\text{Rate of H}_2}{\text{Rate of CH}_4} = \sqrt{\frac{16.0 \text{ g/mol}}{2.0 \text{ g/mol}}} = 2.8$$

So hydrogen effuses 2.8 times faster than CH₄

Effusion:

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Diffusion:

$$\frac{\text{Distance traveled by gas 1}}{\text{Distance traveled by gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Figure 5.25: Plots of PV/nRT versus P for several gases (200 K).

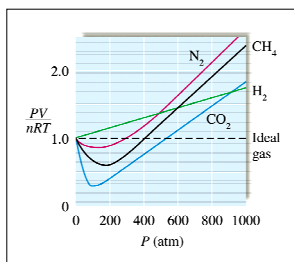


Figure 5.26: Plots of PV/nRT versus P for nitrogen gas at three temperatures.

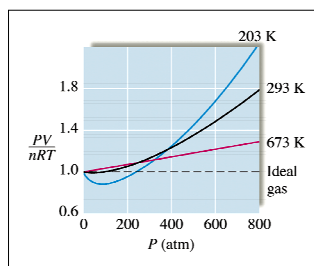


Figure 5.27: (a) Gas at low concentration—relatively few interactions between particles. (b) Gas at high concentration—many more interactions between particles.

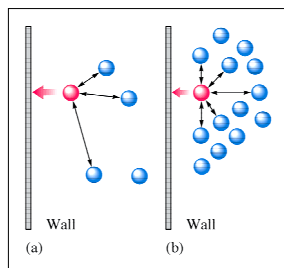


Figure 5.28: Illustration of pairwise interactions among gas particles.

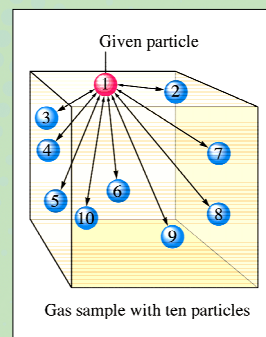
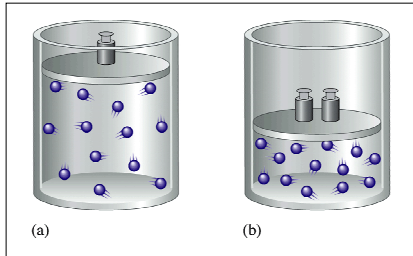


Figure 5.29: The volume taken up by the gas particles themselves is less important at (a) large container volume (low pressure) than at (b) small container volume (high pressure).



Real Gases

$$[P_{\text{obs}} + a(n/V)^2] \times (V - nb) = nRT$$

\uparrow \uparrow
 corrected pressure corrected volume
 $\underbrace{\hspace{10em}}$
 P_{ideal} V_{ideal}

TABLE 5.3
Values of the van der Waals
Constants for Some Common
Gases

Gas	$a \left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \right)$	$b \left(\frac{\text{L}}{\text{mol}} \right)$
He	0.0341	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	1.36	0.0318
Cl ₂	6.49	0.0562
CO ₂	3.59	0.0427
CH ₄	2.25	0.0428
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

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A Problem to Consider

- If sulfur dioxide were an “ideal” gas, the pressure at 0 °C exerted by 1.000 mol occupying 22.41 L would be 1.000 atm. Use the van der Waals equation to estimate the “real” pressure.

Given are the following values for SO₂

$$a = 6.865 \text{ L}^2 \cdot \text{atm} / \text{mol}^2$$

$$b = 0.05679 \text{ L} / \text{mol}$$

A Problem to Consider

- First, let's rearrange the van der Waals equation to solve for pressure.

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$R = 0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}$$

$$T = 273.2 \text{ K} \quad a = 6.865 \text{ L}^2 \cdot \text{atm} / \text{mol}^2$$

$$V = 22.41 \text{ L} \quad b = 0.05679 \text{ L} / \text{mol}$$

A Problem to Consider

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$P = \frac{(1.000 \text{ mol})(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(273.2 \text{ K})}{22.41 \text{ L} - (1.000 \text{ mol})(0.05679 \text{ L} / \text{mol})} - \frac{(1.000 \text{ mol})^2 (6.865 \frac{\text{L}^2 \cdot \text{atm}}{\text{mol}^2})}{(22.41 \text{ L})^2}$$

$$P = 0.989 \text{ atm}$$

- The “real” pressure exerted by 1.00 mol of SO₂ at STP is slightly less than the “ideal” pressure of 1.000 atm.

Real Gases

Must correct ideal gas behavior when at high pressure (smaller volume) and low temperature (attractive forces become important).