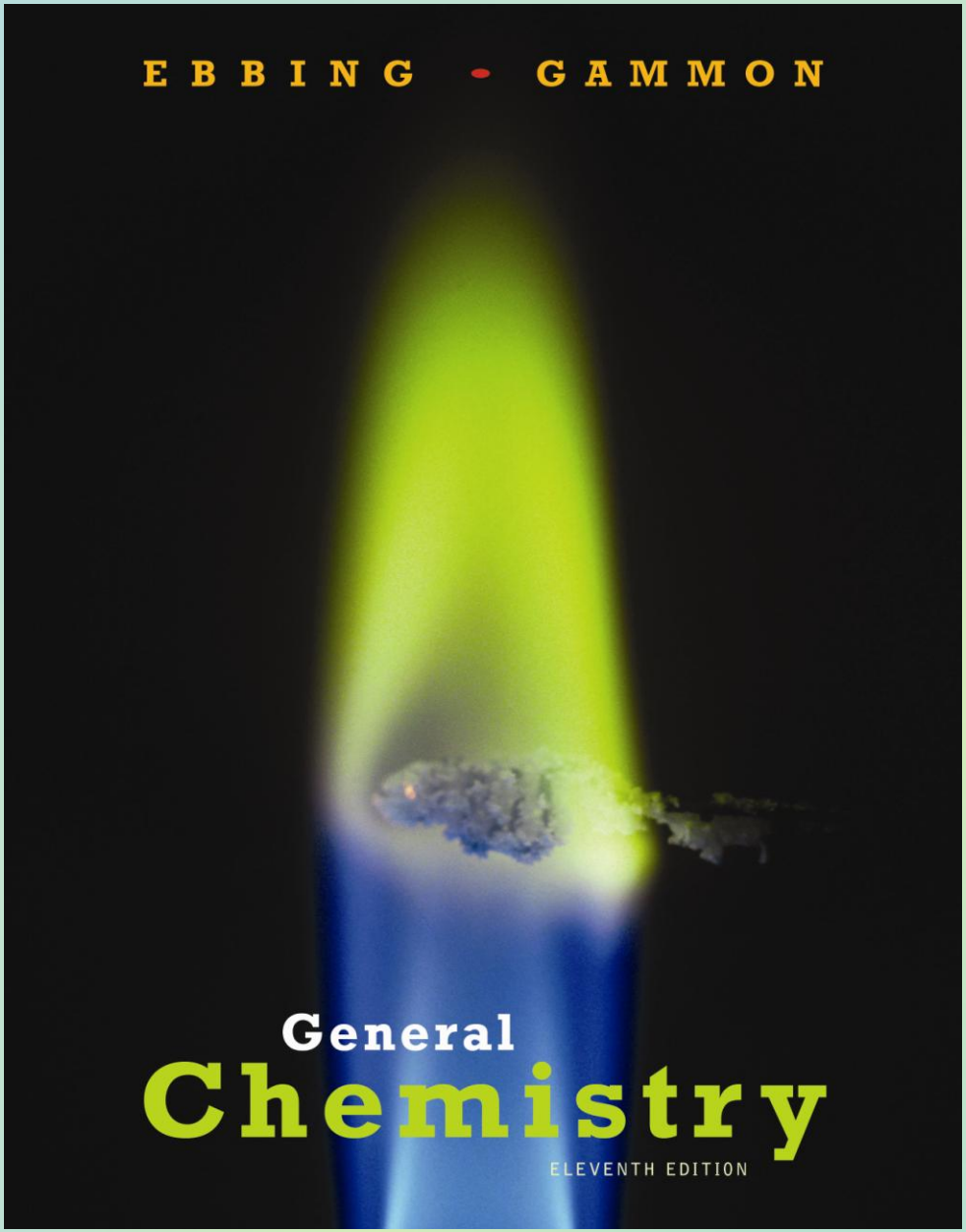


Chapter 5
The Gaseous State

Contents and Concepts

Gas Laws

We will investigate the quantitative relationships that describe the behavior of gases.

- Gas Pressure and Its Measurement
- Empirical Gas Laws
- The Ideal Gas Law
- Stoichiometry Problems Involving Gas Volumes
- Gas Mixtures; Law of Partial Pressures

Kinetic-Molecular Theory

This section will develop a model of gases as molecules in constant random motion.

6. Kinetic Theory of Gases
7. Molecular Speeds; Diffusion and Effusion
8. Real Gases

Learning Objectives

- **Gas Pressure and Its Measurement**
  a. Define *pressure* and its units.
  b. Convert units of pressure.

- **Empirical Gas Laws**
  a. Express Boyle's law in words and as an equation.
  b. Use Boyle's law.
  c. Express Charles's law in words and as an equation.

d. Use Charles's law.
e. Express the combined gas law as an equation.
f. Use the combined gas law.
f. State Avogadro's law.
g. Define *standard temperature and pressure (STP)*.

3. The Ideal Gas Law

a. State what makes a gas an ideal gas.
b. Learn the ideal gas law equation.
c. Derive the empirical gas laws from the ideal gas law.

d. Use the ideal gas law.

e. Calculate gas density.

f. Determine the molecular mass of a vapor.

g. Use an equation to calculate gas density.

4. Stoichiometry Problems Involving Gas Volumes

a. Solve stoichiometry problems involving gas volumes.

5. Gas Mixtures; Law of Partial Pressures

a. Learn the equation for Dalton's law of partial pressures.

b. Define the *mole fraction of a gas*.

c. Calculate the partial pressure and the mole fraction of a gas in a mixture.

d. Describe how gases are collected over water and how to determine the vapor pressure of water.

e. Calculate the amount of gas collected over water.

6. Kinetic Theory of An Ideal Gas

a. List the five postulates of the kinetic theory.

b. Provide a qualitative description of the gas laws based on the kinetic theory.

7. Molecular Speeds; Diffusion and Effusion

a. Describe how the root-mean square (rms) molecular speed of gas molecules varies with temperature.

b. Describe the molecular-speed distribution of gas molecules at different temperatures.

c. Calculate the rms speed of a molecule.

d. Define *effusion* and *diffusion*.

e. Describe how individual gas molecules move while undergoing diffusion.

f. Calculate the ratio of effusion rates of gases.

8. Real Gases

a. Explain how and why a real gas is different from an ideal gas.

b. Use the van der Waals equation.

Gases differ from liquids and solids:

- They are compressible.
- Pressure, volume, temperature, and amount are related.

Pressure

The force exerted per unit area of surface.

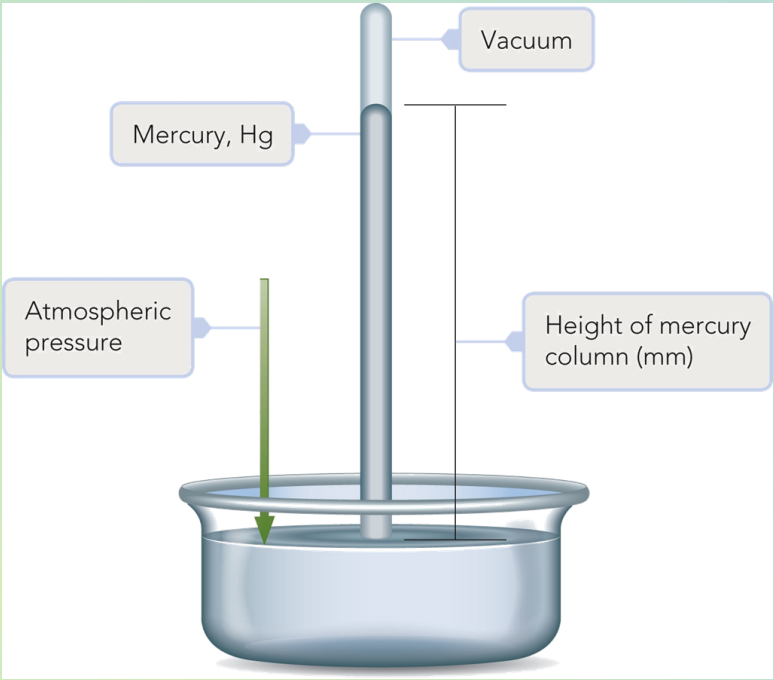
Pascal

The SI unit for pressure; $kg/(m \cdot s^2)$.

Table 5.2 Important Units of Pressure

Unit	Relationship or Definition
Pascal (Pa)	$kg/(m \cdot s^2)$
Atmosphere (atm)	$1\ atm = 1.01325 \times 10^5\ Pa \simeq 101\ kPa$
mmHg, or torr	$760\ mmHg = 1\ atm$
Bar	$1.01325\ bar = 1\ atm$

A **barometer** is a device for measuring the pressure of the atmosphere.



A **manometer** is a device for measuring the pressure of a gas or liquid in a vessel.

Other units used to measure pressure

Millimeters of mercury (mmHg); also called the **torr**

Atmosphere (atm)

Relationship between the pressure *P* and the height *h* of a liquid*:*

$$P = gdh$$

g = constant acceleration of gravity (9.81 m/s^2)

d = density of the liquid in the manometer

Suppose that you set up two barometers like the one shown in Figure 5.2. In one of the barometers you use mercury, and in the other you use water. Which of the barometers would have a higher column of liquid, the one with Hg or H_2O? Explain your answer.

The water column would be higher because its density is less by a factor equal to the density of mercury to the density of water.

Empirical Gas Laws

All gases behave quite simply with respect to temperature, pressure, volume, and molar amount. By holding two of these physical properties constant, it becomes possible to show a simple relationship between the other two properties.

The studies leading to the empirical gas laws occurred from the mid-17th century to the mid-19th century.

Boyle's Law

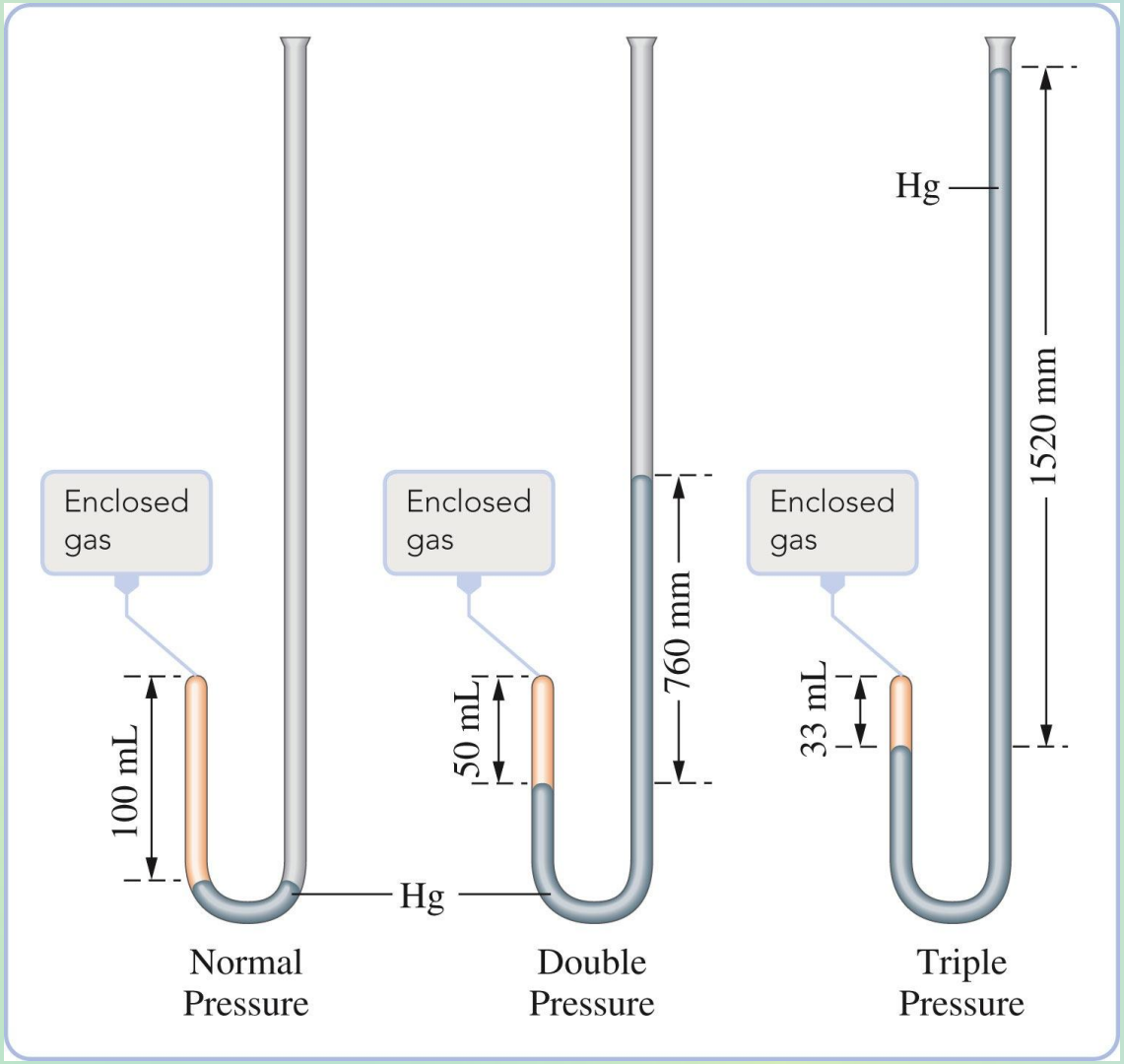
The volume of a sample of gas at constant temperature varies inversely with the applied pressure.

The mathematical relationship: $V \propto \frac{1}{P}$

In equation form: $PV = \text{constant}$

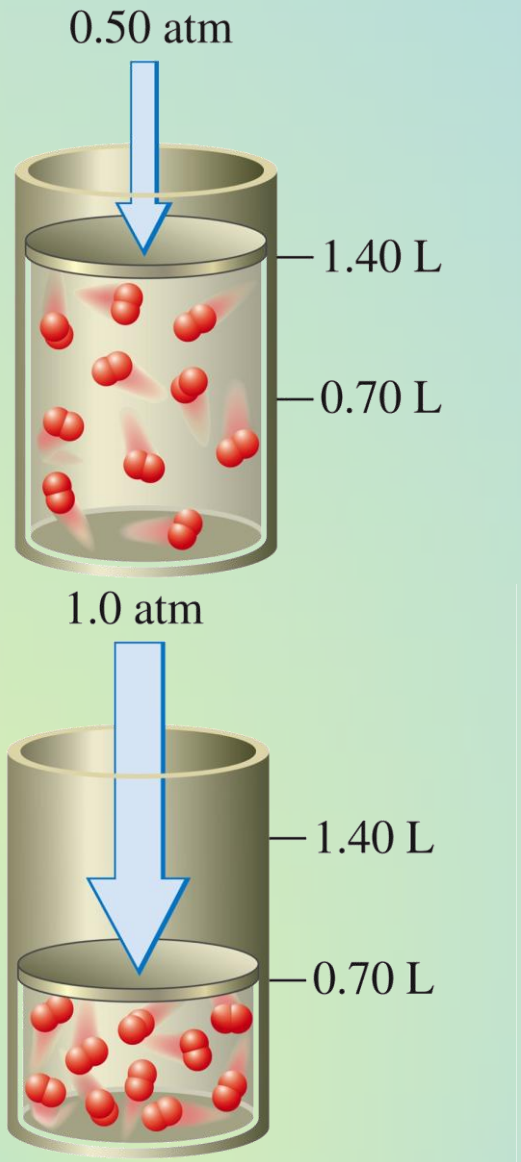
$$P_f V_f = P_i V_i$$

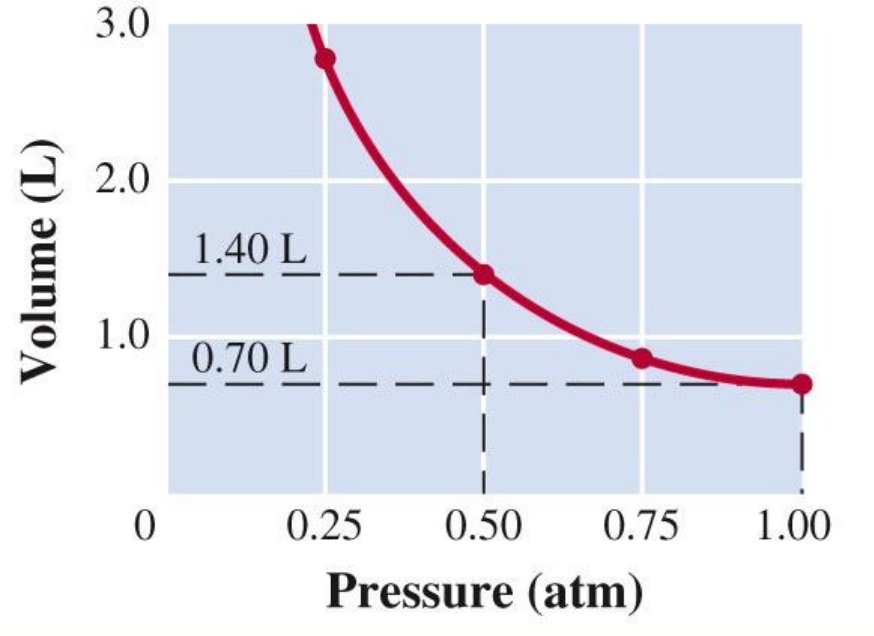
At normal atmospheric pressure, the volume of the gas is 100 mL. When pressure is doubled, the volume is halved. When pressure is tripled, the volume decreases to one-third.

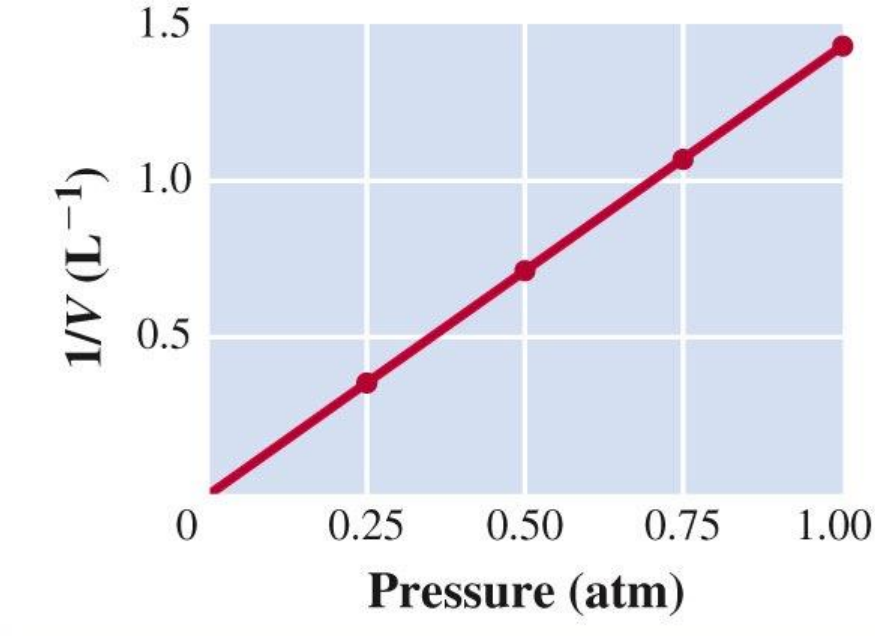


When a 1.00-g sample of O_2 gas at 0°C is placed in a container at a pressure of 0.50 atm, it occupies a volume of 1.40 L.

When the pressure on the O_2 is doubled to 1.0 atm, the volume is reduced to 0.70 L, half the original volume.







Plot of volume vs. pressure for a sample of oxygen.

Plot of 1/V vs. pressure for the same sample.

A volume of air occupying 12.0 dm^3 at 98.9 kPa is compressed to a pressure of 119.0 kPa. The temperature remains constant. Determine the new volume.

$V_i = 12.0\ dm^3$ $\quad V_f = ?$

$P_i = 98.9\ kPa$ $\quad P_f = 119.0\ kPa$

$$V_f = \frac{P_i V_i}{P_f}$$

$$V_f = V_i \times \frac{P_i}{P_f} = 12.0\ dm^3 \times \frac{98.9\ \cancel{kPa}}{119.0\ \cancel{kPa}} = 9.97\ dm^3$$

Charles's Law

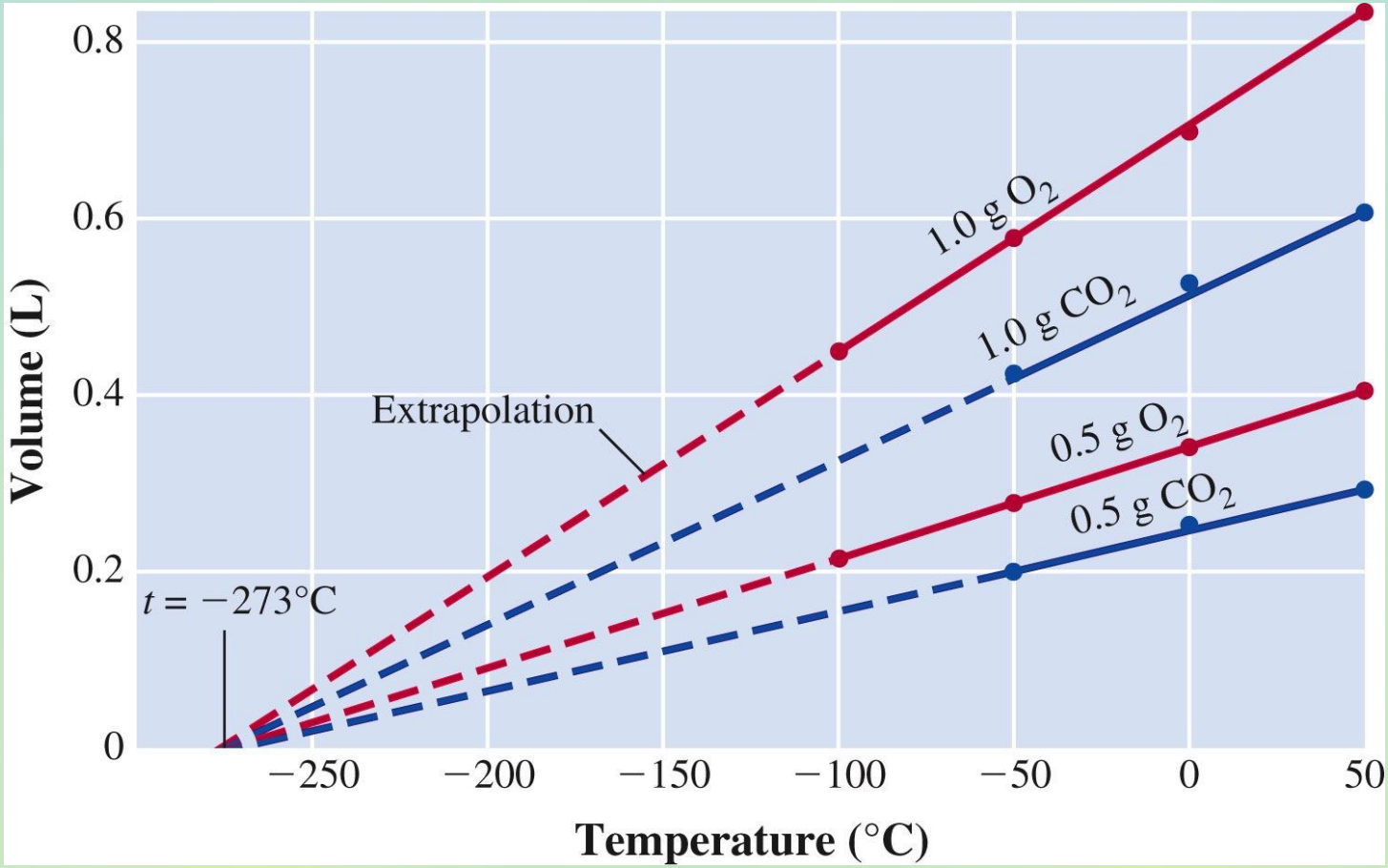
The volume of a sample of gas at constant pressure is directly proportional to the absolute temperature (K).

In equation form: $\frac{V}{T} = \text{constant}$

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

A balloon was immersed in liquid nitrogen (black container) and is shown immediately after being removed. It shrank because air inside contracts in volume.

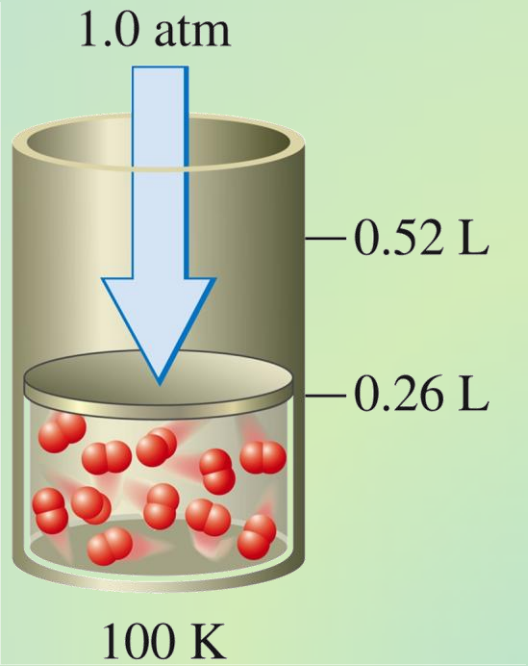
As the air inside warms, the balloon expands to its original size.

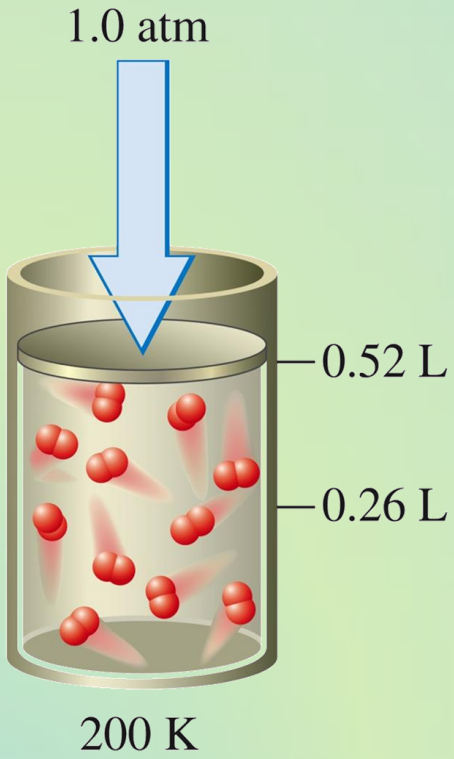


A graph of *V* versus *T* is linear. Note that all lines cross zero volume at the same temperature, −273°C.

A 1.0-g sample of O_2 at 100 K and 1.0 atm of pressure occupies a volume of 0.26 L.

When the absolute temperature of the gas is doubled to 200 K, the volume of O_2 doubles to 0.52 L.





Combined Gas Law

The volume of a certain amount of gas at constant pressure is proportional to the absolute temperature divided by the pressure.

The mathematical relationship: $V \propto \frac{T}{P}$

In equation form: $\frac{PV}{T} = \text{constant}$

$$\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i}$$

According to the Dumas method of determining %N in an organic compound, 39.8 mg of caffeine gives 10.1 cm^3 of nitrogen gas at 23°C and 746 mmHg. Determine the volume of nitrogen at 0°C and 760mmHg.

$$T_i = (23 + 273)\ \text{K} = 296\ \text{K}$$

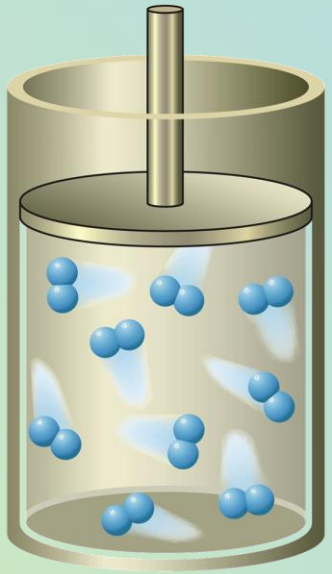
$$T_f = (0 + 273)\ \text{K} = 273\ \text{K}$$

$$V_i = 10.1\ \text{cm}^3 \quad P_i = 746\ \text{mmHg} \quad T_i = 296\ \text{K}$$

$$V_f = ? \quad P_f = 760\ \text{mmHg} \quad T_f = 273\ \text{K}$$

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i} = 10.1\ \text{cm}^3 \times \frac{746\ \cancel{\text{mmHg}}}{760\ \cancel{\text{mmHg}}} \times \frac{273\ \cancel{\text{K}}}{296\ \cancel{\text{K}}} = 9.14\ \text{cm}^3$$

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 H_2 gas to come to a pressure of 20 atm.

a. 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.

b. 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. Decreasing the temperature at a constant pressure results in a decrease in volume. Subsequently increasing the volume at a constant temperature results in a decrease in pressure.

b. Increasing the temperature at a constant pressure results in an increase in volume. Subsequently decreasing the volume at a constant temperature results in an increase in pressure.

Avogadro's Law

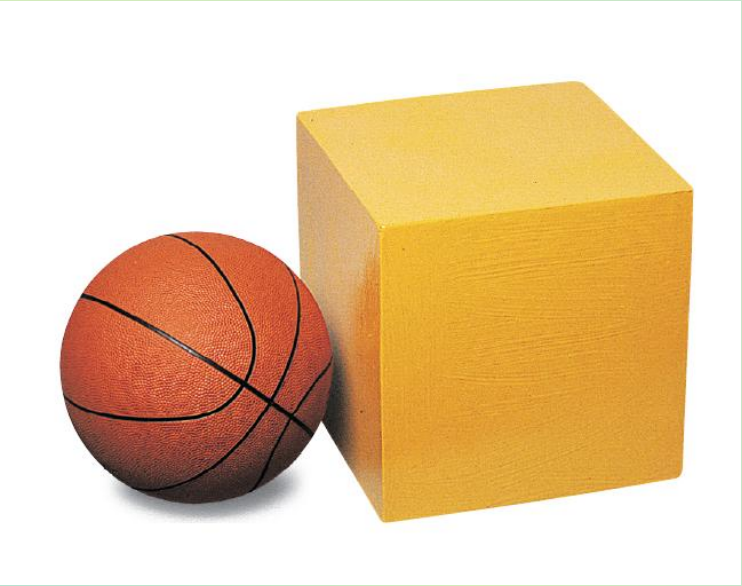
Equal volumes of any two gases at the same temperature and pressure contain the same number of molecules.

Standard Temperature and Pressure (STP)

The reference conditions for gases chosen by convention to be exactly 0°C and 1 atm pressure.

The molar volume of a gas at STP is 22.4 L/mol.

The volume of the yellow box is 22.4 L. To its left is a basketball.



Ideal Gas Law

The ideal gas law is given by the equation

$$PV = nRT$$

The **molar gas constant, R**, is the constant of proportionality that relates the molar volume of a gas to *T*/*P*.

Table 5.5 Molar Gas Constant in Various Units

Value of *R*
0.082058 L·atm/(K·mol)
8.3145 J/(K·mol)*
8.3145 kg·m^2/(s^2·K·mol)
8.3145 kPa·dm^3/(K·mol)
1.9872 cal/(K·mol)*

*The units of pressure times volume are the units of energy—for example, joules (J) or calories (cal).

Prove the following statement: the pressure of a given amount of gas at a fixed volume is proportional to the absolute temperature. This is sometimes called Amontons' law.

Using the ideal gas law:

$$PV = nRT$$

$$P = \left(\frac{nR}{V}\right)T$$

$$P = \text{constant} \times \text{T}$$

$$P \ \alpha \ T$$

Determine the grams of O_2 in a 50.0-L cylinder at 21°C when the O_2 pressure is 15.7 atm.

Variable	*Value*
P	15.7 atm
V	50.0 L
T	(21 + 273) K = 294 K
n	?

Solving the ideal gas law for *n*

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

Substituting the data gives

$$n = \frac{15.7\ \text{atm} \times 50.0\ \text{L}}{0.0821\ \text{L} \cdot \text{atm}/(\text{K} \cdot \text{mol}) \times 294\ \text{K}} = 32.5\ \text{mol}$$

Converting moles into mass of oxygen yields

$$32.5\ \text{mol}\ O_2 \times \frac{32.0\ \text{g}\ O_2}{1\ \text{mol}\ O_2} = 1.04 \times 10^3\ \text{g}\ O_2$$

Gas Density: Molecular-weight Determination

The density of a substance is its mass divided by its volume. Hence, density is influenced by temperature and pressure.

The ideal gas law can be used to calculate the density of a gas at any temperature and pressure.

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

a. Which of the flasks contains the most atoms of gas?

b. Which of the flasks has the greatest density of gas?

c. If the He flask were heated and the Ar flask cooled, which of the three flasks would be at the highest pressure?

d. Say the temperature of the He was lowered while that of the Xe was raised. Which of the three flasks would have the greatest number of moles of gas?

Assume the flasks are closed.

a. All flasks contain the same number of atoms.
b. The gas with the highest molar mass, Xe, has the greatest density.
c. The flask at the highest temperature (the one containing He) has the highest pressure.
d. The number of atoms is unchanged.

Stoichiometry and Gas Volumes

Use the ideal gas law to find moles from a given volume, pressure, and temperature, and vice versa.

Air bags in automobiles can be inflated with nitrogen using the rapid reaction of sodium azide, NaN_3, and iron (III) oxide, Fe_2O_3. How many grams of sodium azide would be required to provide 75.0 L of nitrogen gas at 25°C and 748 mmHg?

The balanced equation is:

$$6NaN_3(s) + Fe_2O_3(s) \longrightarrow 3Na_2O(s) + 2Fe(s) + 9N_2(g)$$

Variable	Value
P	$748\ \cancel{\text{mmHg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 0.984\ \text{atm}$
V	75.0 L
T	(25 + 273) K = 298 K
n	?

Rearranging the ideal gas law to obtain *n*

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

Making substitutions from the data available

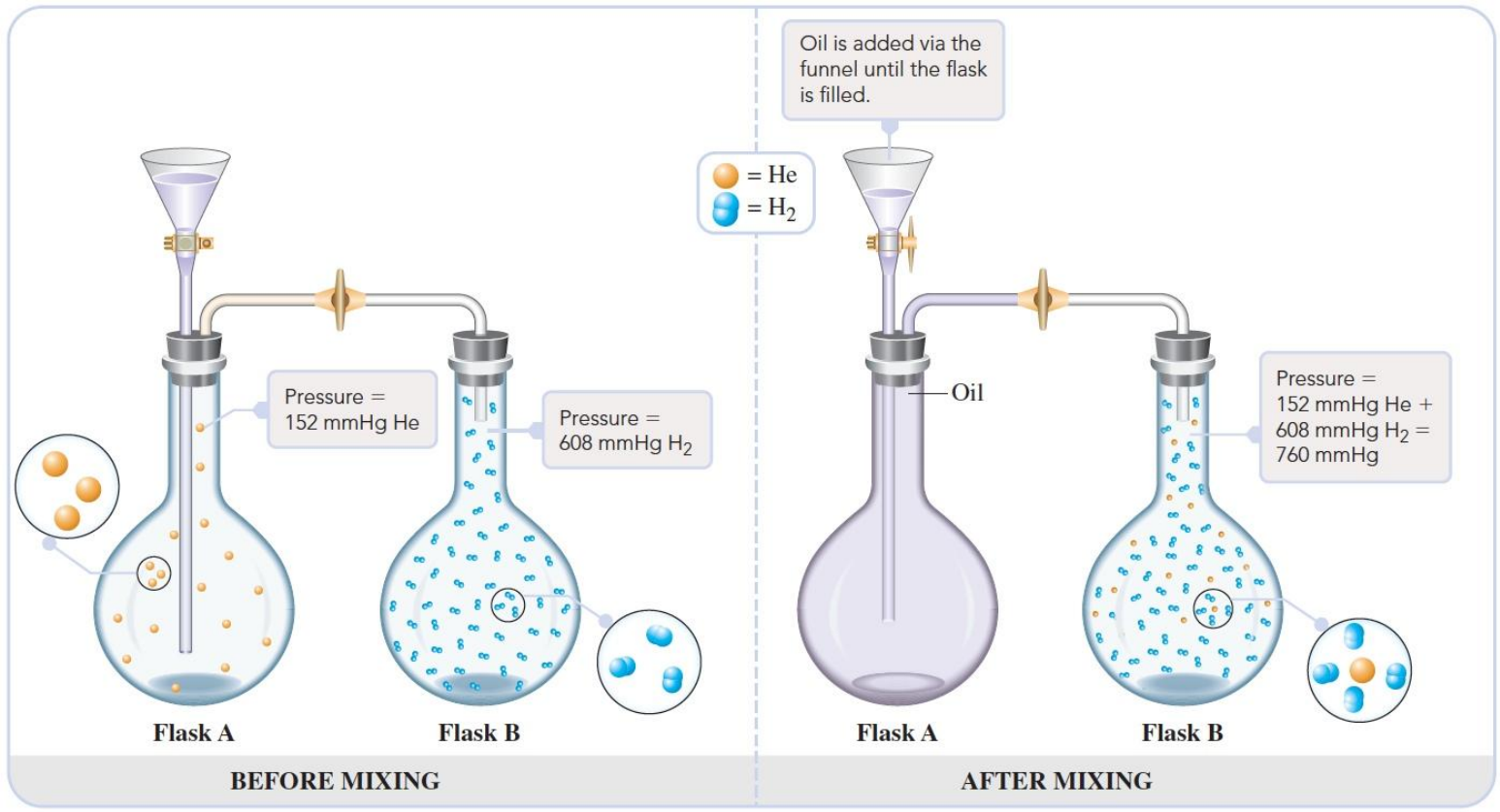
$$n = \frac{0.984 \cancel{\text{atm}} \times 75.0 \cancel{\text{L}}}{0.0821 \cancel{\text{L}} \cdot \cancel{\text{atm}}/(\cancel{\text{K}} \cdot \text{mol}) \times 298 \cancel{\text{K}}} = 3.02 \text{ mol}$$

$$3.02 \cancel{\text{mol N}_2} \times \frac{6 \text{mol NaN}_3}{9 \cancel{\text{mol N}_2}} = 2.01 \text{ mol NaN}_3$$

$$2.01 \cancel{\text{mol NaN}_3} \times \frac{65.01 \text{ g NaN}_3}{1 \cancel{\text{mol NaN}_3}} = \boxed{131 \text{ g NaN}_3}$$

Gas Mixtures

Dalton found that in a mixture of unreactive gases, each gas behaves as if it were the only gas in the mixture as far as pressure is concerned.



Originally (left), flask A contains He at 152 mmHg and flask B contains O_2 at 608 mmHg. Flask A is then filled with oil forcing the He into flask B (right). The new pressure in flask B is 760 mmHg.

Partial Pressure

The pressure exerted by a particular gas in a mixture.

Dalton's Law of Partial Pressures

The sum of the partial pressures of all the different gases in a mixture is equal to the total pressure of the mixture:

$$P = P_A + P_B + P_C + \ldots$$

Mole Fraction

The mole fraction of a component gas is the fraction of moles of that component in the total moles of gas mixture.

A 1.00-L sample of dry air at 25°C and 786 mmHg contains 0.925 g N_2, plus other gases including oxygen, argon, and carbon dioxide.

Determine the partial pressure (in mmHg) of N_2 in the air sample

Determine the mole fraction and mole percent of N_2 in the mixture.

Converting 0.925 g N_2 moles to N_2

$$0.925\ \text{g}\ \cancel{\text{N}_2} \times \frac{1\ \text{mol}\ \text{N}_2}{28.0\ \cancel{\text{g}\ \text{N}_2}} = 0.330\ \text{mol}\ \text{N}_2$$

Substituting into the ideal gas law (25°C = 298 K)

$$P_{\text{N}_2} = \frac{n_{\text{N}_2}\text{RT}}{V}$$

$$= \frac{0.0330\ \cancel{\text{mol}} \times 0.0821\ \cancel{\text{L}}\cdot\text{atm}/(\cancel{\text{K}}\cdot\cancel{\text{mol}}) \times 298\ \cancel{\text{K}}}{1.00\ \cancel{\text{L}}}$$

$$= 0.807\ \text{atm}\ (= 613\ \text{mmHg})$$

Determining the mole fraction of N_2 in the air

Mole fraction of N_2 $\dfrac{P_{N_2}}{P} = \dfrac{613 \cancel{\text{ mmHg}}}{786 \cancel{\text{ mmHg}}} = 0.780 = 78.0\%$

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.

a. 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?

b. How do the pressures of the Ar and the H_2 in the flask compare?

c. How does the total pressure in the flask relate to the pressures of the two gases?

a. Nothing happens to the pressure of H_2.

b. The pressures are equal because the moles are equal.

c. The total pressure is the sum of the pressures of the two gases.

Collecting Gas Over Water

Gases are often collected over water. The result is a mixture of the gas and water vapor.

The partial pressure of water depends only on temperature.

1. Hydrogen, prepared by the reaction of zinc with hydrochloric acid, is led to an inverted tube initially filled with water

2. When the gas-collection tube is adjusted so that the water level in the tube is at the same height as the level in the beaker, the gas pressure in the tube equals the barometric pressure (769 mmHg).

3. The total gas pressure equals the sum of the partial pressure of the hydrogen (752 mmHg) and the vapor pressure of water (17 mm Hg). For clarity, hydrochloric acid is shown in light brown and hydrogen gas in light blue.

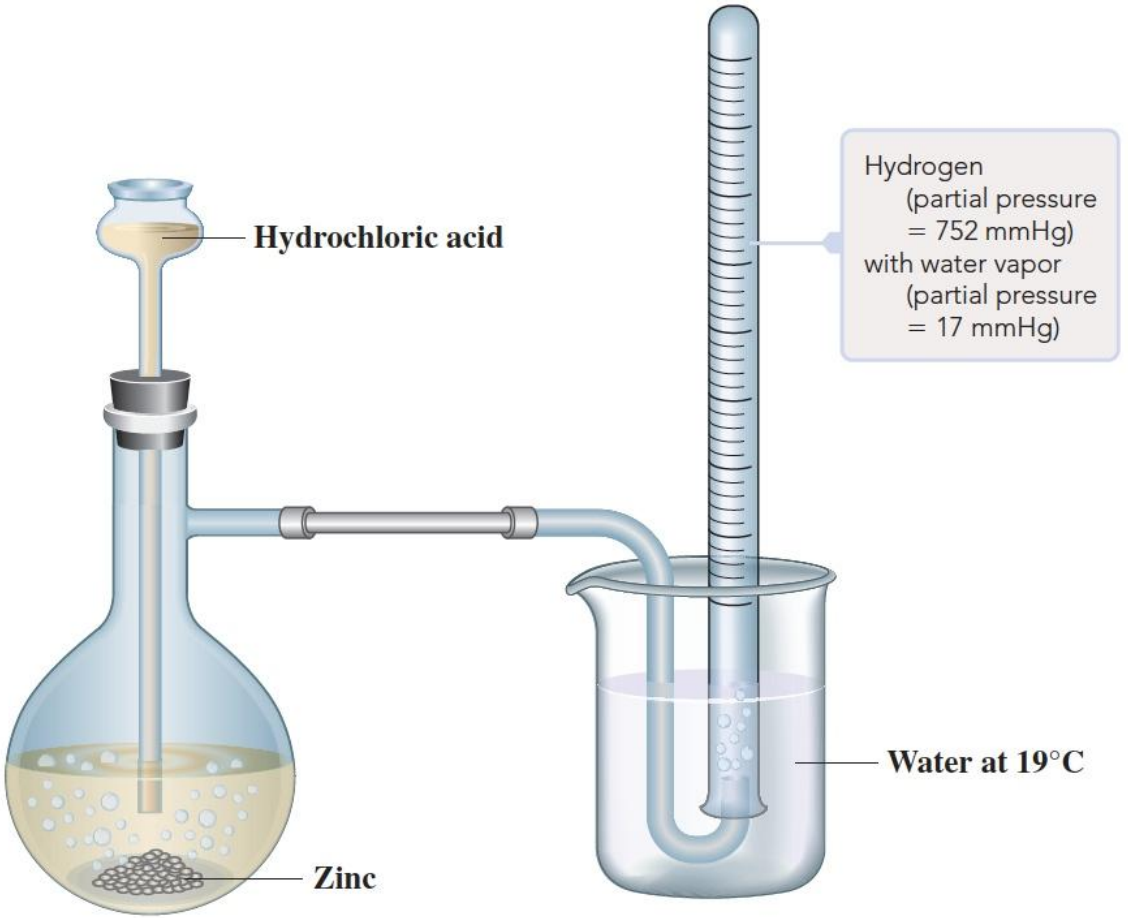


Table 5.6 Vapor Pressure of Water at Various Temperatures*

Temperature (°C)	Pressure (mmHg)
0	4.6
10	9.2
15	12.8
17	14.5
19	16.5
21	18.7
23	21.1
25	23.8
27	26.7
30	31.8
40	55.3
60	149.4
80	355.1
100	760.0

*Appendix B contains a more complete table.

Hydrogen gas is produced by the reaction of HCl on zinc metal.

$$2HCl\,(aq) + Zn(s) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

The gas is collected over water. Determine the mass of hydrogen collected if 156 mL of gas is collected at 19°C and 769 mmHg total pressure.

Using Dalton's law of partial pressures,

$$P = P_{H_2} + P_{H_2O}$$

$$P_{H_2} = P - P_{H_2O} = (769 - 16.5)\ \text{mmHg} = 752\ \text{mmHg}$$

Variable	Value
P	$752\ \cancel{\text{mmHg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 0.989\ \text{atm}$
V	156 mL = 0.156 L
T	(19 + 273) K = 292 K
n	?

Calculating the moles of H_2 collected,

$$n = \frac{PV}{RT} = \frac{0.989\ \cancel{\text{atm}} \times 0.156\ \cancel{\text{L}}}{0.0821\ \cancel{\text{L}} \cdot \cancel{\text{atm}}/(\cancel{\text{K}} \cdot \text{mol}) \times 293\ \cancel{\text{K}}} = 0.00641\ \text{mol}$$

Converting moles of H_2 to grams of H_2

$$0.00664\ \cancel{\text{mol H}_2} \times \frac{2.02\ \text{g H}_2}{1\ \cancel{\text{mol H}_2}} = \boxed{0.0130\ \text{g H}_2}$$

Kinetic-Molecular Theory (Kinetic Theory)
A theory, developed by physicists, that is based on the assumption that a gas consists of molecules in constant random motion.

Kinetic energy is related to the mass and velocity:

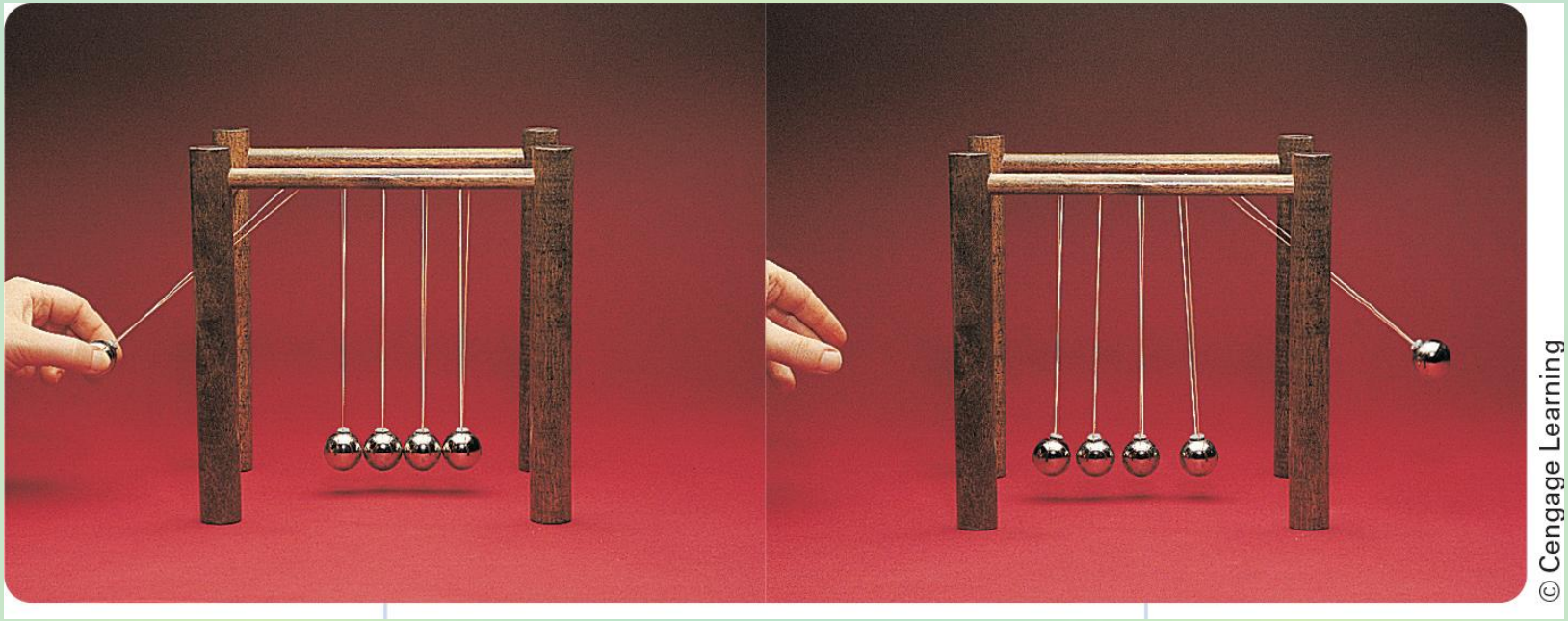
$$E_{\mathrm{K}} = \frac{1}{2} m(\text{speed})^2$$

m = mass

Postulates of the Kinetic Theory

1. Gases are composed of molecules whose size is negligible compared to the average distance between them
2. Molecules move randomly in straight lines in all directions and at various speeds.
3. The forces of attraction or repulsion between two molecules (intermolecular forces) in a gas are very weak or negligible, except when the molecules collide.
4. When molecules collide with each other, the collisions are elastic.
5. The average kinetic energy of a molecule is proportional to the absolute temperature.

An elastic collision is one in which no kinetic energy is lost. The collision on the left causes the ball on the right to swing the same height as the ball on the left had initially, with essentially no loss of kinetic energy.



Each of the gas laws can be derived from the postulates.

For the ideal gas law:

$P \propto$ frequency of collision x average force

The average force depends on the mass of the molecules, *m*, and its average speed, *u*, i.e., it depends on momentum, *mu.*

The frequency of collisions is proportional to the average speed, *u*, and the number of molecules, *N*, and is inversely proportional to the volume, *V*.

$$\mathrm{P}\,\alpha\left(\mathrm{u}\times\frac{1}{\mathrm{V}}\times\mathrm{N}\right)\times mu$$

Rearranging this equation gives

$$PV \propto Nmu^2$$

The average kinetic energy of a molecule of mass m and average speed u is $^1/_2 mu^2$.

Thus PV is proportional to the average kinetic energy of the molecule.

However, the average kinetic energy is also proportional to the absolute temperature. Therefore,

$$PV \propto nT$$

Inserting the proportionality constant, *R*, gives

$$PV = nRT$$

Molecular Speeds

According to kinetic theory, molecular speeds vary over a wide range of values. This distribution depends on temperature, so it increases as the temperature increases.

Root-mean Square (rms) Molecular Speed, *u*

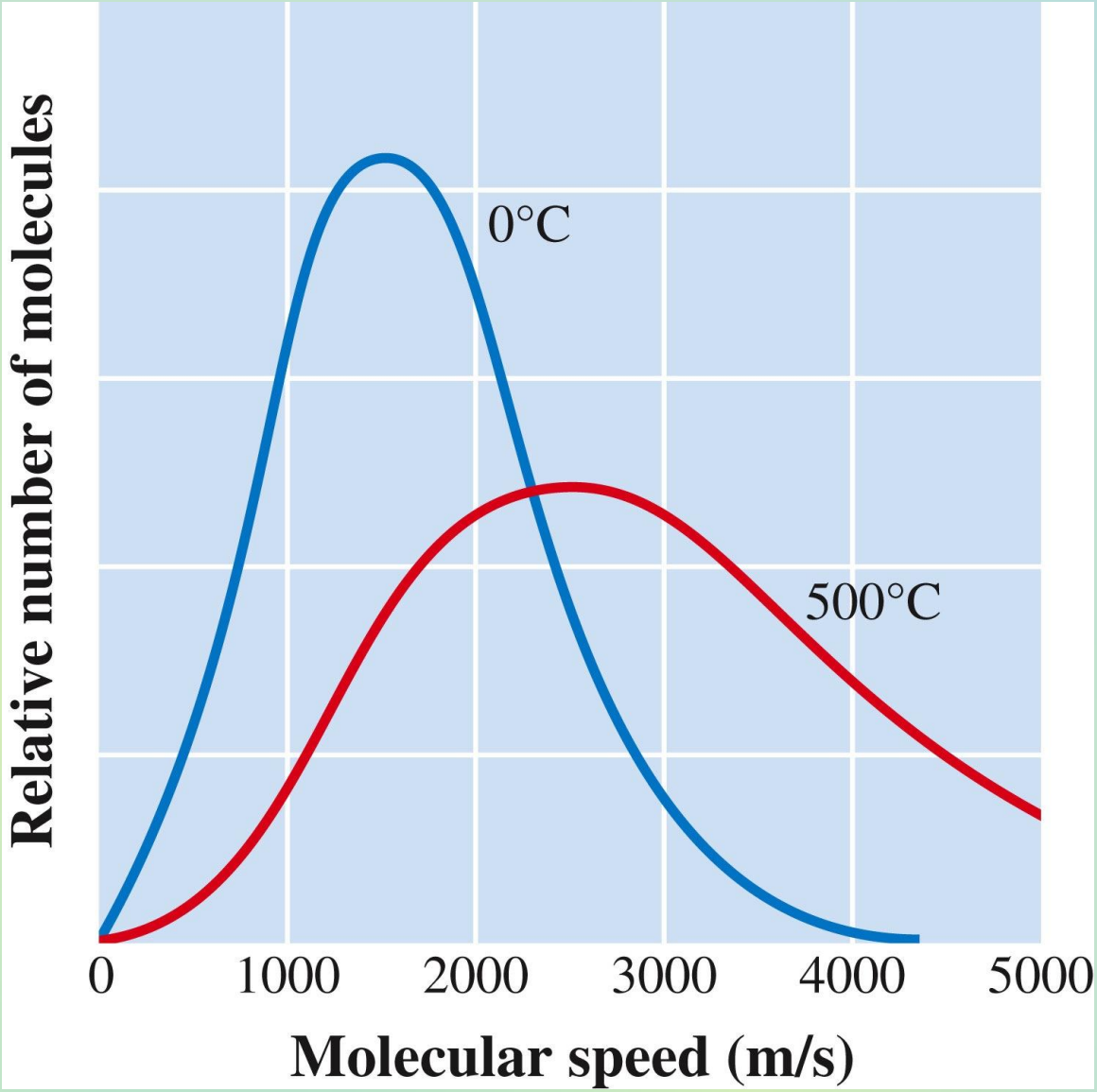
A type of average molecular speed, equal to the speed of a molecule that has the average molecular kinetic energy

$$u = \sqrt{\frac{3RT}{M_m}} = \left(\frac{3\mathrm{RT}}{M_m}\right)^{\frac{1}{2}}$$

When applying the equation, consistent units are to be used.

If SI units are used for R (= 8.31 $kg \cdot m^2/s^2 \cdot K \cdot mol$), T(K) and M_m (kg/mol), rms speed will be in meters per second.

Maxwell predicted the distributions of molecular speeds at various temperatures. The graph shows 0°C and 500°C.

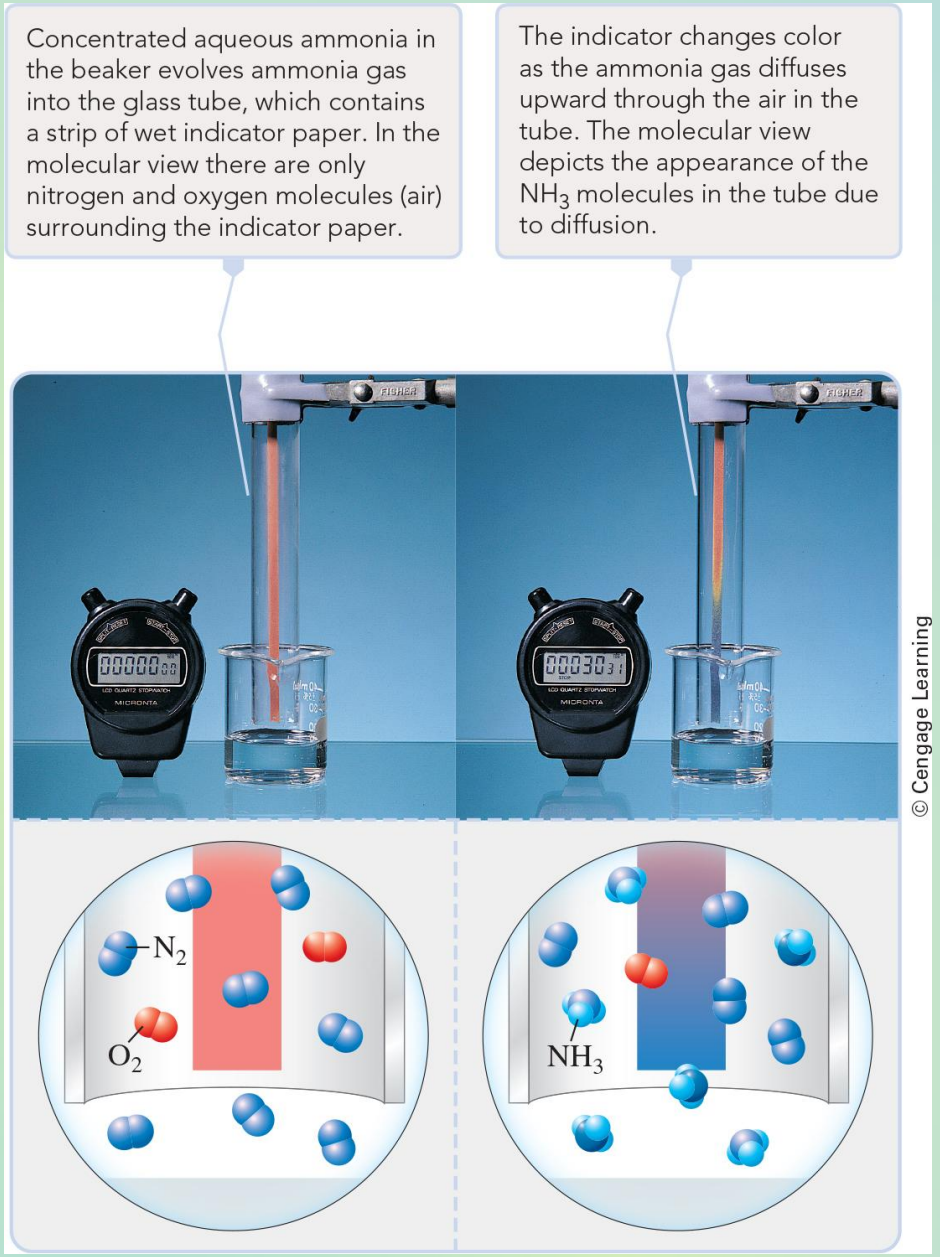


Determine the rms speed of O_2 molecules in a cylinder at 21°C and 15.7 atm.

$$u = \left(\frac{3 \times 8.31\ \text{kg} \cdot \text{m}^2 / (\text{s}^2 \cdot \text{K} \cdot \text{mol}) \times 294\text{K}}{32.0 \times 10^{-3}\ \text{kg/mol}} \right)^{1/2} = 479\ \text{m/s}$$

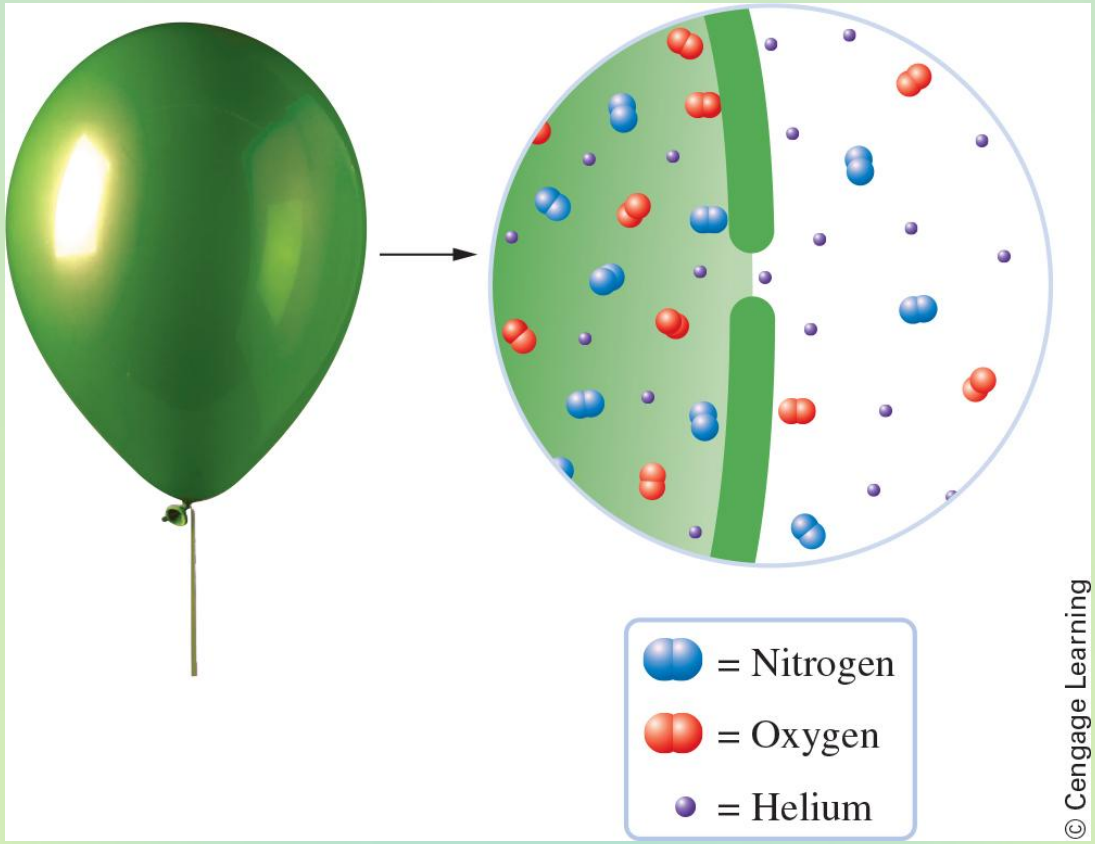
Diffusion

The process whereby a gas spreads out through another gas to occupy the space uniformly.



Effusion

The process by which a gas flows through a small hole in a container. A pinprick in a balloon is one example of effusion.



Graham's Law of Effusion

The rate of effusion of gas molecules through a particular hole is inversely proportional to the square root of the molecular mass of the gas.

$$\text{Rate of effusion of molecules} \propto \frac{1}{\sqrt{M_m}}$$

Calculate the ratio of effusion rates of molecules and CO_2 and SO_2 from the same container and at the same temperature and pressure.

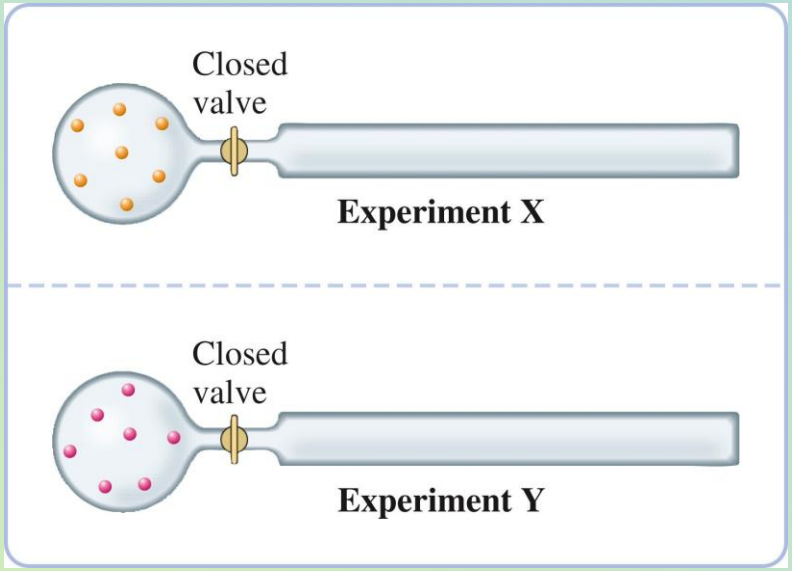
$$\frac{\text{Rate of effusion of } CO2_2}{\text{Rate of effusion of } SO_2} = \frac{\frac{1}{\sqrt{M_m(CO_2)}}}{\frac{1}{\sqrt{M_m(SO_2)}}}$$

$$= \sqrt{\frac{M_m(SO_2)}{M_m(CO_2)}}$$

$$= \sqrt{\frac{64.1 \text{ g/mol}}{44.0 \text{ g/mol}}}$$

$$= 1.21$$

CO_2 diffuses1.21 times faster than sulfur dioxide



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?

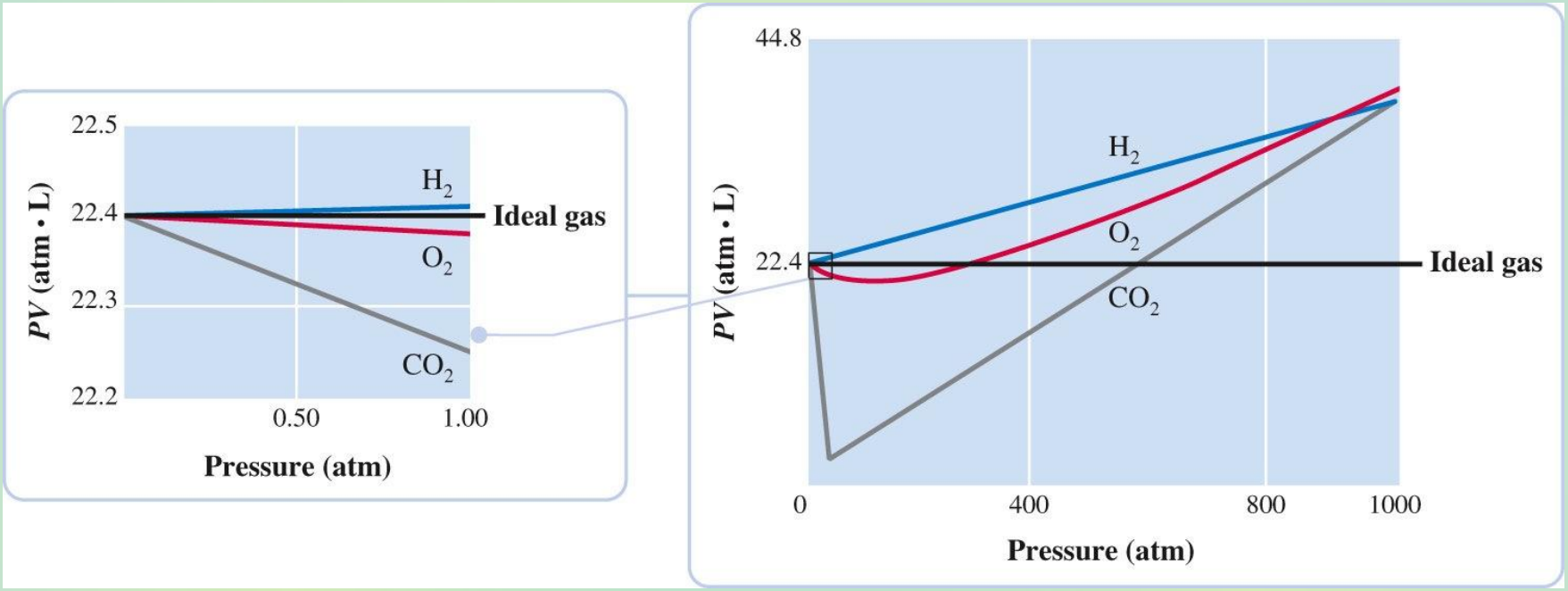
b. If you wanted the Ar to reach the end of the long tube at the same time as the He, what experimental condition (that is, you cannot change the equipment) could you change to make this happen?

a. He will reach the end first because it has a smaller molar mass.

b. Open the valves at two different times, allowing Ar more time by a factor equal to the square root of the ratio of molar masses of Ar to He, or approximately 3.16 times longer.

Real Gases

At high pressure, the relationship between pressure and volume does not follow Boyle's law. This is illustrated in the graph below.



At high pressure, some of the assumptions of the kinetic theory no longer hold true:

1. At high pressure, the volume of the gas molecule is not negligible. (Postulate 1)
2. At high pressure, the intermolecular forces are not negligible. (Postulate 3)

Van der Waals Equation

An equation that is similar to the ideal gas law, but which includes two constants, *a* and *b,* to account for deviations from ideal behavior.

The term V becomes $(V - nb)$.

The term P becomes $\left(P + n^2a/V^2\right)$.

Values for *a* and *b* are found in Table 5.7.

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

If SO_2 were an ideal gas, the pressure at 0.0°C exerted by 1.000 mole occupying 22.41 L would be 1.000 atm. Use the van der Waals equation to estimate the pressure of this volume of 1.000 mol SO_2 at 0.0°C.

Rearranging the van der Waal's equation to give P

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

Substituting values of *R*, *T*, *V*, *a*, and *b*

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

$$= 1.003\ \text{atm} - 0.014\ \text{atm} = \boxed{0.989\ \text{atm}}$$