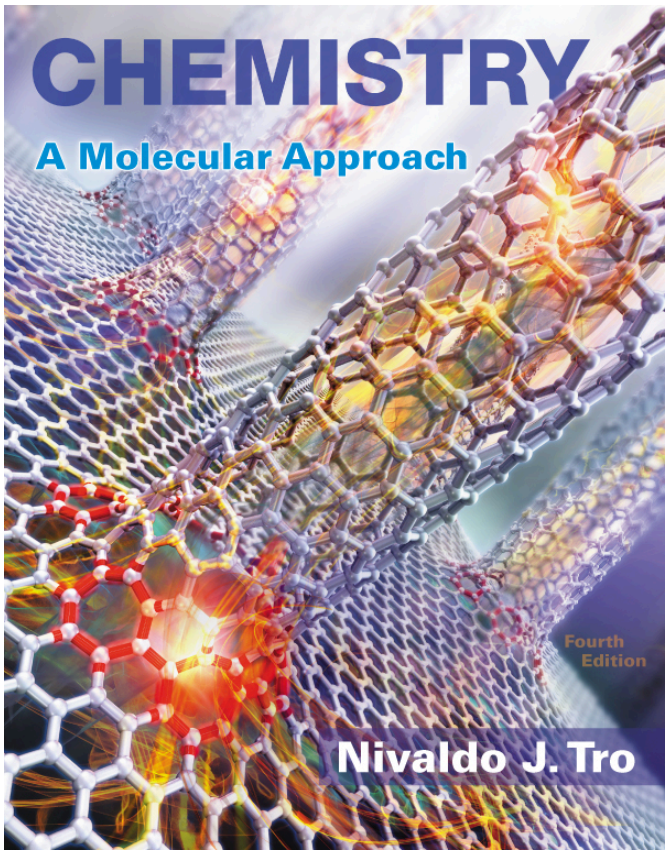

Lecture Presentation

Chapter 5

Gases

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Supersonic Skydiving and the Risk of Decompression

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Gas

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

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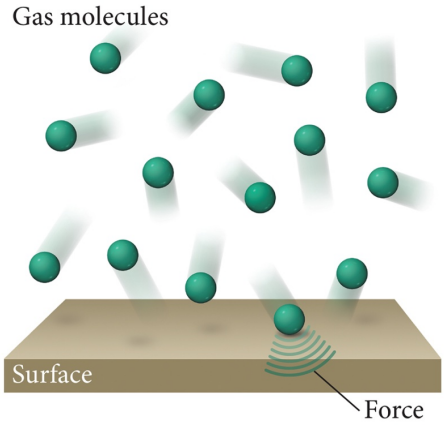
Gas Pressure

- **Pressure** is the force exerted per unit area by gas molecules as they strike the surfaces around them.
- Just as a ball exerts a force when it bounces against a wall, a gaseous atom or molecule exerts a force when it collides with a surface.



Collisions with surfaces create pressure.

$$\text{Pressure} = \frac{\text{force}}{\text{area}} = \frac{F}{A}$$

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Pressure: The Result of Molecular Collision

- Gas pressure is a result of the constant movement of the gas molecules and their collisions with the surfaces around them.
- The pressure of a gas depends on several factors:
  - Number of gas particles in a given volume
  - Volume of the container
  - Average speed of the gas particles

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Gas Pressure

- The total pressure exerted by a gas depends on several factors, including the concentration of gas molecules in the sample.
  - The higher the concentration, the greater the pressure.
- As volume increases, concentration of gas molecules decreases (number of molecules does not change, but since the volume increases, the *concentration* goes down).
  - This, in turn, results in fewer molecular collisions, which results in lower pressure.

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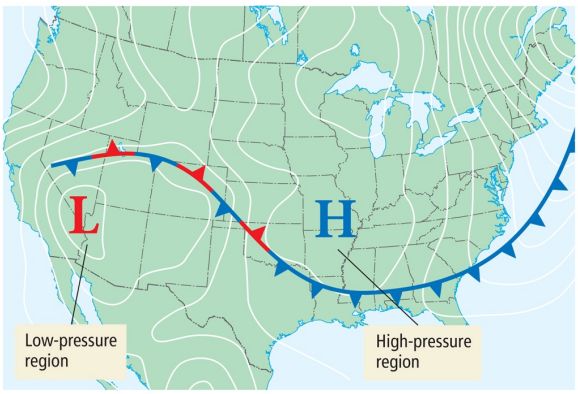
Atmospheric Pressure Effects

- Variation in pressure in Earth's atmosphere creates wind and pressure.
  - The H on this map indicates a region of high pressure, usually associated with clear weather.
  - The L indicates a region of low pressure, usually associated with unstable weather.
- The number of gas particles in a given volume decreases with increasing altitude.
  - *Pressure decreases with increasing altitude.*



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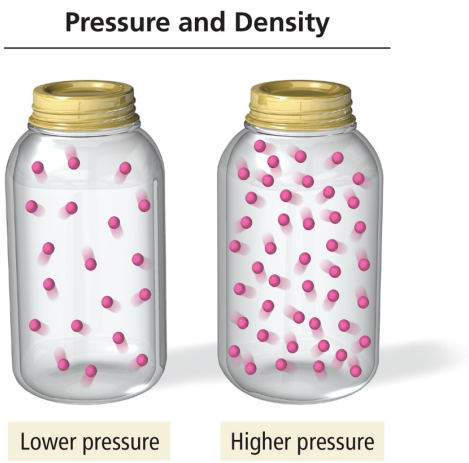
Gas Pressure

- Pressure exerted by a gas is dependent on the number of gas particles in a given volume.
- The fewer 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.



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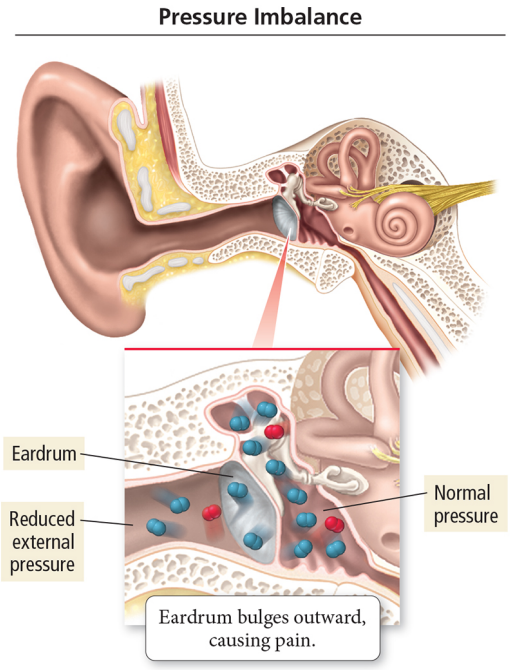
Pressure Imbalance in the Ear

- If there is a difference in pressure across the eardrum membrane, the membrane will be pushed out—what we commonly call a "popped eardrum."



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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.
- A competition is established between the pressures of the atmosphere and the gas.
- The difference in the liquid levels is a measure of the difference in pressure between the gas and the atmosphere.

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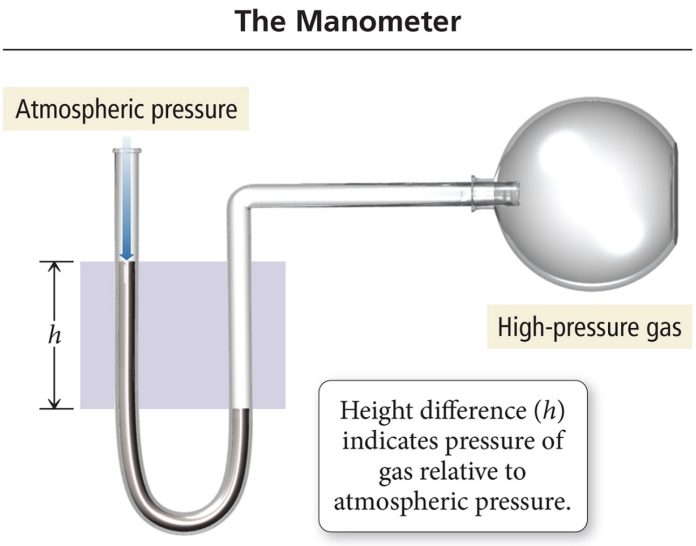
The Manometer



For this sample, the gas pressure is *greater than* the atmospheric pressure; the mercury level on the left side of the tube is *higher than* the level on the right.

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Blood Pressure

- Blood pressure is the force within arteries that drives the circulation of blood throughout the body.
- Blood pressure is measured with an instrument called a sphygmomanometer—an inflatable cuff equipped with a pressure gauge and a stethoscope.

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Blood Pressure

TABLE 5.2 Blood Pressure Ranges

Blood Pressure	Systolic (mmHg)	Diastolic (mmHg)
Hypotension	<100	<60
Normal	100–119	60–79
Prehypertension	120–139	80–89
Hypertension Stage 1	140–159	90–99
Hypertension Stage 2	>160	>100

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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.

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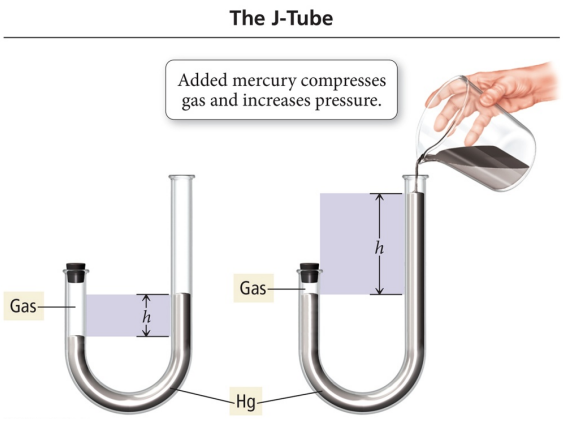
Boyle's Law: Robert Boyle (1627–1691)

- Robert Boyle and Robert Hooke used a J-tube to measure the volume of a sample of gas at different pressures.
- They trapped a sample of air in the J-tube and added mercury to increase the pressure on the gas.



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

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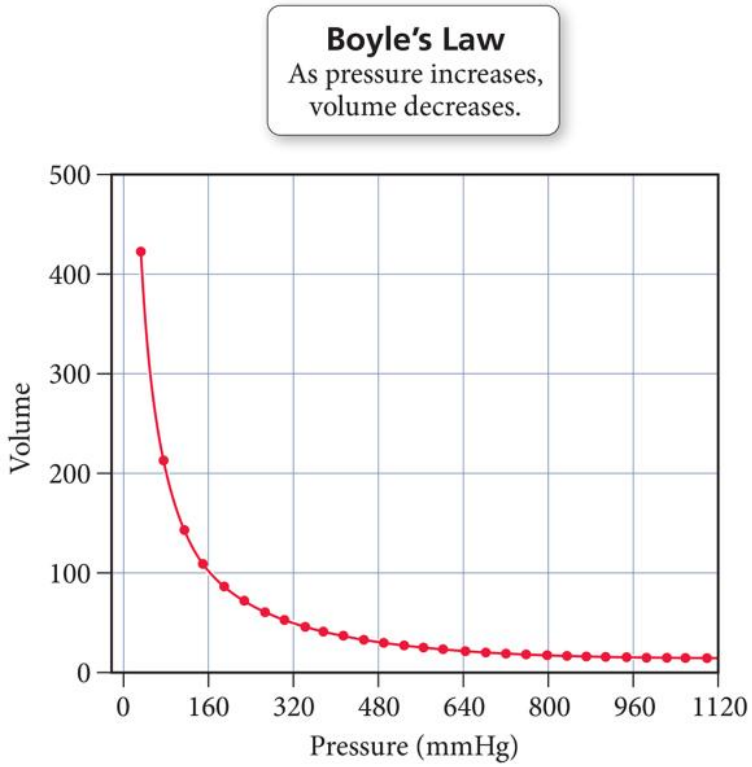
Boyle's Law



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Boyle's Law

- The pressure of a gas is inversely proportional to its volume.
  - Constant *T* and amount of gas.
  - Graph *P* vs. *V* is a curve.
  - Graph *P* vs. 1/*V* is a straight line.
- As *P* increases, *V* decreases by the same factor.
- $P \times V$ = constant
- $P_1 \times V_1 = P_2 \times V_2$

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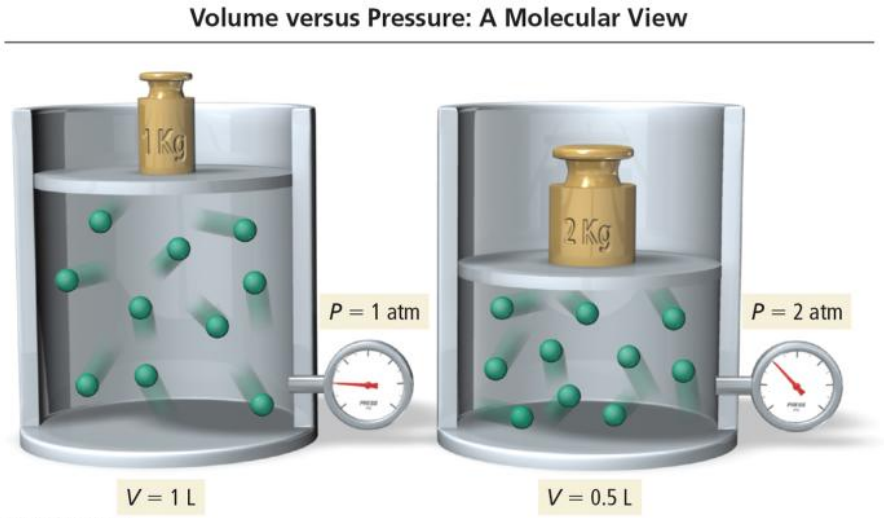
Molecular Interpretation of Boyle's Law



As the volume of a gas sample decreases, gas molecules collide with surrounding surfaces more frequently, resulting in greater pressure.

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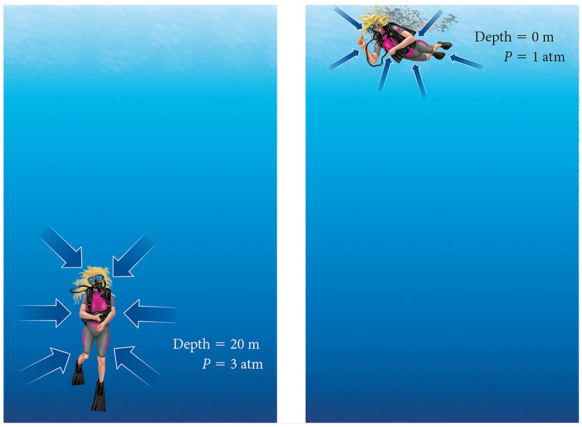
Boyle's Law and Diving

- 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.



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

Always exhale when rising!

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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

(if T is measured in kelvins)

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

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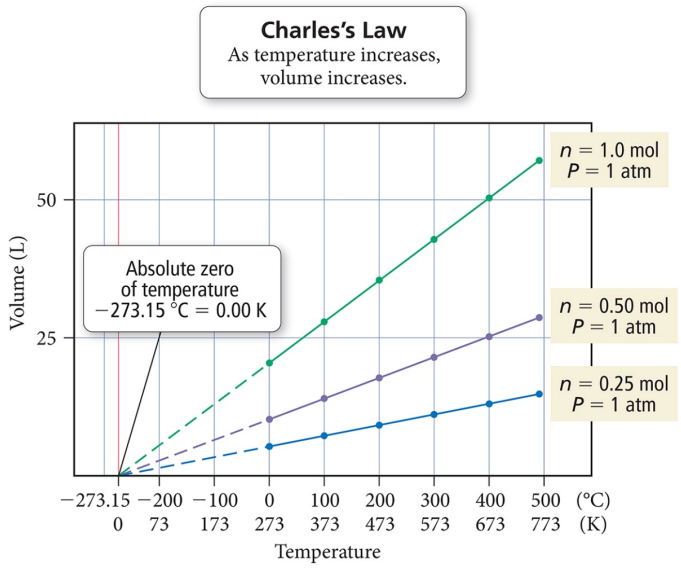
Charles's Law



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**.

The extrapolated lines cannot be measured experimentally because all gases condense into liquids before –273.15 °C is reached.

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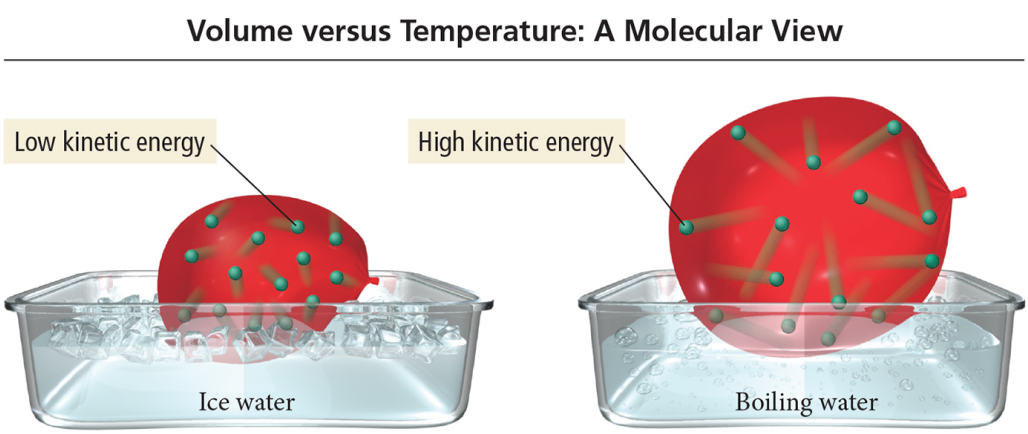
Charles's Law—A Molecular View



If we move a balloon from an ice water bath to a boiling water bath, its volume expands as the gas particles within the balloon move faster (due to the increased temperature) and collectively occupy more space.

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Charles's Law—A Molecular View

- When the temperature of a gas sample increases, the gas particles move faster.
  - Collisions with the walls are more frequent.
  - The force exerted with each collision is greater.
- The only way for the pressure (the force per unit area) to remain constant is for the gas to occupy a larger volume so that collisions become less frequent and occur over a larger area.

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Charles's Law

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Avogadro's Law: Volume and Amount (Moles)

- Volume is directly proportional to the number of gas molecules.
  - ***V*** = constant × ***n***
  - Constant *P* and *T*
  - More gas molecules = larger volume
- Count the number of gas molecules by **moles**.
- Equal volumes of gases contain equal numbers of molecules.
  - ***The gas doesn't matter.***

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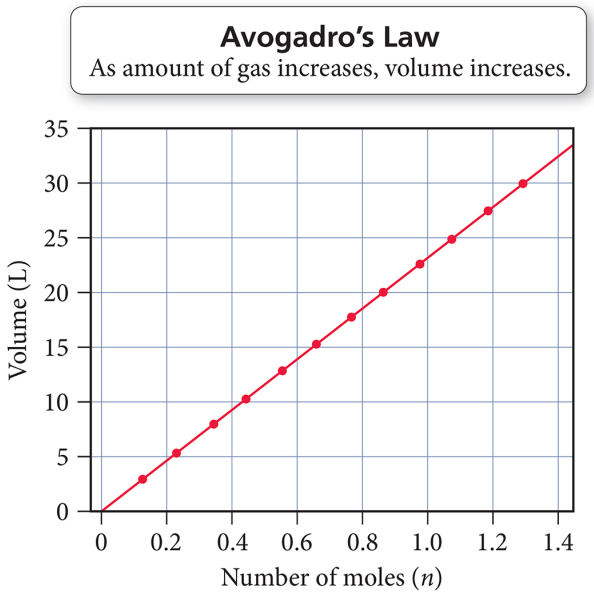
Avogadro's Law



When the amount of gas in a sample increases at constant temperature and pressure, its volume increases in direct proportion because the greater number of gas particles fill more space.

The volume of a gas sample increases linearly with the number of moles of gas in the sample.

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Ideal Gas Law

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

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

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

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

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

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Ideal Gas Law

- By combining the gas laws, we can write a general equation.
- ***R*** is called the **gas constant.**
- The value of ***R*** depends on the units of *P* and *V*.
  - We will use $PV = nRT$ and convert *P* to atm and *V* to liters.
- The other gas laws are found in the ideal gas law if two variables are kept constant.
- The ideal gas law allows us to find one of the variables if we know the other three.

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

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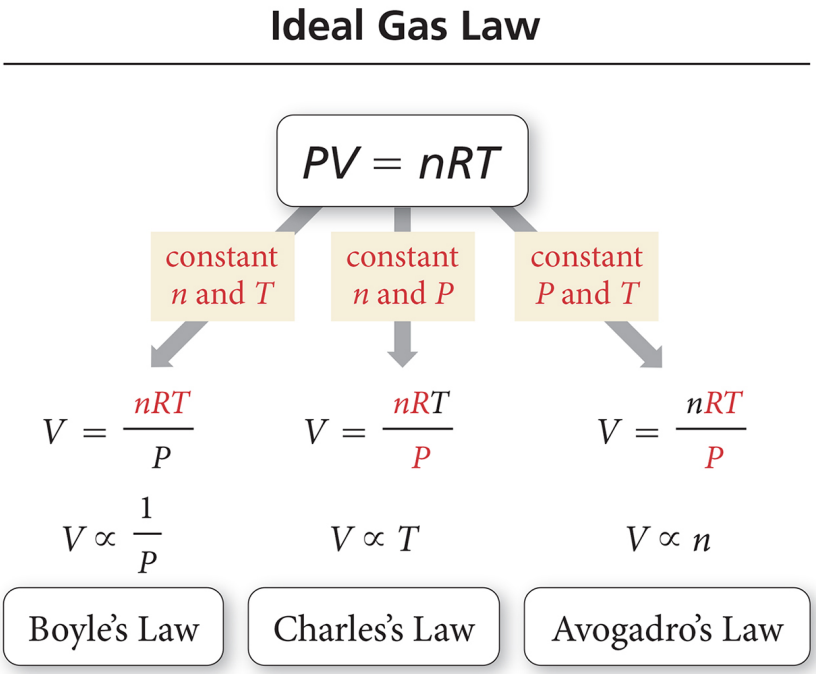
Ideal Gas Law



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Standard Conditions

- Because the volume of a gas varies with pressure and temperature, chemists have agreed on a set of conditions to report our measurements so that comparison is easy.
  - We call these **standard conditions**.
  - STP
- Standard pressure = 1 atm
- Standard temperature = 273 K = 0 ˚C

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Molar Volume

- The volume occupied by one mole of a substance is its **molar volume** at STP (*T* =273 K or 0 ˚C and P = 1atm).

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

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

$$= 22.4 \text{ L}$$

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Molar Volume at STP

- Solving the ideal gas equation for the volume of 1 mol of gas at STP gives 22.4 L.
  - 6.022×10^{23} molecules of gas
  - Notice that the gas is immaterial.
- We call the volume of 1 mole of gas at STP the **molar volume**.
  - It is important to recognize that one mole measurements of different gases have different masses, even though they have the same volume.

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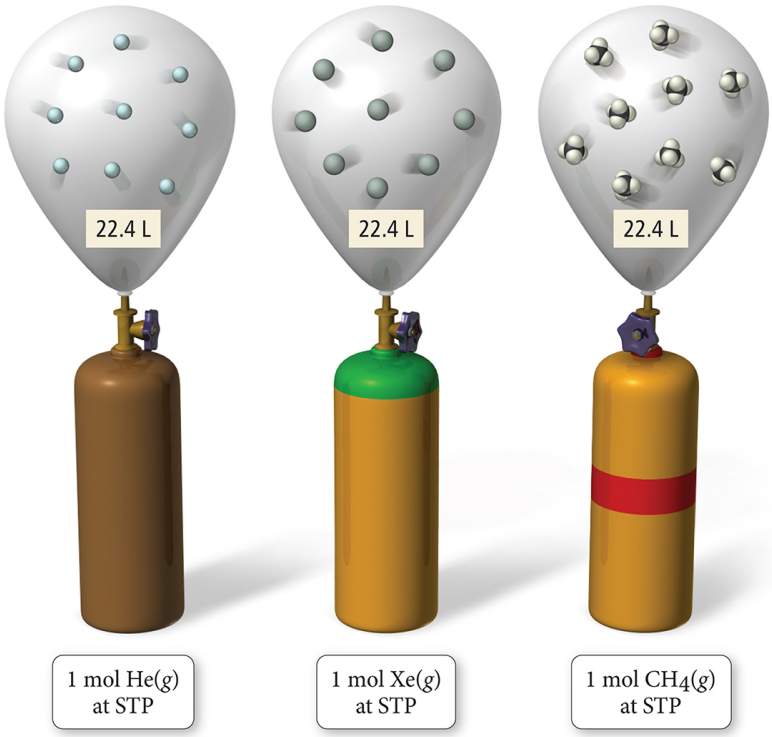
Molar Volume at STP



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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.

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

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Density of a Gas at STP

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

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

$$d_{\text{N}_2} = \frac{28.02\ \text{g/mol}}{22.4\ \text{L/mol}} = 1.25\ \text{g/L}$$

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Gas Density

- **Density is directly proportional to molar mass.**

$$PV = nRT$$

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

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

Molar density | Molar mass | Density in grams/liter

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

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Molar Mass of a Gas

- One of the methods chemists use to determine the molar mass of an unknown substance is to heat a weighed sample until it becomes a gas; measure the temperature, pressure, and volume; and then use the ideal gas law.

$$\text{Molar mass} = \frac{\text{mass } (m)}{\text{moles } (n)}$$

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Mixtures of Gases

- Many gas samples are not pure but are mixtures of gases.
- Dry air, for example, is a mixture containing nitrogen, oxygen, argon, carbon dioxide, and a few other gases in trace amounts.

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

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Mixtures of Gases

- Therefore, in certain applications, the mixture can be thought of as one gas.
  - 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.

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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.

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

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Partial Pressure

- The pressure due to any individual component in a gas mixture is its **partial pressure (P_n)**.
- We can calculate partial pressure from the ideal gas law by assuming that each gas component acts independently.

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

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Dalton's Law of Partial Pressures

- 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) as follows:

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

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

$$P_{total} = P_a + P_b + P_c + \ldots$$

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Dalton's Law of Partial Pressures

P total is the total pressure and P_a, P_b, P_c, . . . are the partial pressures of the components. This relationship is known as Dalton's law of partial pressures.

$$\begin{aligned} P_{total} &= P_a + P_b + P_c + \ldots \\ &= n_a \frac{RT}{V} + n_b \frac{RT}{V} + n_c \frac{RT}{V} + \ldots \\ &= (n_a + n_b + n_c + \ldots) \frac{RT}{V} \\ &= (n_{total}) \frac{RT}{V} \end{aligned}$$

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Mole Fraction

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

$$\frac{P_a}{P_{total}} = \frac{n_a(RT/V)}{n_{total}(RT/V)} = \frac{n_a}{n_{total}} \qquad \chi_a = \frac{n_a}{n_{total}}$$

- The number of moles of a component in a mixture divided by the total number of moles in the mixture is the **mole fraction**.

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

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

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

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Mole Fraction

- The partial pressure of a component in a gaseous mixture is its mole fraction multiplied by the total pressure.
- For gases, the mole fraction of a component is equivalent to its percent by volume divided by 100%.
  - Nitrogen has a 78% composition of air; find its partial pressure.

$$P_{N_2} = 0.78 \times 1.00 \text{ atm}$$
$$= 0.78 \text{ atm}$$

$$P_{total} = P_{N_2} + P_{O_2} + P_{Ar}$$
$$P_{total} = 0.78 \text{ atm} + 0.21 \text{ atm} + 0.01 \text{ atm}$$
$$= 1.00 \text{ atm}$$

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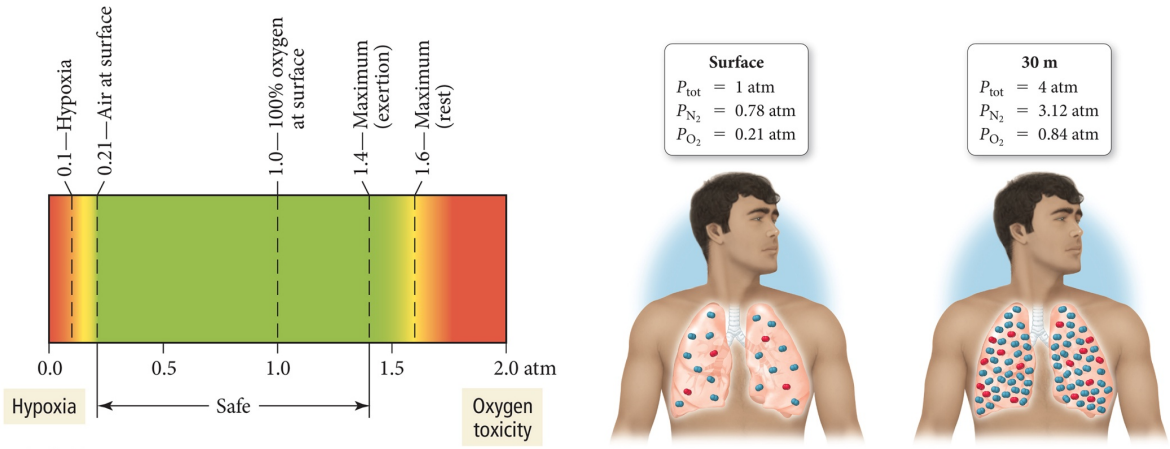
Deep-Sea Diving and Partial Pressures



When a diver breathes compressed air, the abnormally high partial pressure of oxygen in the lungs leads to an elevated concentration of oxygen in body tissues.

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Collecting Gases

- Gases are often collected by having them displace water from a container.
- The problem is that, because water evaporates, there is also water vapor in the collected gas.
- The partial pressure of the water vapor, called the **vapor pressure**, depends only on the temperature.
  - You can use a table to find out the partial pressure of the water vapor in the gas you collect.
  - If you collect a gas sample with a total pressure of 758.2 mmHg* at 25 ˚C, the partial pressure of the water vapor will be 23.78 mmHg, so the partial pressure of the dry gas will be 734.4 mmHg. (See Table 5.4.)

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Vapor Pressure of Water

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		

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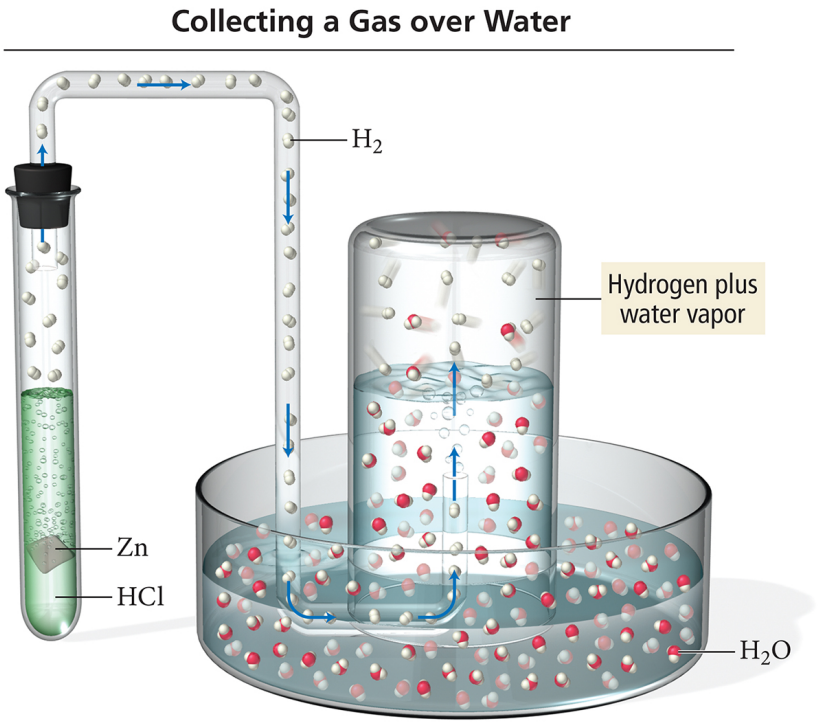
Collecting Gas by Water Displacement



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Reactions Involving Gases

- In reactions involving reactants or products, we often specify the quantity of a gas in terms of its volume at a given temperature and pressure.
  - 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.

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

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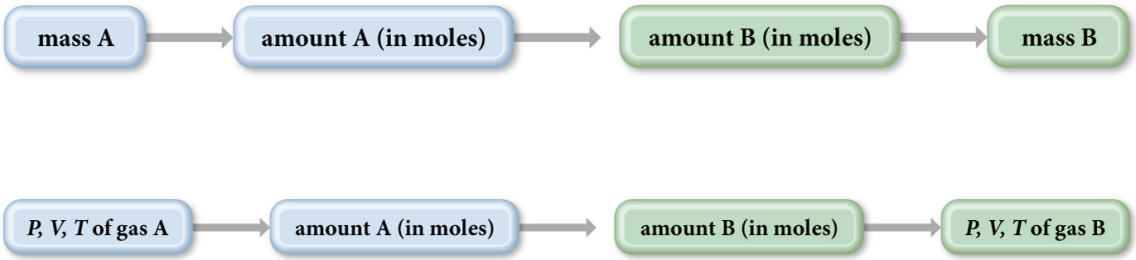
Reactions Involving Gases

- When gases are at STP, use 1 mol = 22.4 L.
- The pressures here could also be partial pressures.
- The general conceptual plan for these kinds of calculations is as follows:



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Molar Volume and Stoichiometry

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

$$2\ H_2\ (g) + O_2\ (g) \longrightarrow 2\ H_2O\ (g)$$

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Properties of Gases

- Expand to completely fill their container
- Take the shape of their container
- Low density, much less than solid or liquid state
- Compressible
- Mixtures of gases are always homogeneous fluids.

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Kinetic Molecular Theory

- 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.

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Kinetic Molecular Theory

- The particles of the gas (either atoms or molecules) are constantly moving.
- The attraction between particles is negligible.
- When the moving gas particles hit another gas particle or the container, they do not stick, but they bounce off and continue moving in another direction.
- There is a lot of empty space between the gas particles compared to the size of the particles.

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Kinetic Molecular Theory

- The average kinetic energy of the gas particles is directly proportional to the Kelvin temperature.
  - As you raise the temperature of the gas, the average speed of the particles increases.
    - But not all the gas particles 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*.
    - Any kinetic energy lost by one particle is completely gained by the other.

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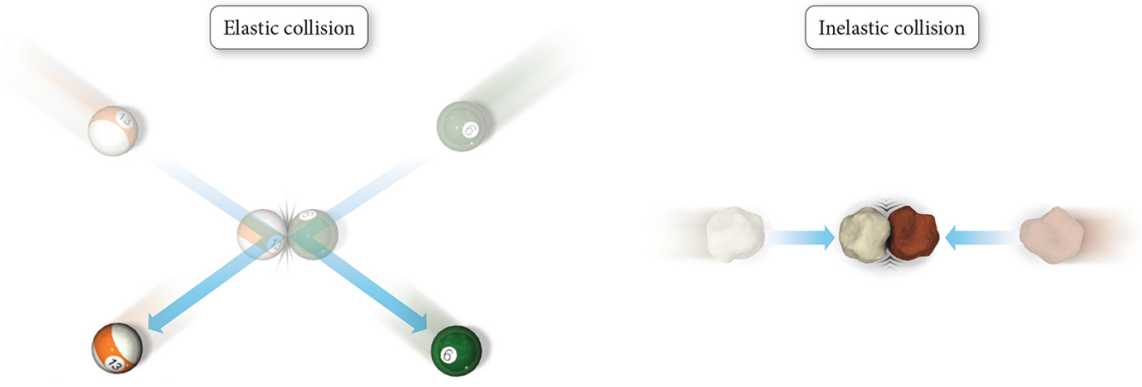
Kinetic Molecular Theory



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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.

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

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Gas Laws Explained—Boyle's Law

- Boyle's law states that the volume of a gas is inversely proportional to the pressure.
  - Decreasing the volume forces the molecules into a smaller space.
- More molecules will collide with the container at any one instant, increasing the pressure.

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Gas Laws Explained—Charles's Law

- Charles's law states that 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.

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Gas Laws Explained—Avogadro's Law

- Avogadro's law states that 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.

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Gas Laws Explained—Dalton'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.

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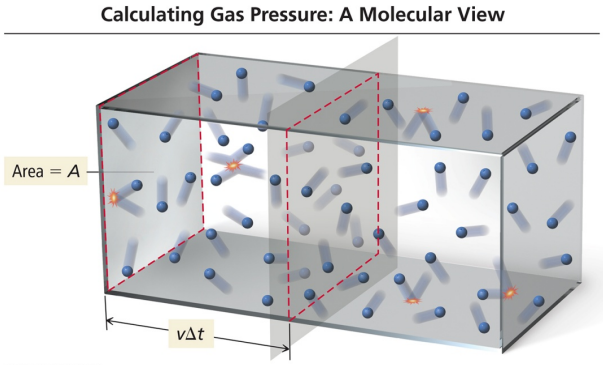
Kinetic Molecular Theory and the Ideal Gas Law

- The kinetic molecular theory is a quantitative model that implies $PV = nRT$.
- The pressure on a wall of a container occupied by particles in constant motion is the total force on the wall (due to the collisions) divided by the area of the wall.



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

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Temperature and Molecular Velocities

- Average kinetic energy of the gas molecules depends on the average mass and velocity.

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

- Gases in the same container have the same temperature; therefore, they have the same average kinetic energy.
- If they have different masses, the only way for them to have the same kinetic energy is to have different average velocities.
  - Lighter particles will have a faster average velocity than more massive particles.

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

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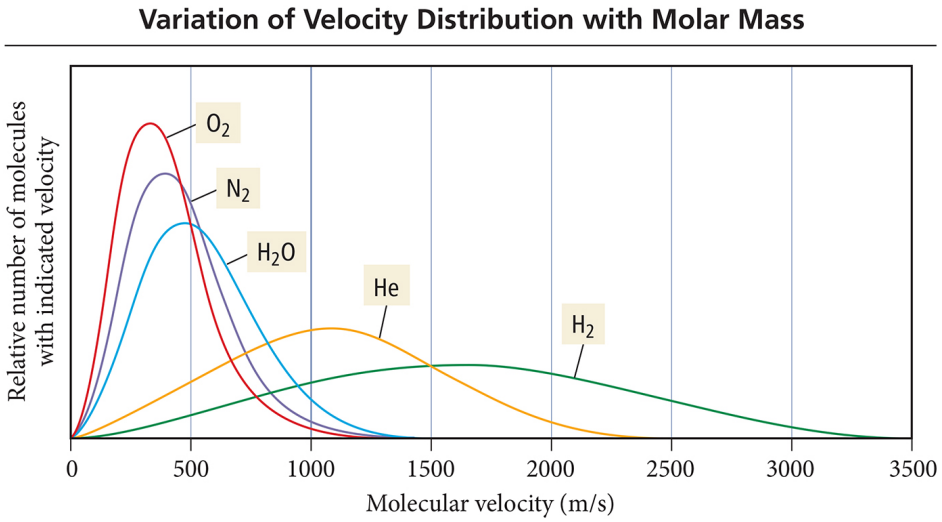
Molecular Speed versus Molar Mass

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



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Temperature and Molecular Velocities

- $KE_{avg} = \frac{1}{2}N_A m u^2$
  - N_A is Avogadro's number.
- $KE_{avg} = (3/2)RT$
  - R is the gas constant in energy units, 8.314 J/mol · K.
    - 1 J = 1 kg · m^2/s^2
- Equating and solving we get the following:
  - N_A · mass = molar mass in kg/mol

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

As temperature increases, the average velocity increases.

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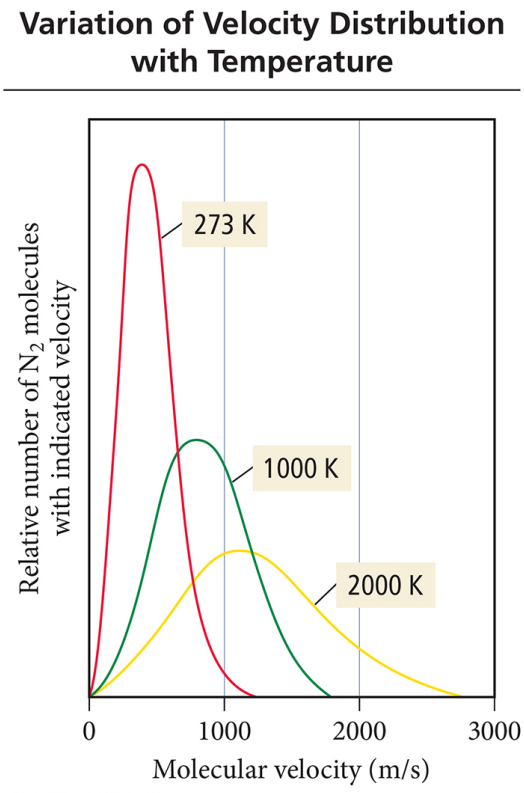
Temperature versus Molecular Speed

- As the temperature of a gas sample increases, the velocity distribution of the molecules shifts toward higher velocity.
  - The distribution function "spreads out," resulting in more molecules with faster speeds.



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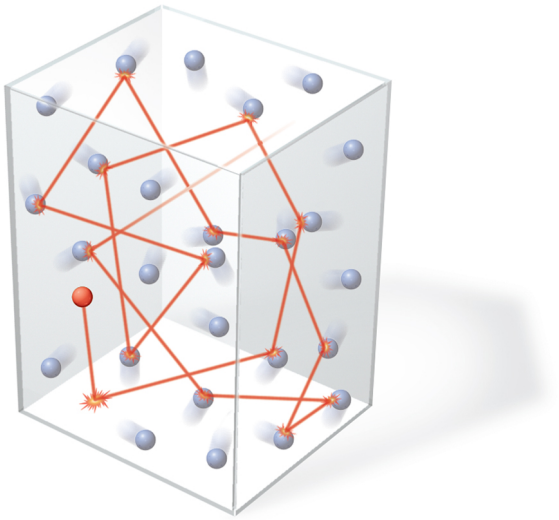
Mean Free Path

- 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.

Typical Gas Molecule Path

The average distance between collisions is the mean free path.



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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.

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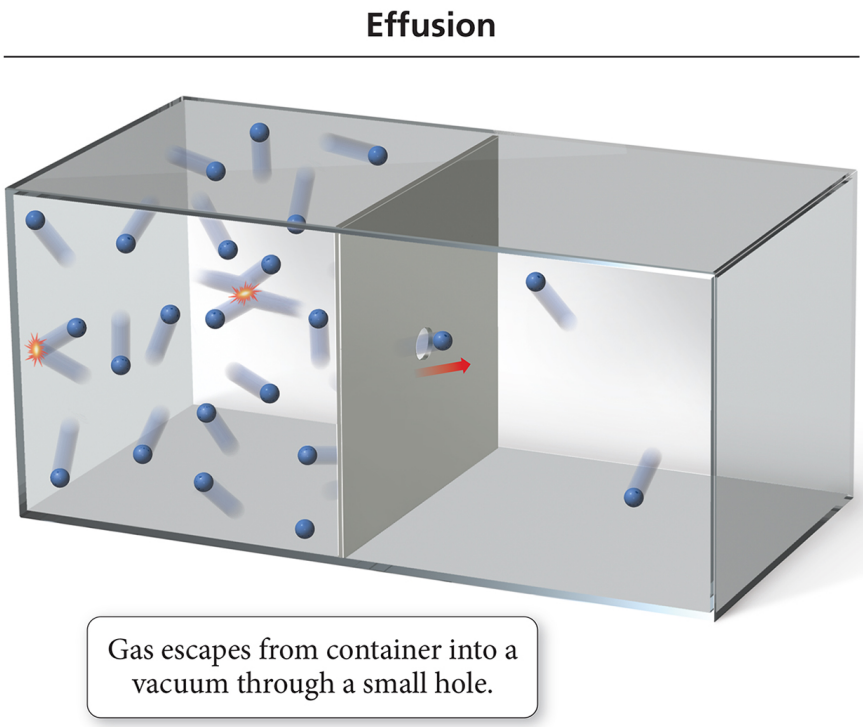
Effusion



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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:

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

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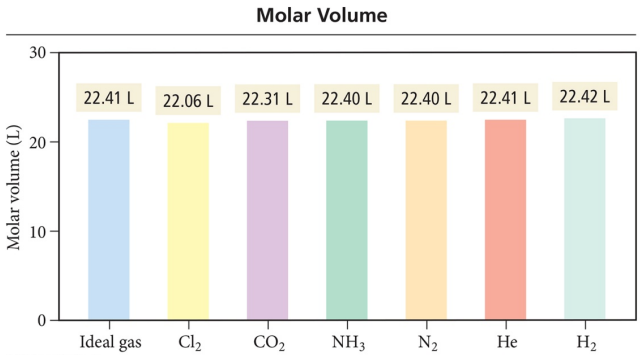
Real Gases

- Real gases often do not behave like ideal gases at high pressure or low temperature.
- Ideal gas laws assume
  1. no attractions between gas molecules.
  2. gas molecules do not take up space.
     - Based on the kinetic molecular theory
- At low temperatures and high pressures these assumptions are not valid.



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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.

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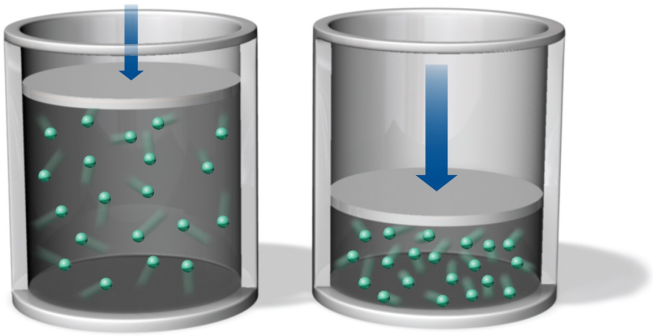
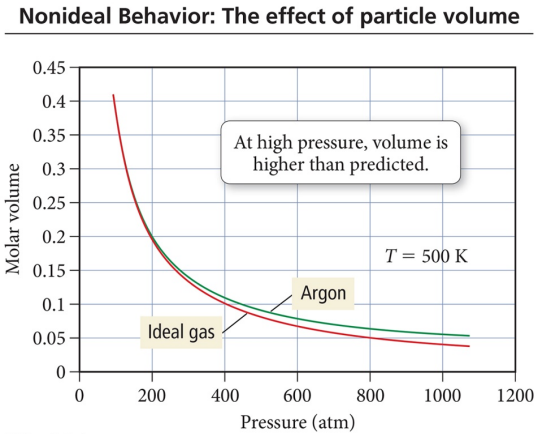
Real Gas Behavior





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.

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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.

$$V = \frac{nRT}{P} \quad \Rightarrow \quad V = \frac{nRT}{P} + nb$$

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The Effect of Intermolecular Attractions

- At high temperature, the pressures of the gases are nearly identical to that of an ideal gas.
- But at lower temperatures, the pressures of the gases are *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.

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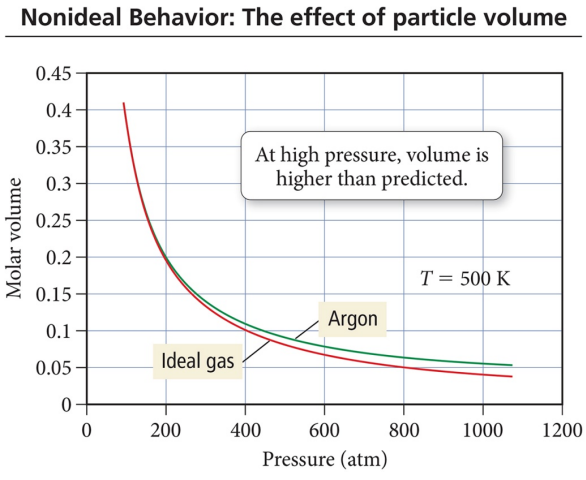
The Effect of Intermolecular Attractions

- 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.



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

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Van der Waals's Equation

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

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

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

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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.

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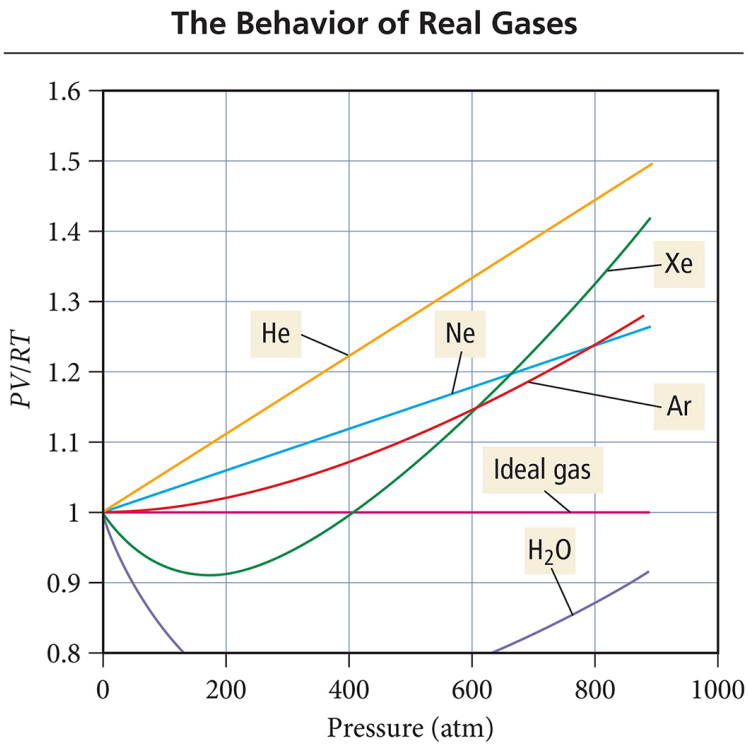
Real versus Ideal Behavior



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