# Chapter 5
# Gases

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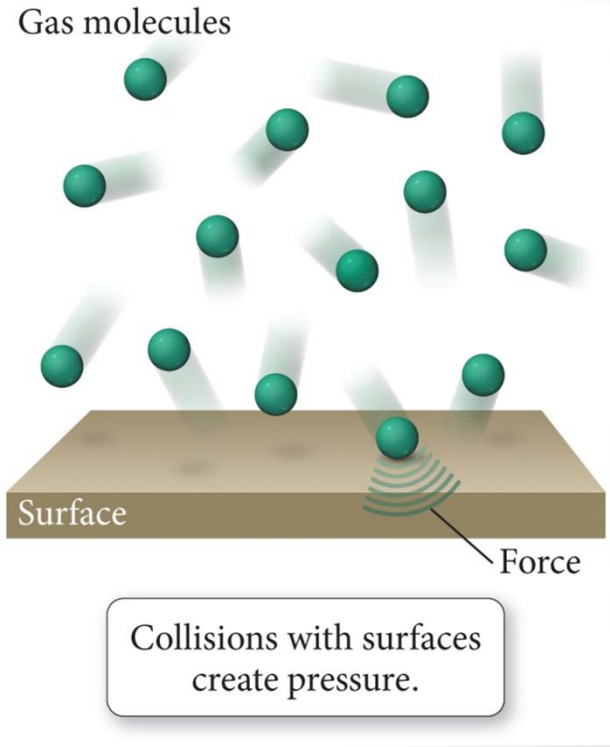
# Gas

- Gases are composed of particles that are moving around very fast in their container(s).
- These particles moves in straight lines until they collides with either the container wall or another particle, then they bounce off.
- A snapshot of these particles in a gas, will reveal that there is a lot of empty space
  in there

# Gas Pressure

- **Pressure** is the force exerted per unit area by gas molecules as they strike the surfaces around them.

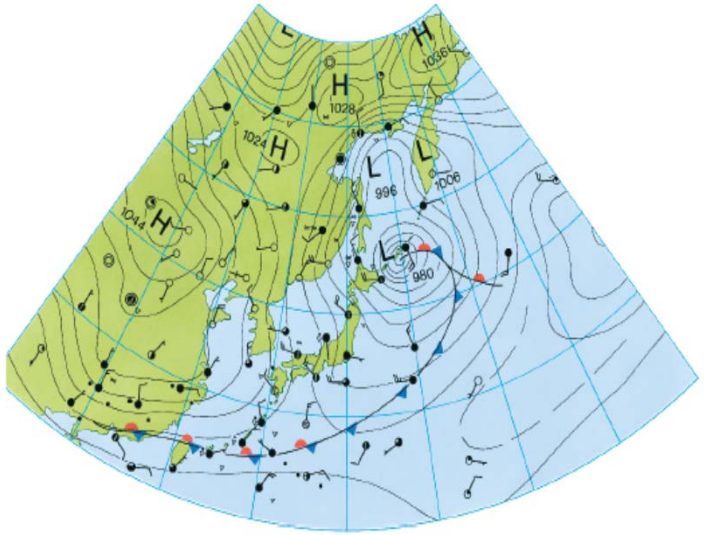
$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$



# Pressure of a gas

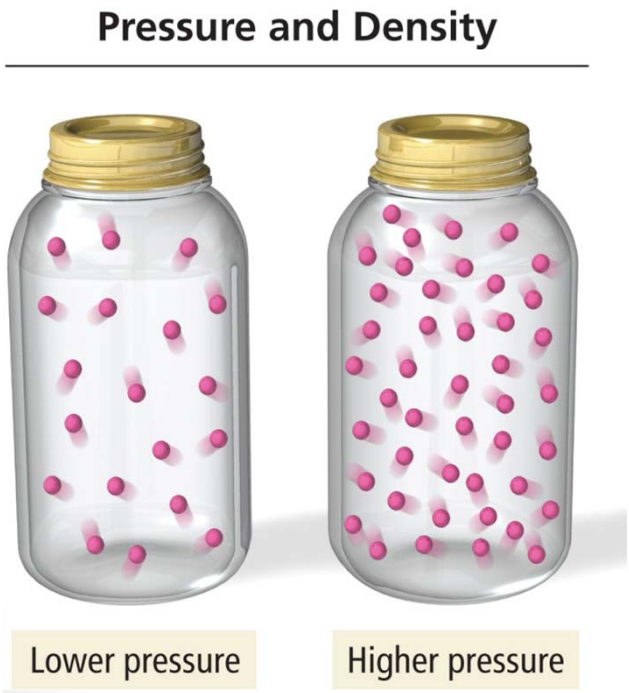
- The pressure of a gas depends on several factors:
  - ✓ Number of gas particles in a given volume
    - ➢ The higher the concentration, the greater the pressure.
  - ✓ Volume of the container
    - ➢ This in turn results in fewer molecular collisions, which results in lower pressure.
  - ✓ Average speed of the gas particles (Temperature)

# Atmospheric Pressure Effects




- Variation in pressure in Earth's atmosphere creates wind, and changes in pressure help us to predict weather.
  - ✓ The H's in this map indicate regions of high pressure, usually associated with clear weather.
  - ✓ The L's indicate regions of low pressure, usually associated with unstable weather.
- ➢ The number of gas particles in a given volume decreases with increasing altitude.
  - ✓ Hence, **pressure decreases** with **increasing altitude.**

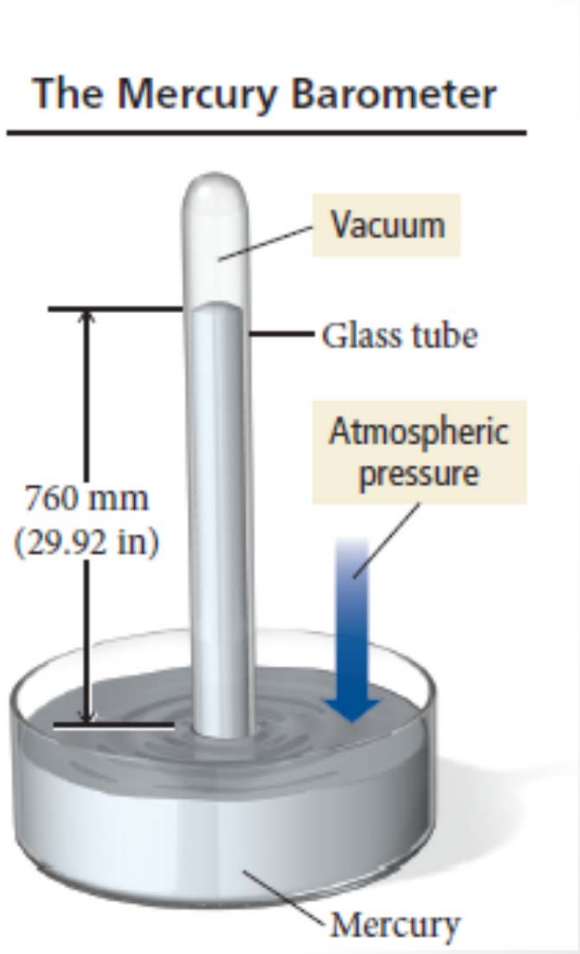
# Pressure




- Pressure exerted by a gas is dependent on the number of gas particles in a given volume.
- The fewer the gas particles, the lower the force per unit area and the lower the pressure.
  - ✓ A low density of gas particles results in low pressure. A high density of gas particles results in high pressure.

# Pressure Units

- Pressure is measured in several different units. A common unit of pressure, the **millimeter of mercury (mmHg)** , originates from how pressure is measured with a **barometer**



# Pressure Units

**TABLE 5.1 Common Units of Pressure**

| Unit | Abbreviation | Average Air Pressure at Sea Level |
|---|---|---|
| Pascal (1 $N/m^2$) | Pa | 101,325 Pa |
| Pounds per square inch | psi | 14.7 psi |
| Torr (1 mmHg) | torr | 760 torr (exact) |
| Inches of mercury | in Hg | 29.92 in Hg |
| Atmosphere | atm | 1 atm |

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

$$1 \text{ atm} = 760 \text{ mmHg}$$

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

$$1 \text{ atm} = 101{,}325 \text{ Pa}$$

*1atm*=14.7*psi*

The SI unit of pressure is the **pascal (Pa)** ,

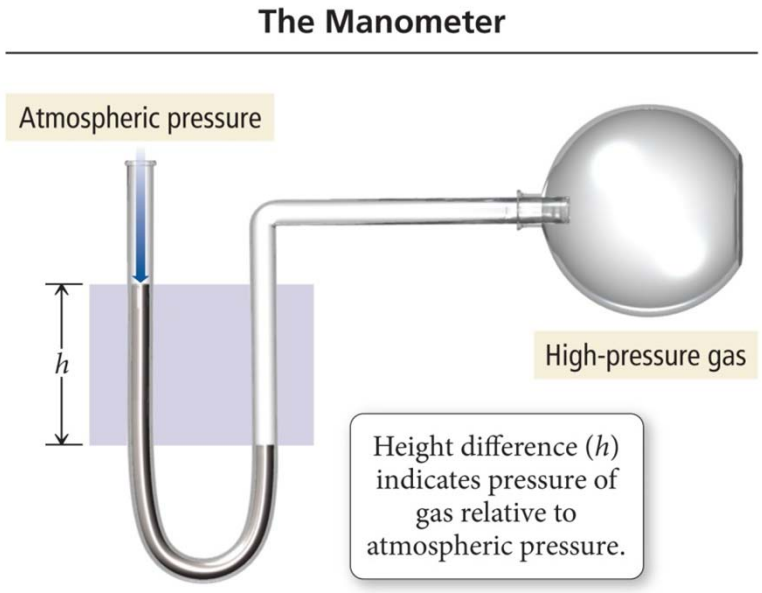
# EXAMPLE 5.1 Converting between Pressure Units

- A high-performance road bicycle tire is inflated to a total pressure of 132 psi. What is this pressure in mmHg?

**SOLUTION**

$$132\ \text{psi} \times \frac{1\ \text{atm}}{14.7\ \text{psi}} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 6.82 \times 10^3\ \text{mmHg}$$

# The Manometer

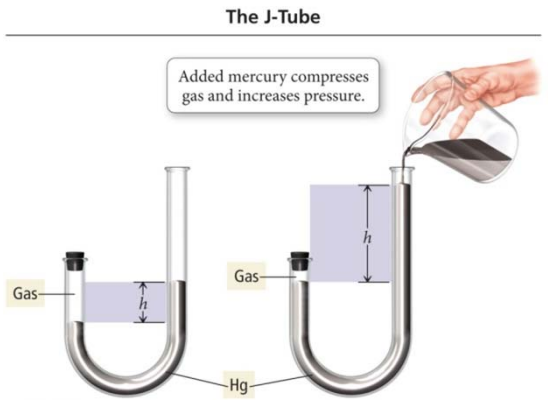


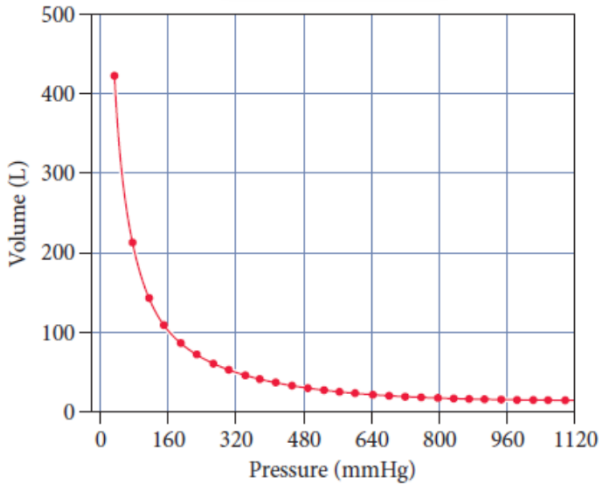

- The pressure of a gas trapped in a container can be measured with an instrument called a **manometer**.
- Manometers are U-shaped tubes partially filled with a liquid that are connected to the gas sample on one side and open to the air on the other.
- The difference in the liquid levels is a measure of the difference in pressure between the gas and the atmosphere.

# The Simple Gas Laws

- There are four basic properties of a gas: pressure (*P*), volume (*V*), temperature (*T*), and amount in moles (*n*).
  - ✓ These properties are interrelated—when one changes, it affects the others.
  - ✓ The *simple gas laws* describe the relationships between pairs of these properties.

# Boyle's Law: Robert Boyle (1627–1691)




- They observed an *inverse relationship* between volume and pressure.
- Hence, an increase in one causes a decrease in the other.

Boyle's law: $V \propto \frac{1}{P}$ (constant $T$ and $n$)

$P \times V$ = constant

$P1 \times V1 = P2 \times V2$

# Boyle's Law and Diving


- For every 10 m of depth, a diver experiences approximately one additional atmosphere of pressure due to the weight of the surrounding water.
- At 20 m, for example, the diver experiences approximately 3 atm of pressure.

# Boyle's Law and Diving

- If a diver holds his or her breath and rises to the surface quickly, the outside pressure drops to 1 atm.
  - ✓ According to Boyle's law, what should happen to the volume of air in the lungs?

SOL:

Because the pressure is decreasing by a factor of 3, the volume will expand by a factor of 3, causing damage to internal organs

# EXAMPLE 5.2 Boyle's Law

- As discussed in the opening section of this chapter, you inhale by increasing your lung volume. A woman has an initial lung volume of 2.75 L, which is filled with air at an atmospheric pressure of 1.02 atm. If she increases her lung volume to 3.25 L without inhaling any additional air, what is the pressure in her lungs?

**SOLUTION**

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{V_1}{V_2}\mathrm{P}_1$$

$$= \frac{2.75\ \cancel{\mathrm{L}}}{3.25\ \cancel{\mathrm{L}}}\,1.02\ \mathrm{atm}$$

$$= 0.863\ \mathrm{atm}$$

# Charles's Law: Volume and Temperature

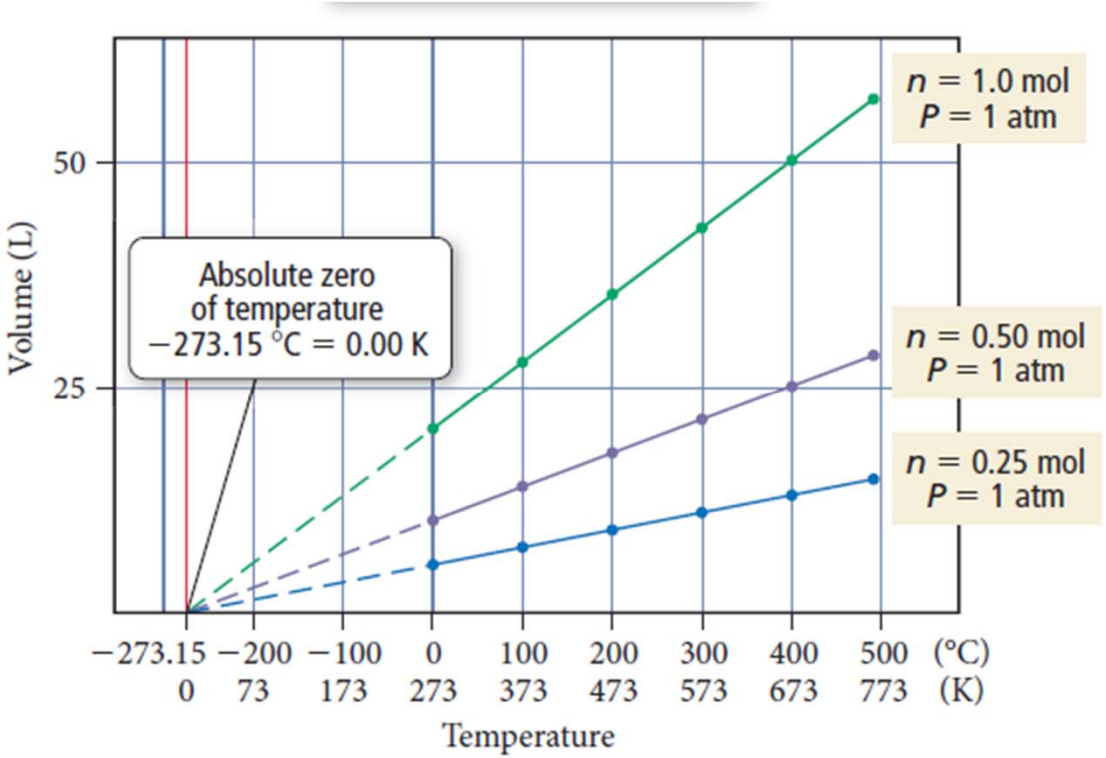
- The volume of a fixed amount of gas at a constant pressure increases linearly with increasing temperature in kelvins:
  - ✓ The volume of a gas increases with increasing temperature.
- Kelvin $T$ = Celsius $T$ + 273
- V = constant × $T$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Charles's law: $V \propto T$ (constant $P$ and $n$)

T: Kelvin *Temp*

# Charles's Law

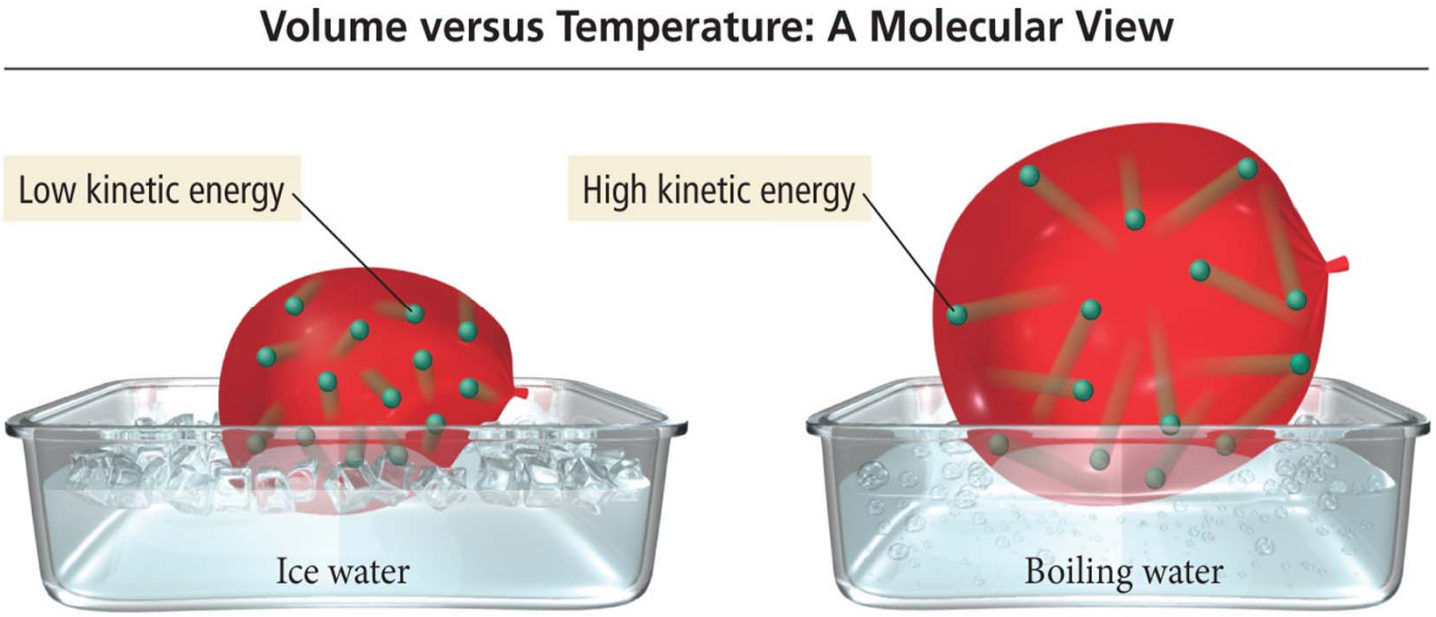



If the lines are extrapolated back to a volume of "0," they all show the same temperature, −273.15 °C = 0 K, called **absolute zero**



Charles's law: $V \propto T$ (constant $P$ and $n$)

# Charles's Law – A Molecular View




$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

# EXAMPLE 5.3 Charles's Law

- A sample of gas has a volume of 2.80 L at an unknown temperature. When the sample is submerged in ice water at $T$ = 0.00 C, its volume decreases to 2.57 L. What was its initial temperature (in K and in ˚C)?

**SOLUTION**

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_1 = \frac{V_1}{V_2} T_2$$

$$= \frac{2.80 \text{ L}}{2.57 \text{ L}} 273.15 \text{ K}$$

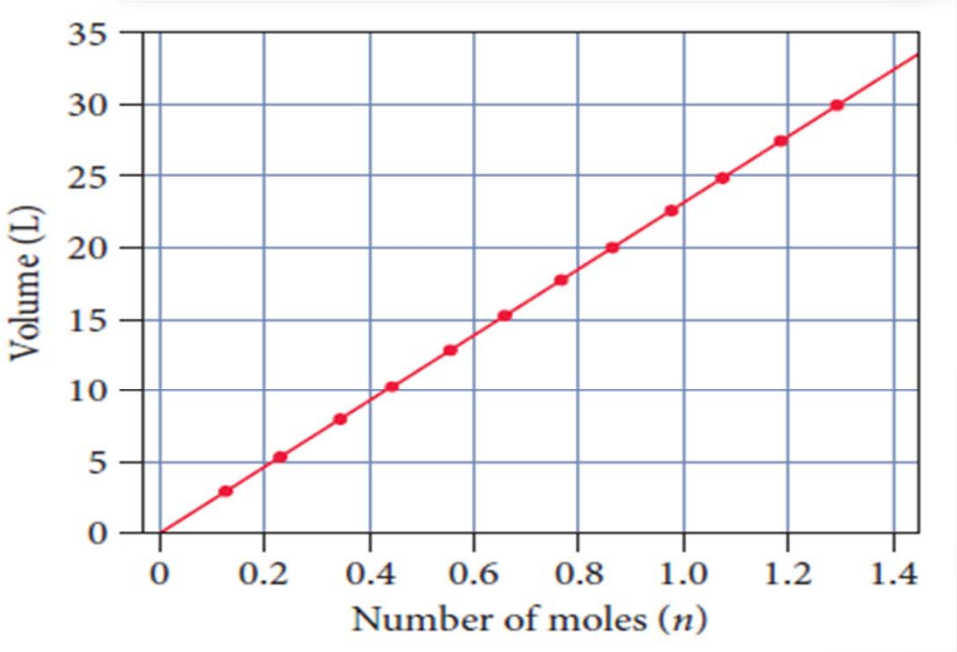
$$= 297.6 \text{ K}$$

$$T_2\,(\text{K}) = 0.00 + 273.15 = 273.15\,\text{K}$$

$$T_1\,(^\circ\text{C}) = 297.6 - 273.15 = 24\,^\circ\text{C}$$

# Avogadro's Law: Volume and Amount (in Moles)

- The relationship between volume and amount is linear. This relationship, first stated formally by Amadeo Avogadro, is **Avogadro's law** .




Avogadro's law: $V \propto n$ (constant $T$ and $P$)

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

# EXAMPLE 5.4 Avogadro's Law

- A male athlete in a kinesiology research study has a lung volume of 6.15 L during a deep inhalation. At this volume, his lungs contain 0.254 moles of air. During exhalation, his lung volume decreases to 2.55 L. How many moles of gas did the athlete exhale? Assume constant temperature and pressure.

**SOLUTION**

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

$$n_2 = \frac{V_2}{V_1} n_1 = \frac{2.55\ \cancel{L}}{6.15\ \cancel{L}} 0.254\ \text{mol}$$

$$= 0.105\ \text{mol}$$

$$\text{moles exhaled} = 0.254\,\text{mol} - 0.105\,\text{mol}$$

$$= 0.149\,\text{mol}$$

# 5.4 The Ideal Gas Law

- The relationships that we have discussed so far can be combined into a single law that encompasses all of them.

$$V \propto \frac{1}{P} \qquad \text{(Boyle's law)}$$

$$V \propto T \qquad \text{(Charles's law)}$$

$$V \propto n \qquad \text{(Avogadro's law)}$$

Combining these three expressions, we find that $V$ is proportional to $nT/P$:

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

# The Ideal Gas Law

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

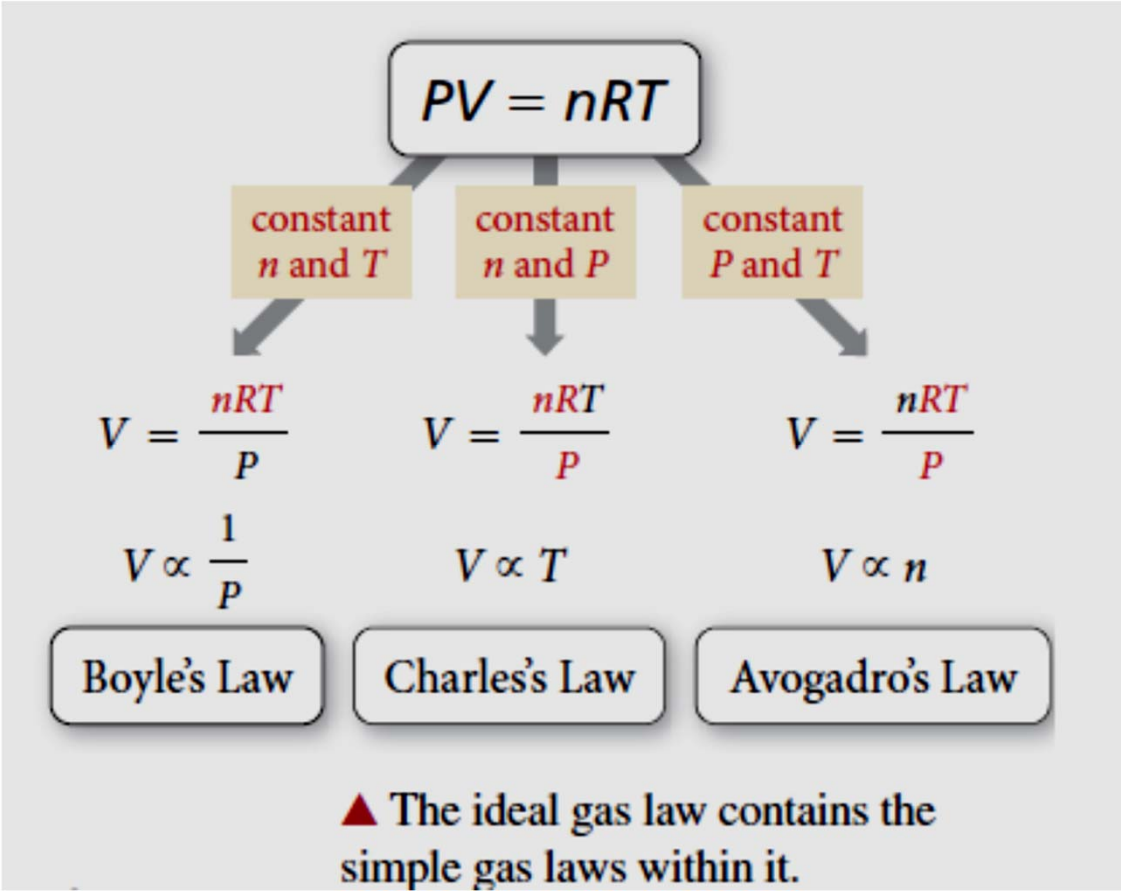
$$PV = nRT$$

This equation is the **ideal gas law**

*R* , the **ideal gas constant**

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

# The Ideal Gas Law




▲ The ideal gas law contains the simple gas laws within it.

# EXAMPLE 5.6 Ideal Gas Law II

- Calculate the number of moles of gas in a 3.24 L basketball inflated to a *total pressure* of 24.3 psi at 25 °C. (Note: The *total pressure* is not the same as the pressure read on a pressure gauge such as the type used for checking a car or bicycle tire. That pressure, called the *gauge pressure* , is the *difference* between the total pressure and atmospheric pressure. In this case, if atmospheric pressure is 14.7 psi, the gauge pressure would be 9.6 psi. However, for calculations involving the ideal gas law, you must use the *total pressure* of 24.3 psi.)

# Sol:

**GIVEN:** $P = 24.3\,\text{psi}, V = 3.24\ \text{L}, T(^\circ\text{C}) = 25\,^\circ\text{C}$

**FIND:** $n$

**SOLUTION**

$$PV = nRT$$

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

$$P = 24.3\ \text{psi} \times \frac{1\ \text{atm}}{14.7\ \text{psi}} = 1.6531\ \text{atm}$$

$$T\,(\text{K}) = 25 + 273 = 298\ \text{K}$$

$$n = \frac{1.6531\ \text{atm} \times 3.24\ \text{L}}{0.08206\ \dfrac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298\ \text{K}} = 0.219\ \text{mol}$$

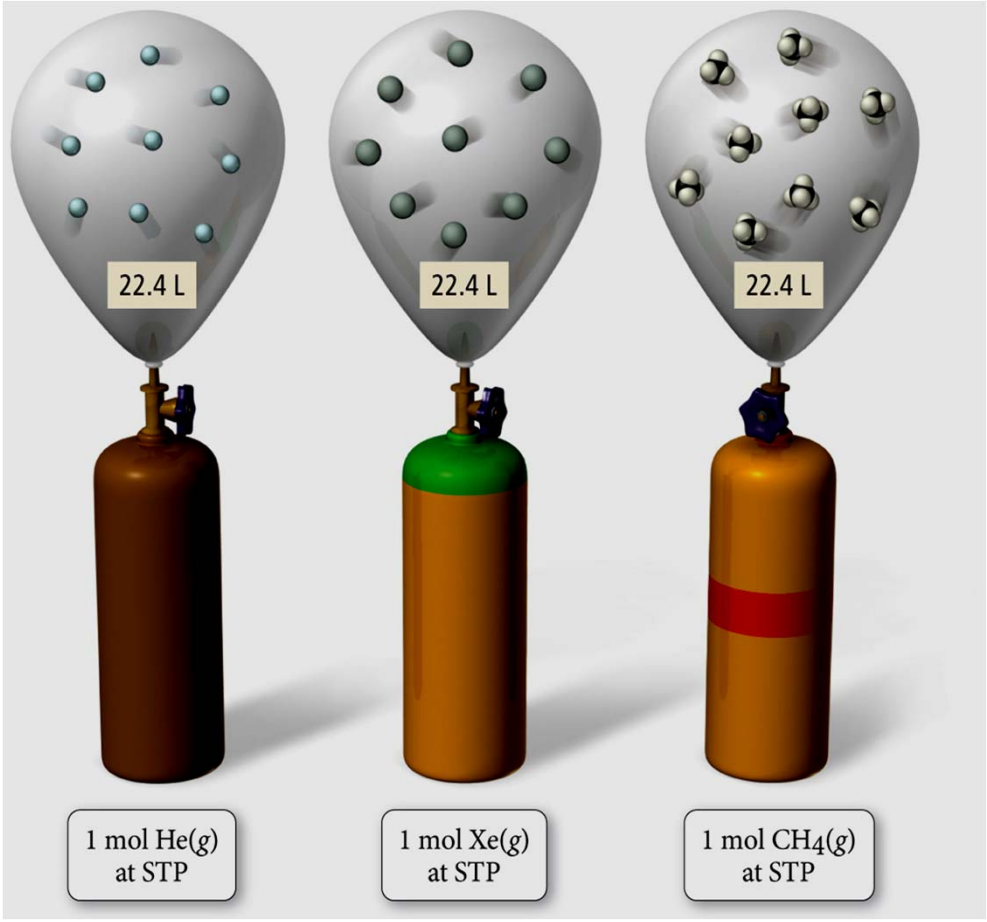
# 5.5 Applications of the Ideal Gas Law: Molar Volume, Density, and Molar Mass of a Gas

- The volume occupied by one mole of a substance is its **molar volume**.
- For gases, we often specify the molar volume under conditions known as **standard temperature** ( $T$ = 0 °C or 273 K) **and pressure** ( $P$ = 1.00 atm), abbreviated as **STP** .
- **molar volume of** Ideal gas at STP

$$V = \frac{nRT}{P} = \frac{1.00 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 273 \text{ K}}{1.00 \text{ atm}}$$

$$= 22.4 \text{ L}$$

# Molar Volume at STP



# Density of a Gas at STP

- Density is the ratio of mass to volume.
- Density of a gas is generally given in g/L.
- The mass of 1 mole = molar mass.
- The volume of 1 mole at STP = 22.4 L.

$$\text{Density} = \frac{\text{molar mass}}{\text{molar volume}}$$

# Density of a Gas at STP

- For example, the densities of helium and nitrogen gas at STP are as follows:

$$d_{\mathrm{He}} = \frac{4.00\ \mathrm{g/mol}}{22.4\ \mathrm{L/mol}} = 0.179\ \mathrm{g/L}$$

$$d_{\mathrm{N_2}} = \frac{28.02\ \mathrm{g/mol}}{22.4\ \mathrm{L/mol}} = 1.25\ \mathrm{g/L}$$

# Gas Density

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{\cancel{\text{moles}}}{\text{liter}} \times \frac{\text{grams}}{\cancel{\text{mole}}} = \frac{\text{grams}}{\text{liter}}$$

Molar density | Molar mass | Density in grams/liter

$$d = \frac{P\mathcal{M}}{RT}$$

# EXAMPLE 5.7 Density

Calculate the density of nitrogen gas at 125 °C and a pressure of 755 mmHg.

**SOLUTION**

$$T(\text{K}) = 125 + 273 = 398\ \text{K}$$

$$P = 755\ \cancel{\text{mmHg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}}$$

$$= 0.99342\ \text{atm}$$

$$d = \frac{PM}{RT}$$

$$= \frac{0.99342\ \cancel{\text{atm}}\left(28.02 \frac{\text{g}}{\cancel{\text{mol}}}\right)}{0.08206 \frac{\text{L} \cdot \cancel{\text{atm}}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}}(398\ \cancel{\text{K}})}$$

$$= 0.852\ \text{g/L}$$

# Mixtures of Gases

- Dry air, for example, is a mixture containing nitrogen, oxygen, argon, carbon dioxide, and a few other gases in trace amounts.
  - ✓ Even though air is a mixture, we can measure the pressure, volume, and temperature of air as if it were a pure substance.
  - ✓ We can calculate the total moles of molecules in an air sample, knowing *P*, *V*, and *T*, even though they are different molecules.

**TABLE 5.3 Composition of Dry Air**

| Gas | Percent by Volume (%) |
|---|---|
| Nitrogen ($N_2$) | 78 |
| Oxygen ($O_2$) | 21 |
| Argon (Ar) | 0.9 |
| Carbon dioxide ($CO_2$) | 0.04 |

# Partial Pressure

- The pressure of a single gas in a mixture of gases is called its **partial pressure.**
- We can calculate the partial pressure of a gas if
  - ✓ we know what fraction of the mixture it composes and the total pressure,
  - ✓ or we know the number of moles of the gas in a container of known volume and temperature.
- The sum of the partial pressures of all the gases in the mixture equals the total pressure:
  - ✓ Dalton's law of partial pressures
  - ✓ Gases behave independently

$$P_{\text{total}} = P_{\text{a}} + P_{\text{b}} + P_{\text{c}} + \ldots$$

# Partial Pressure

- The pressure due to any individual component in a gas mixture is its **partial pressure ( $P_n$ )** .

$$P_n = n_n \frac{RT}{V}$$

- For a multicomponent gas mixture, we calculate the partial pressure of each component
- from the ideal gas law and the number of moles of that component ( $n_n$ )

$$P_a = n_a \frac{RT}{V}; \quad P_b = n_b \frac{RT}{V}; \quad P_c = n_c \frac{RT}{V}; \ldots$$

# Dalton's Law of Partial Pressures

- The sum of the partial pressures of the components in a gas mixture equals the total pressure:

$$P_{\text{total}} = P_{\text{a}} + P_{\text{b}} + P_{\text{c}} + \ldots$$

$$\begin{aligned} P_{\text{total}} &= P_{\text{a}} + P_{\text{b}} + P_{\text{c}} + \ldots \\ &= n_{\text{a}}\frac{RT}{V} + n_{\text{b}}\frac{RT}{V} + n_{\text{c}}\frac{RT}{V} + \ldots \\ &= (n_{\text{a}} + n_{\text{b}} + n_{\text{c}} + \ldots)\frac{RT}{V} \\ &= (n_{\text{total}})\frac{RT}{V} \end{aligned}$$

$$\frac{P_{\text{a}}}{P_{\text{total}}} = \frac{n_{\text{a}}(RT/V)}{n_{\text{total}}(RT/V)} = \frac{n_{\text{a}}}{n_{\text{total}}}$$

# Mole Fraction

- The ratio of the partial pressure a single gas contributes and total pressure is equal to the mole fraction.

$$\chi_a = \frac{n_a}{n_{total}}$$

$$\frac{P_a}{P_{total}} = \frac{n_a}{n_{total}}$$

$$P_a = \frac{n_a}{n_{total}} P_{total} = \chi_a P_{total}$$

$$P_a = \chi_a P_{total}$$

# EXAMPLE 5.9 Total Pressure and Partial Pressures

- A 1.00 L mixture of helium, neon, and argon has a total pressure of 662 mmHg at 298 K. If the partial pressure of helium is 341 mmHg and the partial pressure of neon is 112 mmHg, what mass of argon is present in the mixture?

**GIVEN:** $P_{He} = 341$ mmHg, $P_{Ne} = 112$ mmHg,
$P_{total} = 662$ mmHg,
$V = 1.00$ L, $T = 298$ K

**SOLUTION**

$$P_{\text{total}} = P_{\text{He}} + P_{\text{Ne}} + P_{\text{Ar}}$$

$$P_{\text{Ar}} = P_{\text{total}} - P_{\text{He}} - P_{\text{Ne}}$$

$$= 662 \text{ mmHg} - 341 \text{ mmHg} - 112 \text{ mmHg}$$

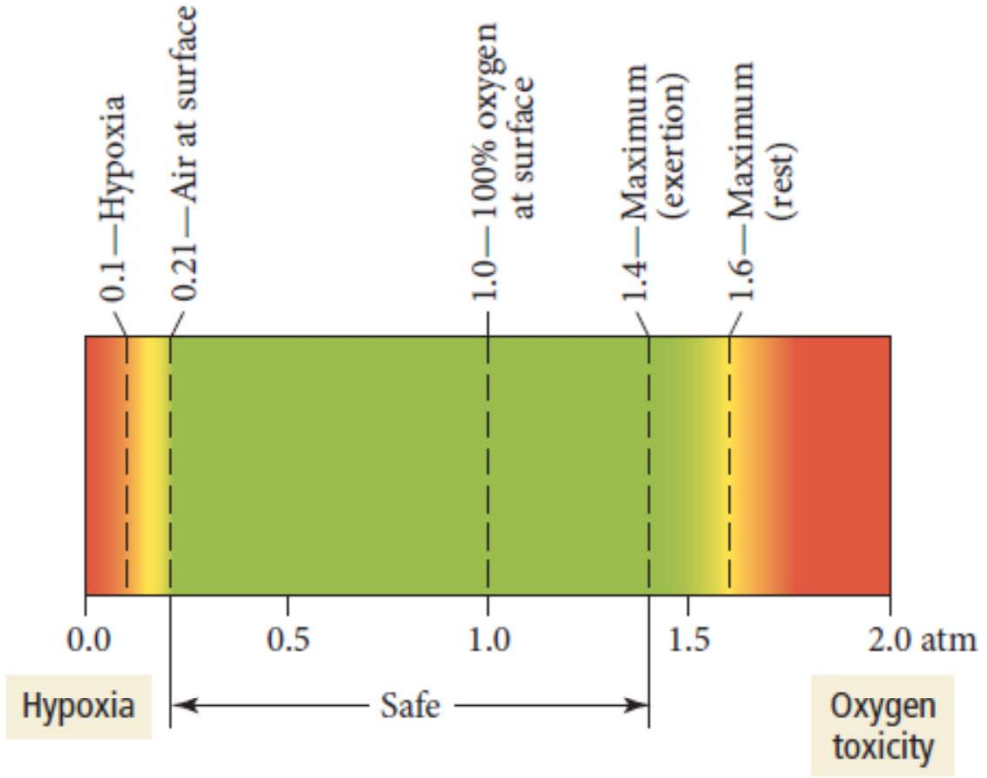
$$= 209 \text{ mmHg}$$

$$209 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.275 \text{ atm}$$

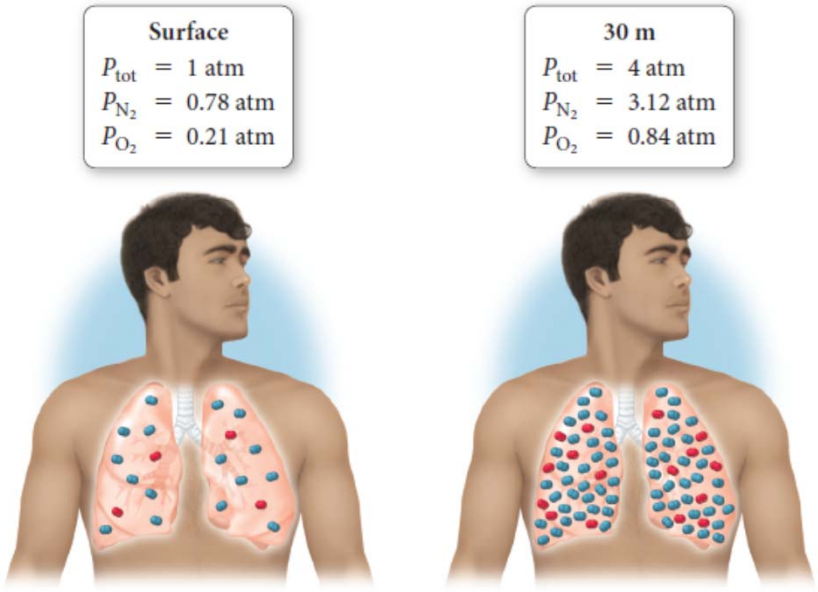
$$n = \frac{PV}{RT} = \frac{0.275 \text{ atm}(1.00 \text{ L})}{0.08206 \dfrac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}(298 \text{ K})} = 1.125 \times 10^{-2} \text{ mol Ar}$$

$$1.125 \times 10^{-2} \text{ mol Ar} \times \frac{39.95 \text{ g Ar}}{1 \text{ mol Ar}} = 0.449 \text{ g Ar}$$

# Deep-Sea Diving and Partial Pressures




▲ **FIGURE 5.13** Oxygen Partial Pressure Limits The partial pressure of oxygen in air at sea level is 0.21 atm. Partial pressures of oxygen below 0.1 atm and above 1.4 atm are dangerous to humans.




- When $P_{N2}$ increases beyond about 4 atm, a condition called nitrogen narcosis or *rapture of the deep* results.
- To avoid oxygen toxicity and nitrogen narcosis, deep-sea divers—those who descend beyond 50 m—breathe specialized mixtures of gases. One common mixture is heliox, a mixture of helium and oxygen.

# EXAMPLE 5.10 Partial Pressures and Mole Fractions

- A 12.5 L scuba diving tank contains a helium–oxygen (heliox) mixture made up of 24.2 g of He and 4.32 g of $O_2$ at 298 K. Calculate the mole fraction and partial pressure of each component in the mixture and the total pressure of the mixture.

**GIVEN:** $m_{He} = 24.2$ g, $m_{O_2} = 4.32$ g, $V = 12.5$ L, $T = 298$ K

**FIND:** $\chi_{He}$, $\chi_{O_2}$, $P_{He}$, $P_{O_2}$, $P_{total}$

Sol:

$$24.2\ \text{g He} \times \frac{1\ \text{mol He}}{4.00\ \text{g He}} = 6.05\ \text{mol He}$$

$$4.32\ \text{g } O_2 \times \frac{1\ \text{mol } O_2}{32.00\ \text{g } O_2} = 0.135\ \text{mol } O_2$$

$$\chi_{He} = \frac{n_{He}}{n_{He} + n_{O_2}} = \frac{6.05}{6.05 + 0.135} = 0.97817$$

$$\chi_{O_2} = \frac{n_{O_2}}{n_{He} + n_{O_2}} = \frac{0.135}{6.05 + 0.135} = 0.021827$$

$$P_{total} = \frac{\left(n_{He} + n_{O_2}\right)RT}{V}$$

$$= \frac{(6.05\ \text{mol} + 0.135\ \text{mol})\left(0.08206\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(298\ \text{K})}{12.5\ \text{L}}$$

$$= 12.099\ \text{atm}$$

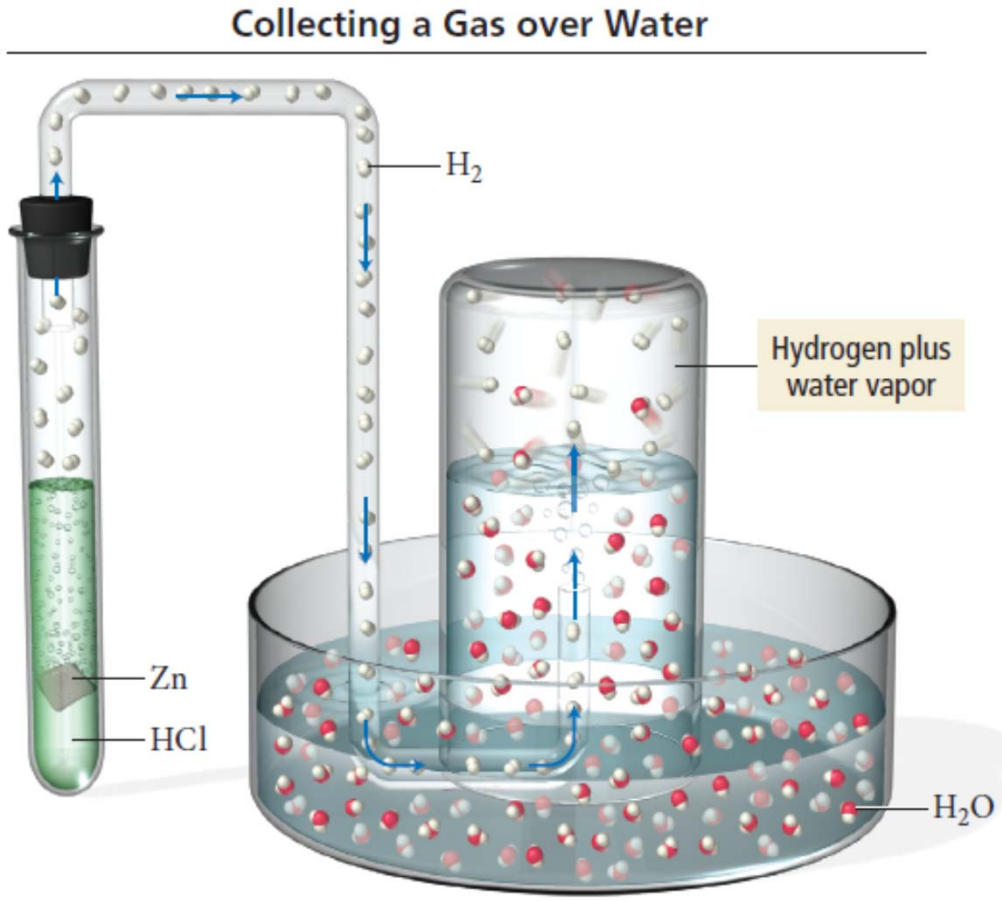
$$P_{He} = \chi_{He}\, P_{total} = 0.97817 \times 12.099\ \text{atm}$$

$$= 11.8\ \text{atm}$$

$$P_{O_2} = \chi_{O_2} P_{total} = 0.021827 \times 12.099\ \text{atm}$$

$$= 0.264\ \text{atm}$$

# Collecting Gases over Water



- The partial pressure of water in the mixture, called its **vapor pressure** , depends on temperature

**TABLE 5.4 Vapor Pressure of Water versus Temperature**

| Temperature (°C) | Pressure (mmHg) | Temperature (°C) | Pressure (mmHg) |
|---|---|---|---|
| 0 | 4.58 | 55 | 118.2 |
| 5 | 6.54 | 60 | 149.6 |
| 10 | 9.21 | 65 | 187.5 |
| 15 | 12.79 | 70 | 233.7 |
| 20 | 17.55 | 75 | 289.1 |
| 25 | 23.78 | 80 | 355.1 |
| 30 | 31.86 | 85 | 433.6 |
| 35 | 42.23 | 90 | 525.8 |
| 40 | 55.40 | 95 | 633.9 |
| 45 | 71.97 | 100 | 760.0 |
| 50 | 92.6 | | |

- Suppose we collect the hydrogen gas over water at a total pressure of 758.2 mmHg and a temperature of 25 °C. What is the partial pressure of the hydrogen gas

$$P_{\text{total}} = P_{H_2} + P_{H_2O}$$

$$758.2 \text{ mmHg} = P_{H_2} + 23.78 \text{ mmHg}$$

Therefore,

$$P_{H_2} = 758.2 \text{ mmHg} - 23.78 \text{ mmHg}$$

$$= 734.4 \text{ mmHg}$$

# EXAMPLE 5.11 Collecting Gases over Water

- In order to determine the rate of photosynthesis, the oxygen gas emitted by an aquatic plant is collected over water at a temperature of 293 K and a total pressure of 755.2 mmHg. Over a specific time period, a total of 1.02 L of gas is collected. What mass of oxygen gas (in grams) is formed?

**GIVEN:** $V = 1.02\ \text{L}, P_{\text{total}} = 755.2\ \text{mmHg}, T = 293\ \text{K}$

**FIND:** $\text{g O}_2$

**SOLUTION**

$$P_{O_2} = P_{\text{total}} - P_{H_2O}\,(20\,^\circ\text{C})$$

$$= 755.2\ \text{mmHg} - 17.55\ \text{mmHg}$$

$$= 737.65\ \text{mmHg}$$

$$n_{O_2} = \frac{P_{O_2}V}{RT}$$

$$737.65\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.97059\ \text{atm}$$

$$n_{O_2} = \frac{P_{O_2}V}{RT} = \frac{0.97059\ \text{atm}\,(1.02\ \text{L})}{0.08206\ \dfrac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\,(293\ \text{K})}$$

$$= 4.1175 \times 10^{-2}\ \text{mol}$$

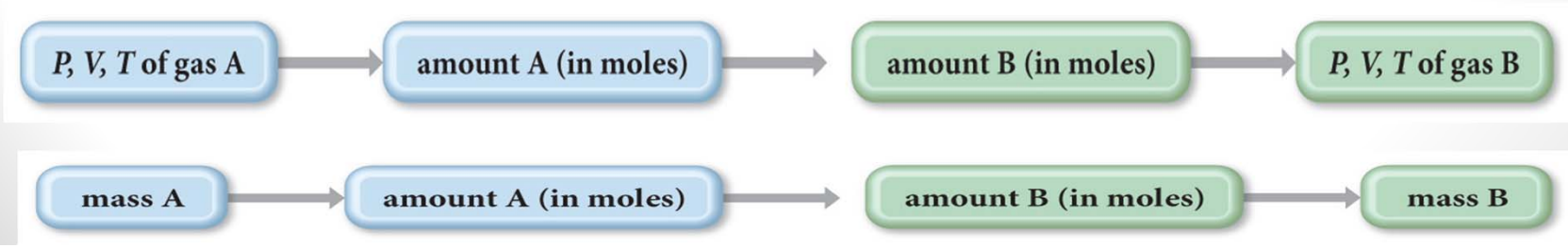
$$4.1175 \times 10^{-2}\ \text{mol}\ O_2 \times \frac{32.00\ \text{g}\ O_2}{1\ \text{mol}\ O_2} = 1.32\ \text{g}\ O_2$$

# 5.7 Gases in Chemical Reactions: Stoichiometry Revisited

Avogadro's law: $V \propto n$ (constant $T$ and $P$)

- As we have seen, stoichiometry involves relationships between amounts in moles.
- For stoichiometric calculations involving gases, we can use the ideal gas law to determine the amounts in moles from the volumes, or to determine the volumes from the amounts in moles.

$$n = \frac{PV}{RT} \qquad V = \frac{nRT}{P}$$



# EXAMPLE 5.12 Gases in Chemical Reactions

Methanol ($CH_3OH$) can be synthesized by the reaction:

$$CO(g) + 2\,H_2(g) \rightarrow CH_3OH(g)$$

What volume (in liters) of hydrogen gas, at a temperature of 355 K and a pressure of 738 mmHg, do we need to synthesize 35.7 g of methanol?

**GIVEN:** 35.7 g $CH_3OH$,
$T = 355$ K, $P = 738$ mmHg

**FIND:** $V_{H_2}$

# Sol:

$$35.7\ \text{g}\ \cancel{\text{CH}_3\text{OH}} \times \frac{1\ \text{mol}\ \text{CH}_3\text{OH}}{32.04\ \text{g}\ \cancel{\text{CH}_3\text{OH}}} = 1.1142\ \text{mol}\ \text{CH}_3\text{OH}$$

$$1.1142\ \text{mol}\ \cancel{\text{CH}_3\text{OH}} \times \frac{2\ \text{mol}\ \text{H}_2}{1\ \text{mol}\ \cancel{\text{CH}_3\text{OH}}} = 2.2284\ \text{mol}\ \text{H}_2$$

$$V_{\text{H}_2} = \frac{n_{\text{H}_2}RT}{P}$$

$$P = 738\ \cancel{\text{mmHg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 0.97105\ \text{atm}$$

$$V_{\text{H}_2} = \frac{(2.2284\ \cancel{\text{mol}})\left(0.08206 \frac{\text{L} \cdot \cancel{\text{atm}}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}}\right)(355\ \cancel{\text{K}})}{0.97105\ \cancel{\text{atm}}}$$

$$= 66.9\ \text{L}$$

# EXAMPLE 5.13 Using Molar Volume in Gas Stoichiometric Calculations

How many grams of water form when 1.24 L of $H_2$ gas at STP completely reacts with $O_2$?

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$

**GIVEN:** 1.24 L $H_2$

**FIND:** g $H_2O$

1 mol = 22.4 L (at STP)

**Sol:**

$$1.24\ \text{L}\ H_2 \times \frac{1\ \text{mol}\ H_2}{22.4\ \text{L}\ H_2} \times \frac{2\ \text{mol}\ H_2O}{2\ \text{mol}\ H_2O} \times \frac{18.02\ \text{g}\ H_2O}{1\ \text{mol}\ H_2O} = 0.998\ \text{g}\ H_2O$$

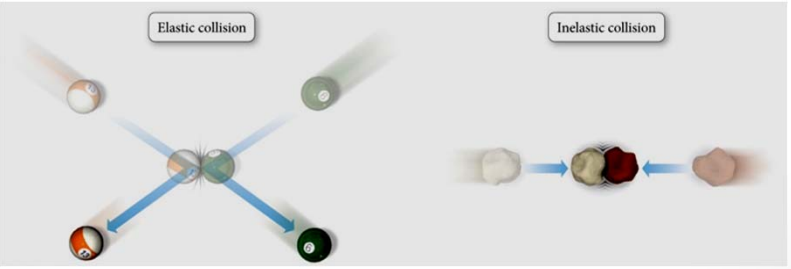
# 5.8 Kinetic Molecular Theory: A Model for Gases

- The simplest model for the behavior of gases is the **kinetic molecular theory**.
- In this theory, a gas is modeled as a collection of particles (either molecules or atoms, depending on the gas) in constant motion.

# Kinetic Molecular Theory

The basic postulates (or assumptions) of kinetic molecular theory are:

- The size of a particle is negligibly small.
- The average kinetic energy of a particle is proportional to the temperature in kelvins.
  - As you raise the temperature of the gas, the average speed of the particles increases. But not all the gas articles are moving at the same speed!
- The collision of one particle with another (or with the walls of its container) is completely elastic.
  - This means that when two particles collide, they may *exchange energy*, but there is no overall *loss of energy*

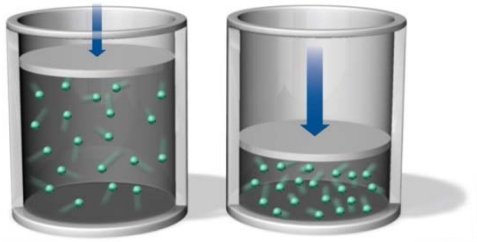


# The Nature of Pressure

- Because the gas particles are constantly moving, they strike the sides of the container with a force.
- The result of many particles in a gas sample exerting forces on the surfaces around them is a constant pressure.

- Boyle's Law says that the volume of a gas is inversely proportional to the pressure. More molecules w the container at any one instant, increasing the

$$P = \frac{F}{A}$$



# Gas Laws Explained – Charles"s Law

- Charles' s Law : the volume of a gas is directly proportional to the absolute temperature.
  - ✓ According to kinetic molecular theory, when we increase the temperature of a gas, the average speed, and thus the average kinetic energy, of the particles increases.
  - ✓ The greater volume spreads the collisions out over a greater surface area, so that the pressure is unchanged.

Charles's law: $V \propto T$ (constant $P$ and $n$)

# Gas Laws Explained – Avogadro"s Law

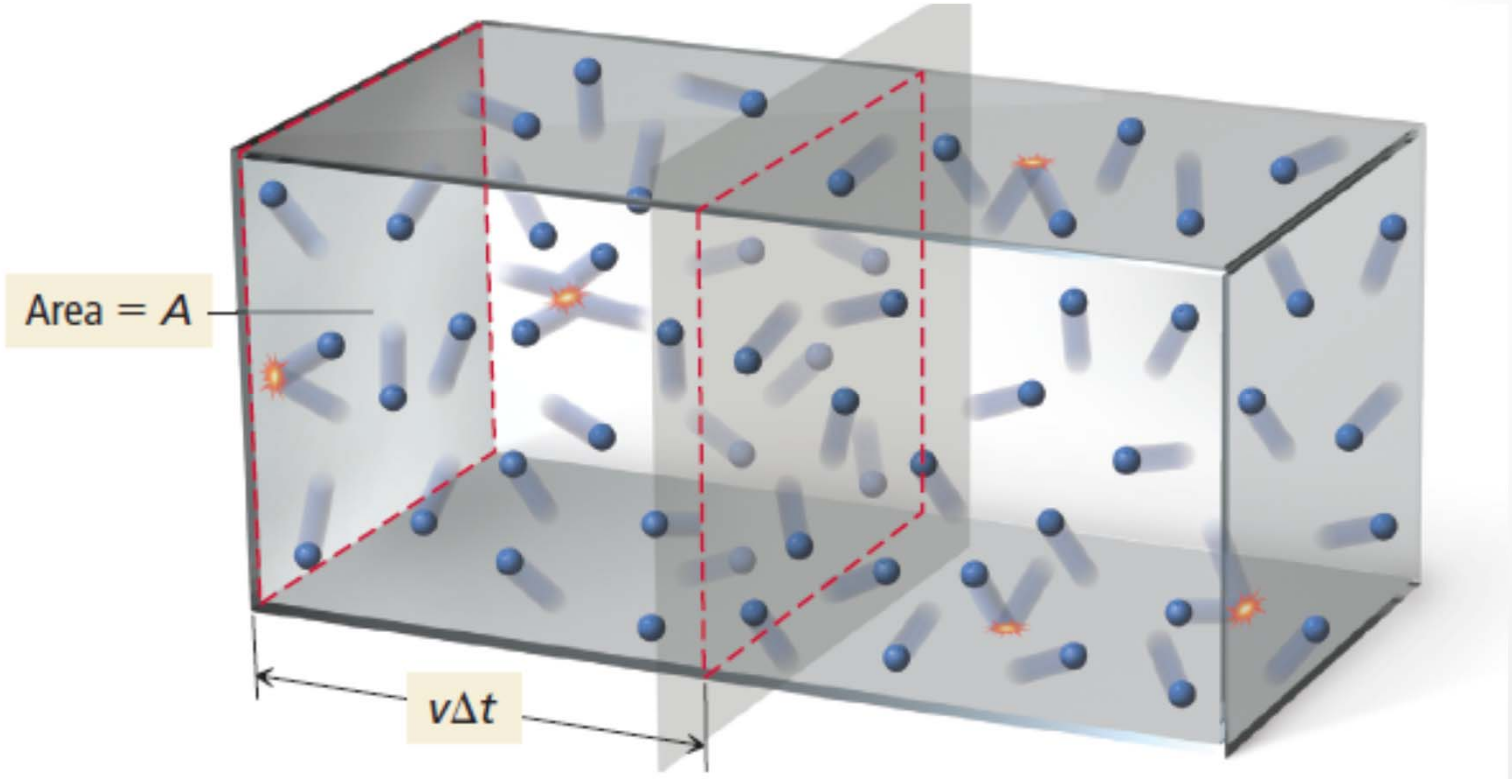
- Avogadro's Law: the volume of a gas is directly proportional to the number of gas molecules
  - Increasing the number of gas molecules causes more of them to hit the wall at the same time.
  - To keep the pressure constant, the volume must then increase.

Avogadro's law: $V \propto n$ (constant $T$ and $P$)

# Gas Laws Explained – Dalto's Law

- Dalton's law: the total pressure of a gas mixture is the sum of the partial pressures.
- According to kinetic molecular theory, the particles have negligible size and they do not interact.
  - ✓ Particles of different masses have the same average kinetic energy at a given temperature.
  - ✓ Because the average kinetic energy is the same, the total pressure of the collisions is the same.

# Kinetic Molecular Theory and the Ideal Gas Law



# Kinetic Molecular Theory and the Ideal Gas Law

$$P = \frac{F_{\text{total}}}{A}$$

$$F_{\text{collision}} = m\frac{\Delta v}{\Delta t}$$

$$F_{\text{collision}} = m\frac{2v}{\Delta t}$$

Number of collisions $\propto$ number of particles within $v\,\Delta t$

$$\propto v\,\Delta t \times A \times \frac{n}{V}$$

Volume

Density of particles

$$F_{\text{total}} = F_{\text{collision}} \times \text{number of collisions}$$

$$\propto m\frac{2v}{\Delta t} \times v\,\Delta t \times A \times \frac{n}{V}$$

$$\propto mv^2 \times A \times \frac{n}{V}$$

$$P = \frac{F_{\text{total}}}{A}$$

$$\propto \frac{mv^2 \times A \times \frac{n}{V}}{A}$$

$$P \propto mv^2 \times \frac{n}{V}$$

# Kinetic Molecular Theory and the Ideal Gas Law

$$P = \frac{F_{\text{total}}}{A}$$

$$\propto \frac{mv^2 \times \cancel{A} \times \frac{n}{V}}{\cancel{A}}$$

$$P \propto mv^2 \times \frac{n}{V}$$

$$mv^2 \propto T$$

$$P \propto \frac{T \times n}{V}$$

$$PV \propto nT$$

$$PV = nRT$$

# Temperature and Molecular Velocities

- According to kinetic molecular theory, particles of different masses have the same average kinetic energy at a given temperature.
- The kinetic energy of a particle depends on its mass and velocity according to the equation

$$\mathrm{KE} = \frac{1}{2}mv^2$$

- In a gas mixture at a given temperature, lighter particles travel faster (on average) than heavier ones.
- the root mean square velocity ($u_{rms}$) of a particle

$$u_{rms} = \sqrt{\overline{u^2}}$$

$$\mathrm{KE}_{avg} = \tfrac{1}{2} N_A m \overline{u^2}$$

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

$$(1/2)\, N_A m \overline{u^2} = (3/2)RT$$

$$\overline{u^2} = \frac{(3/2)RT}{(1/2)N_A m} = \frac{3RT}{N_A m}$$

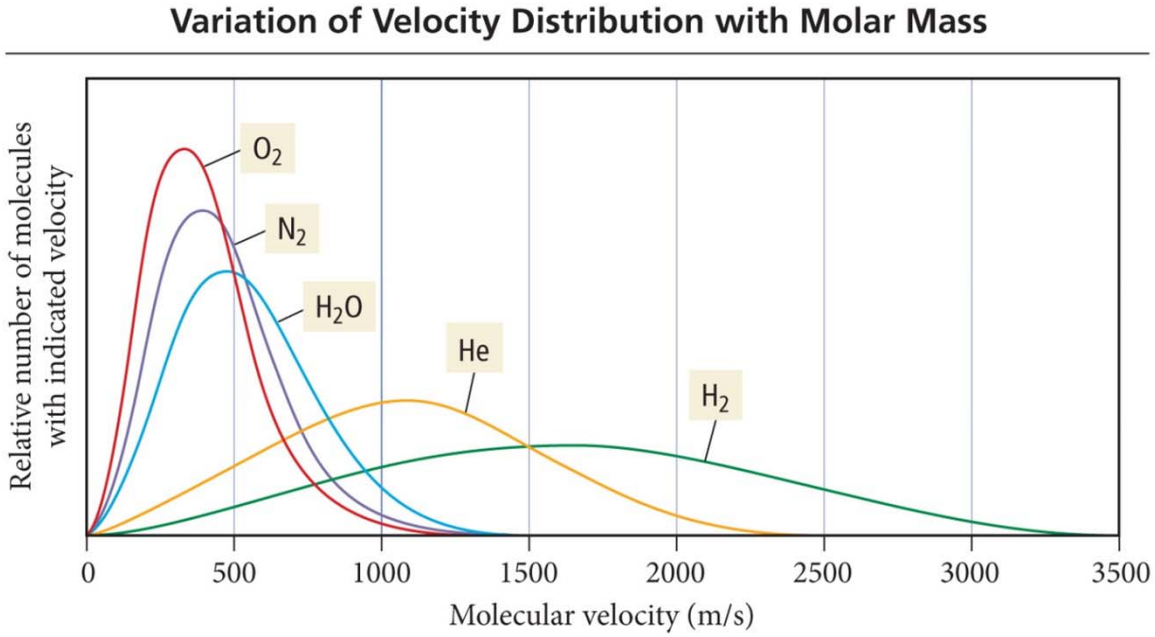
$$\sqrt{\overline{u^2}} = u_{rms} = \sqrt{\frac{3RT}{N_A m}}$$

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

# Molecular Speed versus Molar Mass

- To have the same average kinetic energy, heavier molecules must have a slower average speed.

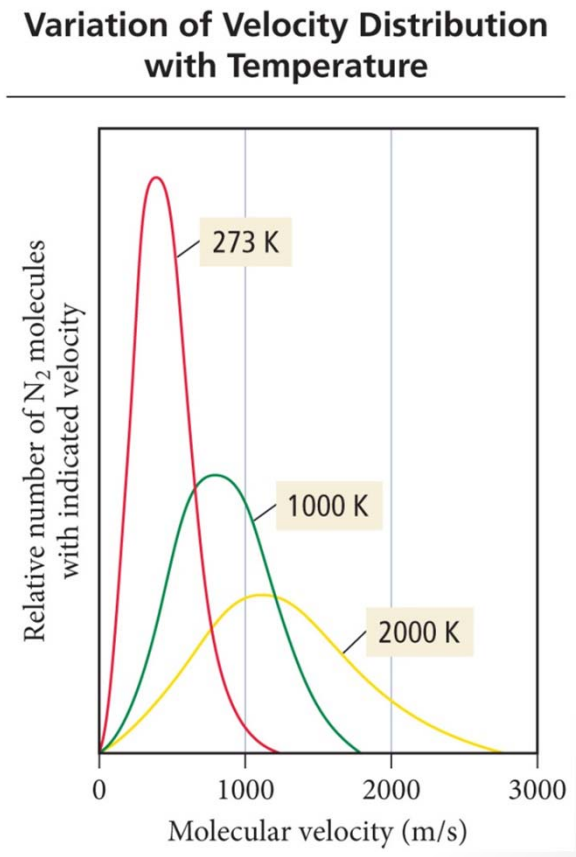
$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$



# Temperature versus Molecular Speed

- As the temperature of a gas sample increases, the velocity distribution of the molecules shifts toward higher velocity.

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$



# EXAMPLE 5.14 Root Mean Square Velocity

- Calculate the root mean square velocity of oxygen molecules at 25 °C.

$$T = 25 + 273 = 298\ \text{K}$$

$$\mathcal{M} = \frac{32.00\ \text{g O}_2}{1\ \text{mol O}_2} \times \frac{1\ \text{kg}}{1000\ \text{g}} = \frac{32.00 \times 10^{-3}\ \text{kg O}_2}{1\ \text{mol O}_2}$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

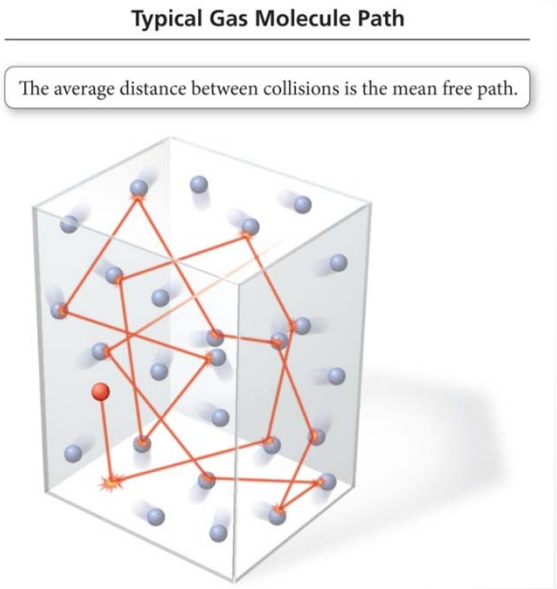
$$= \sqrt{\frac{3\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(298\ \text{K})}{\frac{32.00 \times 10^{-3}\ \text{kg O}_2}{1\ \text{mol O}_2}}}$$

$$= \sqrt{2.32 \times 10^5 \frac{\text{J}}{\text{kg}}}$$

$$= \sqrt{2.32 \times 10^5 \frac{\frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}{\text{kg}}} = 482\ \text{m/s}$$

# Mean Free Path

- Molecules in a gas travel in straight lines until they collide with another molecule or the container.
- The average distance a molecule travels between collisions is called the **mean free path.**
- Mean free path decreases as the pressure increases.

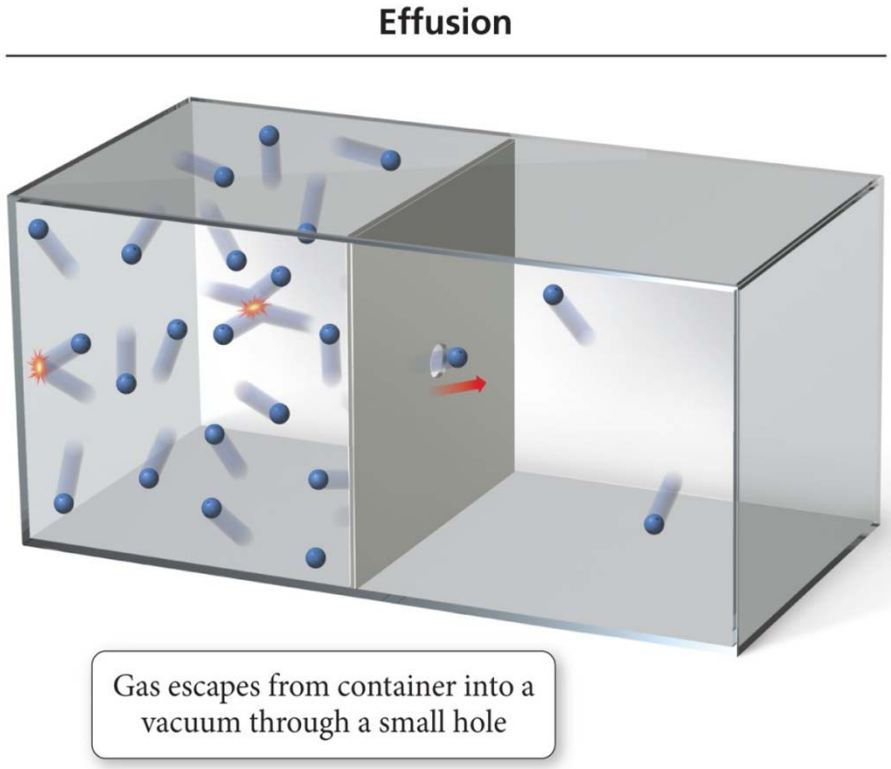


# Diffusion and Effusion

- The process of a collection of molecules spreading out from high concentration to low concentration is called **diffusion.**
- The process by which a collection of molecules escapes through a small hole into a vacuum is called **effusion.**
  - ✓ The rates of diffusion and effusion of a gas are both related to its rms average velocity.
  - ✓ For gases at the same temperature, this means that the rate of gas movement is inversely proportional to the square root of its molar mass.

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

# Effusion


Effusion
Gas escapes from container into a vacuum through a small hole

# Graham's Law of Effusion

- For two different gases at the same temperature, the ratio of their rates of effusion is given by the following equation

$$\frac{\text{rate}_A}{\text{rate}_B} = \sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

# EXAMPLE 5.15 Graham's Law of Effusion

- An unknown gas effuses at a rate that is 0.462 times that of nitrogen gas (at the same temperature). Calculate the molar mass of the unknown gas in g/mol.

Sol:

$$\frac{\text{rate}_{\text{unk}}}{\text{rate}_{\text{N}_2}} = \sqrt{\frac{\mathcal{M}_{\text{N}_2}}{\mathcal{M}_{\text{unk}}}}$$

$$\mathcal{M}_{\text{unk}} = \frac{\mathcal{M}_{\text{N}_2}}{\left(\frac{\text{rate}_{\text{unk}}}{\text{rate}_{\text{N}_2}}\right)^2}$$

$$= \frac{28.02 \text{ g/mol}}{(0.462)^2}$$

$$= 131 \text{ g/mol}$$

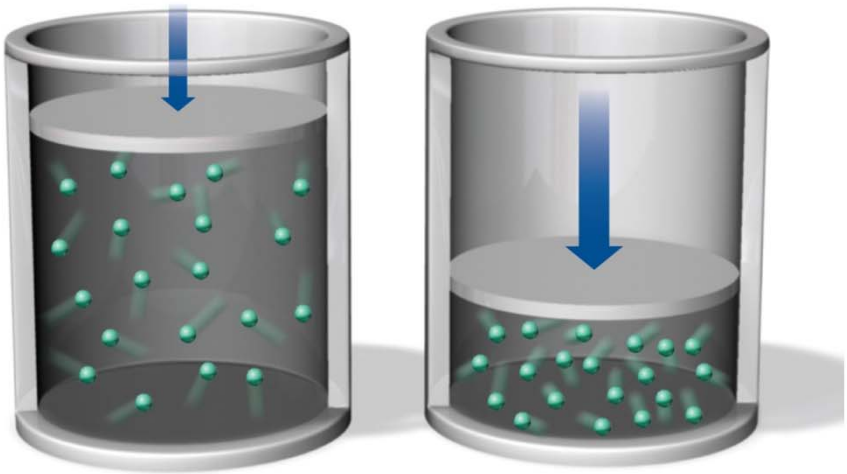
# Real Gases

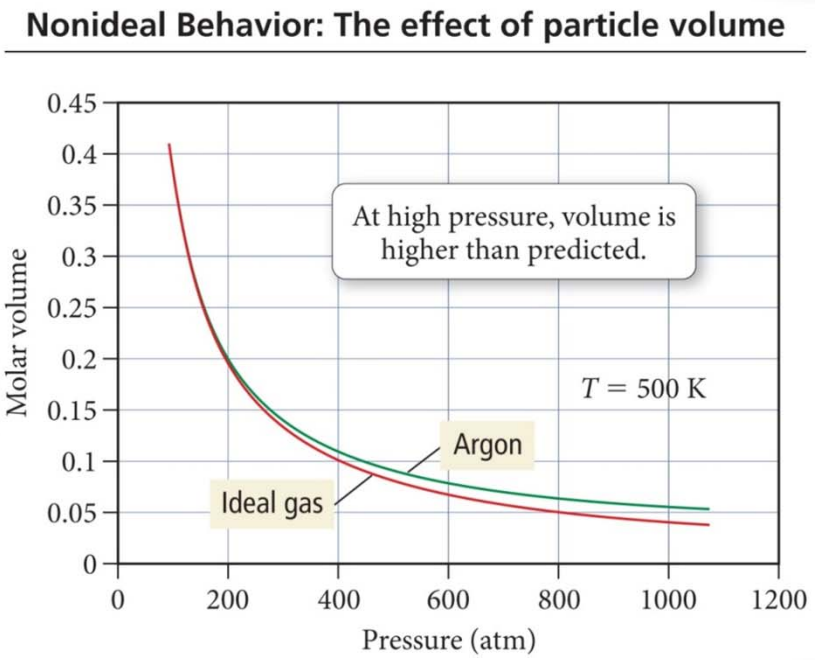
- Ideal gas laws assume
  - no attractions between gas molecules.
  - gas molecules do not take up space.
    - Based on the kinetic-molecular theory
- At low temperatures and high pressures these assumptions are not valid.

# The Effect of the Finite Volume of Gas Particles

- At low pressures, the molar volume of argon is nearly identical to that of an ideal gas.
- But as the pressure increases, the molar volume of argon becomes *greater than* that of an ideal gas.
    - At the higher pressures, the argon atoms themselves occupy a significant portion of the gas volume, making the actual volume greater than that predicted by the ideal gas law.

# Real Gas Behavior






Because real molecules take up space, the molar volume of a real gas is larger than predicted by the ideal gas law at high pressures.

# Modification of the Ideal Gas Equation

- In 1873, Johannes van der Waals (1837–1923) modified the ideal gas equation to fit the behavior of real gases at high pressure.
- The molecular volume makes the real volume larger than the ideal gas law would predict.
- van der Waals modified the ideal gas equation to account for the molecular volume.
  - ✓ ***b*** is called a **van der Waals constant** and is different for every gas because their molecules are different sizes.

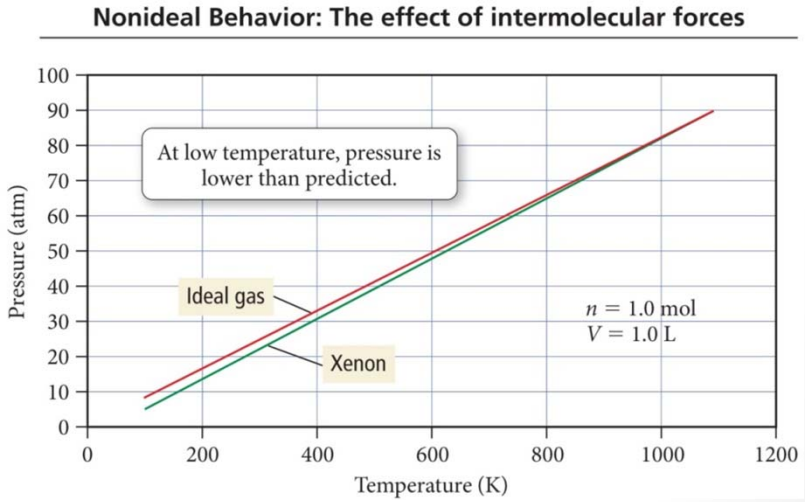
$$V = \frac{nRT}{P} \qquad V = \frac{nRT}{P} + nb$$

# The Effect of Intermolecular Attractions

- At high temperature, the pressure of the gases is nearly identical to that of an ideal gas.
- But at lower temperatures, the pressure of gases is *less than* that of an ideal gas.
  - ✓ At the lower temperatures, the gas atoms spend more time interacting with each other and less time colliding with the walls, making the actual pressure less than that predicted by the ideal gas law.

- Van der Waals modified the ideal gas equation to account for the intermolecular attractions.
  - ✓ *a* is another **van der Waals constant** and is different for every gas because their molecules have different strengths of attraction.

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



# Van der Waals Equation

- Combining the equations to account for molecular volume and intermolecular attractions we get the following equation.

$$[P + a(\frac{n}{V})^2] \times [V - nb] = nRT$$

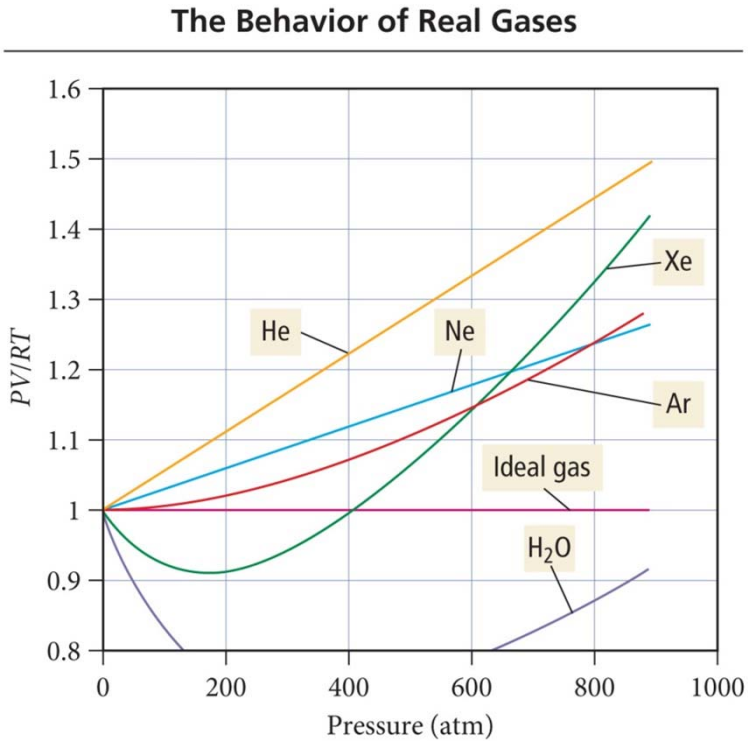
Correction for intermolecular forces

Correction for particle volume

**TABLE 5.5 Van der Waals Constants for Common Gases**

| Gas | $a\,(L^2 \cdot atm/mol^2)$ | $b$ (L/mol) |
|---|---|---|
| He | 0.0342 | 0.02370 |
| 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 |
| $H_2O$ | 5.46 | 0.0305 |
| $CH_4$ | 2.25 | 0.0428 |
| $CO_2$ | 3.59 | 0.0427 |
| $CCl_4$ | 20.4 | 0.1383 |

# Real Gases




- A plot of *PV*/*RT* versus *P* for 1 mole of a gas shows the difference between real and ideal gases.
- It reveals a curve that shows the *PV*/*RT* ratio for a real gas is generally lower than ideal for "low" pressures — meaning that the most important factor is the intermolecular attractions.
- It reveals a curve that shows the *PV*/*RT* ratio for a real gas is generally higher than ideal for "high" pressures— meaning that the most important factor is the molecular volume.