# Chapter 10: Gases

Learning Outcomes:

➤Calculate pressure and convert between pressure units with an emphasis on torr and atmospheres.

➤Calculate P, V, n, or T using the ideal-gas equation.

➤Explain how the gas laws relate to the ideal-gas equation and apply the gas laws in calculations.

➤Calculate the density or molecular weight of a gas.

➤Calculate the volume of gas consumed or formed in a chemical reaction.

➤Calculate the total pressure of a gas mixture given its partial pressures or given information for calculating partial pressures.

➤Describe the kinetic-molecular theory of gases and how it explains the pressure and temperature of a gas, the gas laws, and the rates of effusion and diffusion.

➤Explain why intermolecular attractions and molecular volumes cause real gases to deviate from ideal behavior at high pressure or low temperature.

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Characteristics of Gases

Unlike liquids and solids, gases:

- – expand spontaneously to fill their containers

- – are highly compressible

- – have extremely low densities

- – have indefinite shape

- – can diffuse and mix rapidly with other gases in the same container (different gases in a mixture do not separate upon standing)
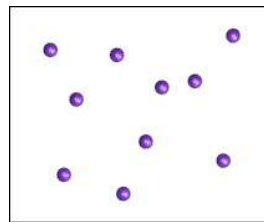
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TABLE 10.1 Some Common Compounds That Are Gases at Room Temperature

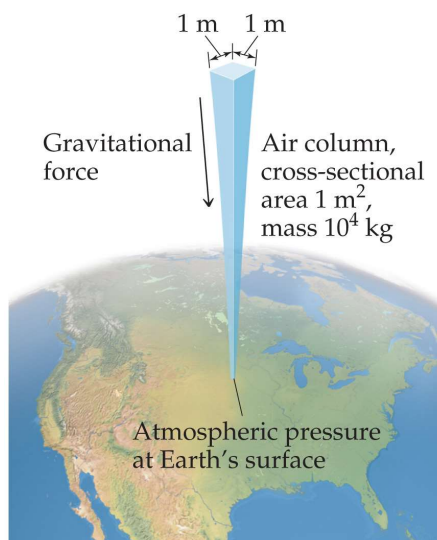| Formula	Name	Characteristics
HCN	Hydrogen cyanide	Very toxic, slight odor of bitter almonds
H_2S	Hydrogen sulfide	Very toxic, odor of rotten eggs
CO	Carbon monoxide	Toxic, colorless, odorless
CO_2	Carbon dioxide	Colorless, odorless
CH_4	Methane	Colorless, odorless, flammable
C_2H_4	Ethene (Ethylene)	Colorless, ripens fruit
C_3H_8	Propane	Colorless, odorless, bottled gas
N_2O	Nitrous oxide	Colorless, sweet odor, laughing gas
NO_2	Nitrogen dioxide	Toxic, red-brown, irritating odor
NH_3	Ammonia	Colorless, pungent odor
SO_2	Sulfur dioxide	Colorless, irritating odor

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Pressure

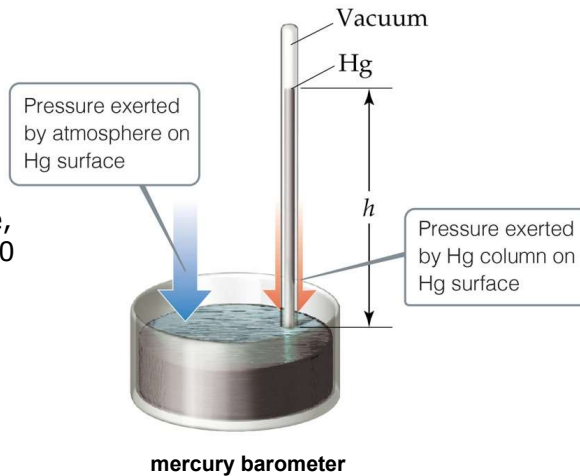- Pressure is the force acting on an object per unit an area.

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

- SI Unit of force newton (N)

  1 N = 1 kg·m/s^2

- SI unit of pressure pascal (Pa)

  1 Pa = 1 N/m^2

  1 bar = 10^5 Pa = 100 kPa

1 m   1 m

Gravitational force

Air column, cross-sectional area 1 m^2, mass 10^4 kg

Atmospheric pressure at Earth's surface

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Units of Pressure

- If a tube is completely filled with mercury and then inverted into a container of mercury open to the atmosphere, the mercury will rise 760 mm up the tube.
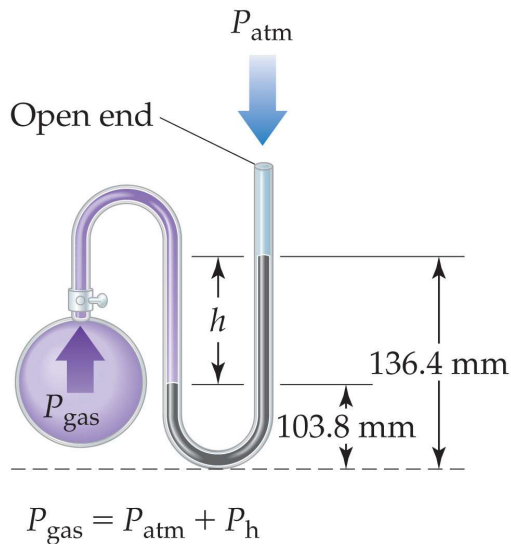- Normal atmospheric pressure at sea level is referred to as standard atmospheric pressure.

Vacuum

Hg

Pressure exerted by atmosphere on Hg surface

h

Pressure exerted by Hg column on Hg surface

mercury barometer

1 mm Hg = 1 torr

1.00 atm = 760 torr = 101.325 kPa
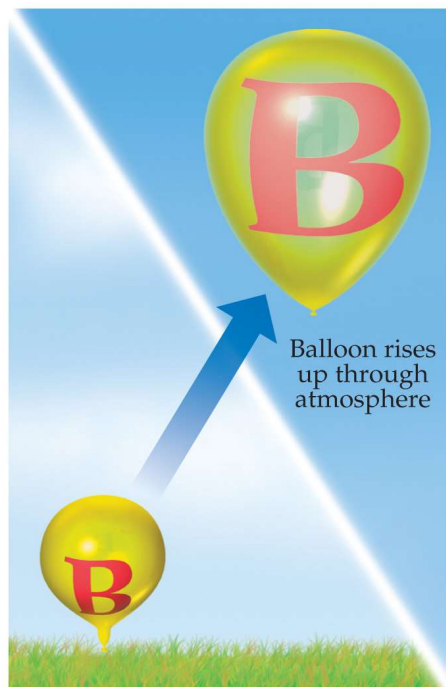
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Manometer

P_{atm}

Open end

h

P_{gas}

136.4 mm

103.8 mm

The manometer is used to measure the difference in pressure between atmospheric pressure and that of a *gas* in a vessel.

$$P_{gas} = P_{atm} + P_h$$

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Variables to describe gases

- P, pressure of the container

- *V*, volume of the container

- *T*, Kelvin temperature of the gas

- *n*, number of molecules in the container

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Balloon rises up through atmosphere

Boyle's Law:

The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.

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Boyle's Law

The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.

- PV = a constant.
- Compare two conditions: $P_1V_1 = P_2V_2$.
- A graph of V vs. P, it will *not* be linear. However, a graph of V vs. $1/P$ *will* result in a linear relationship!
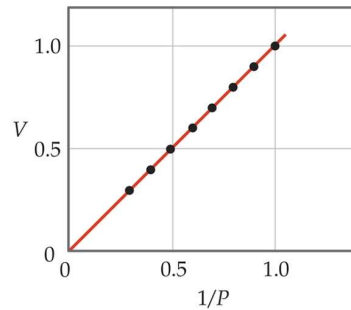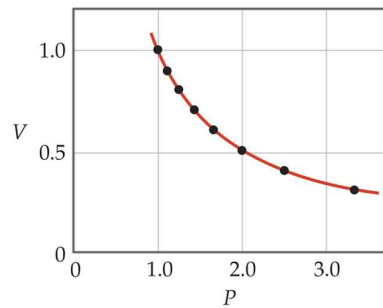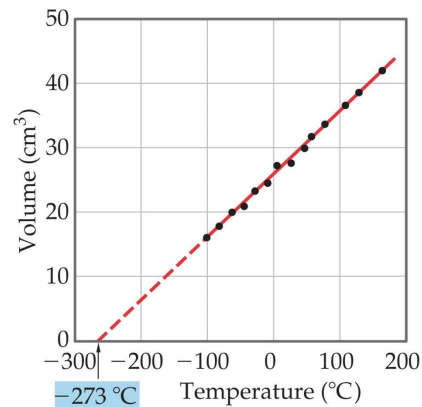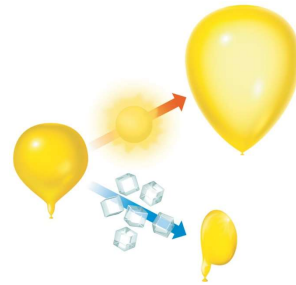

$V = constant \times (1/P)$

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Charles's Law

- The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.

$$\frac{V}{T} = constant$$

$$V = constant \times T$$

$$V_1/T_1 = V_2/T_2$$

A plot of V versus T will be a straight line.

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Avogadro's Law

	He	N_2	CH_4
Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0 °C	0 °C	0 °C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.

$$V = \text{constant} \times n \quad \text{and} \quad V_1/n_1 = V_2/n_2$$

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Ideal-Gas Equation

- Noting:

    $V \propto 1/P$ (Boyle's law)
    $V \propto T$ (Charles's law)
    $V \propto n$ (Avogadro's law)

- Combining these,

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

- The constant of proportionality is known as R, the gas constant.

TABLE 10.2 Numerical Values of the Gas Constant R in Various Units

Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m^3-Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit

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Ideal-Gas Equation

The relationship $V \propto \dfrac{nT}{P}$

then becomes $V = R\,\dfrac{nT}{P}$

$$PV = nRT$$

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

- Ideal gas particles: have no volume and are not attracted/ repelled by each other.
- Brings together gas properties.
- STP (standard temperature and pressure) = 0 °C, 273.15 K, 1 atm.

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Example

A flashbulb contains 2.4×10^{-4} mol of O_2 gas at a pressure of 1.9 atm and a temperature of 19 °C. What is the volume of the flashbulb in cubic cm?

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Example

Typically, when a person coughs, he or she first inhales about 2.50 L of air at 1.00 atm and 25 °C. The epiglottis and the vocal cords then shut, trapping the air in the lungs, where it is warmed to 37 °C and compressed to a volume of about 1.70 L by the action of the diaphragm and chest muscles. The sudden opening of the epiglottis and vocal cords releases this air explosively. Just prior to this release, what is the approximate pressure of the gas inside the lungs?

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Molar Volumes at STP

$$V = \frac{nRT}{P}$$
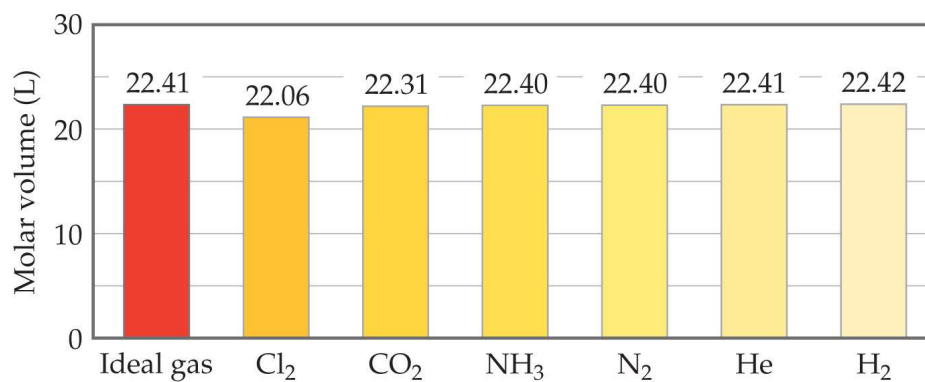
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What is an ideal gas?

Gas molecules

- have no volume.

- have no attraction or repulsion for each other.

- are in constant, random, and rapid motion.

- collide without losing energy.

- have an average kinetic energy that is proportional to their Kelvin temperature. KE α T.

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Densities of Gases

If we divide both sides of the ideal-gas equation by V and by RT, we get

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

- We know that

moles $\times$ molar mass = mass

$$n \times M = m$$

- Multiplying both sides by the molar mass (M) gives

$$\frac{m}{V} = \frac{PM}{RT}$$

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

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Molar Mass

We can manipulate the density equation to enable us to find the molecular mass of a gas:

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

Becomes

$$M = \frac{dRT}{P}$$

Example

Diethyl ether $(C_2H_5)_2O$ vaporizes at room temperature. If the vapor exerts a pressure of 233 mm Hg in a flask at 25 °C, what is the density of the vapor?

Example
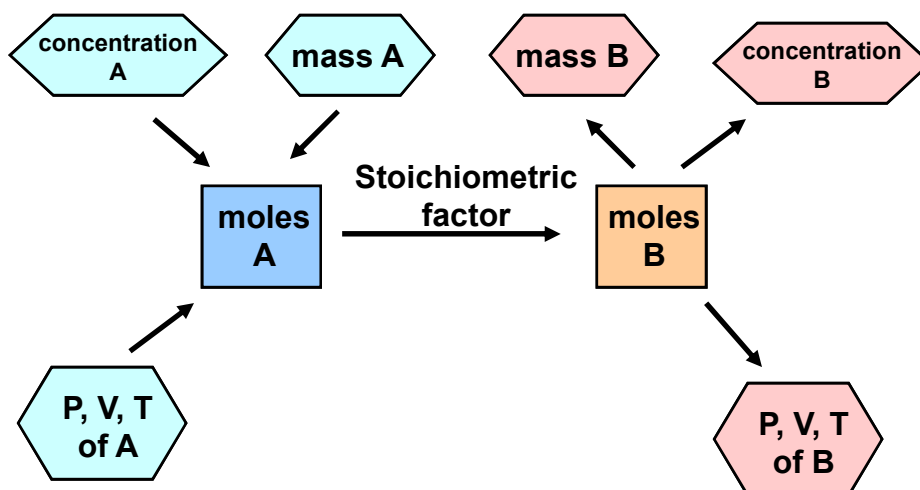
If 8.00 L of a gas at STP has a mass of 19.2 g, calculate the molar mass of the gas.

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Stoichiometry problems

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Example

Hydrazine gas, N_2H_4, will react with oxygen gas to form nitrogen gas and liquid water. Assume the oxygen gas needed for the reaction is in a 450. L tank at 23 °C. What must be the oxygen pressure (in kPa) in the tank to have enough oxygen to consume 1.00 kg of hydrazine completely?

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Dalton's Law of Partial Pressures

- The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.
- **Partial pressure** is the pressure exerted by a particular component of a gas mixture.

$$P_{total} = P_1 + P_2 + P_3 + \dots$$

The pressure of each gas (1, 2, etc) in the mixture is called its partial pressure (P_1, P_2, etc), and can be related to the total pressure by the gas' mole fraction (X):

$$P_1 = X_1 \, P_{total}$$
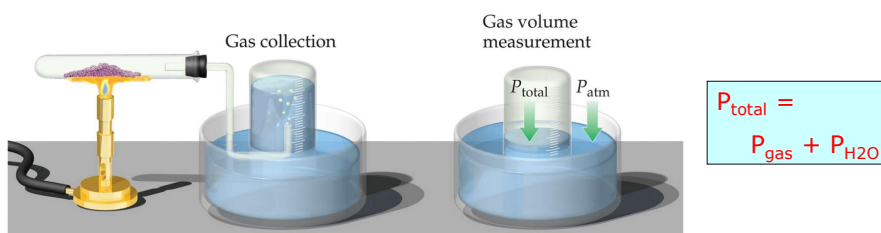
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Example

A cylinder of compressed gas is labeled

(composition mol%)   4.5% H_2S

3.0% CO_2

balance N_2

The pressure gauge attached to the cylinder reads 46.0 atm. Calculate the partial pressure of each gas (in atm).

Partial Pressures

Gas collection

Gas volume measurement

P_{total} P_{atm}

$P_{total} =$
$P_{gas} + P_{H2O}$

- When one collects a gas over water, there is water vapor mixed in with the gas.

- To find only the pressure of the desired gas, one must subtract the vapor pressure of water from the total pressure.

Example

Hydrogen gas is produced when zinc reacts with sulfuric acid. If 159 mL of wet hydrogen gas is collected over water at 24 °C and a barometric pressure of 738 torr, how many grams of Zn have been consumed? The vapor pressure of H_2O at 24 °C is 22.38 torr.

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Kinetic-Molecular Theory

Pressure inside container comes from collisions of gas molecules with container walls.
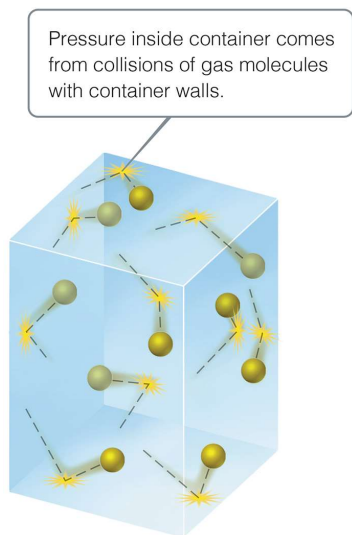
This is a model that explains why

- gases expand when heated at constant pressure
- gas pressure increases when the gas is compressed at constant T

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Kinetic-molecular theory

1. Gases consist of large number of molecules that are in continuous, random motion.

2. The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.

3. Attractive and repulsive (intermolecular) forces between molecules are negligible.

4. Energy can be *transferred* between molecules during collisions, but the **average** kinetic energy (KE) of the molecules does not change with time (if T is constant). The collisions are perfectly elastic.

5. The average KE of the molecules is proportional to the absolute temperature. At any given temperature the molecules of all gases have the same average KE.

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$\varepsilon = 1/2mu^2$
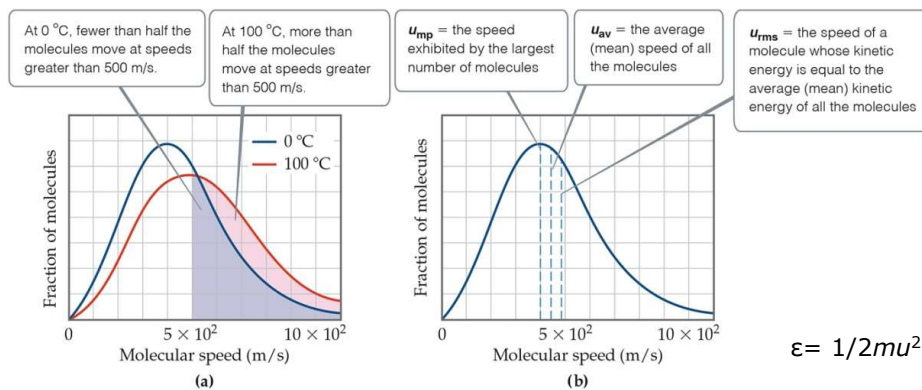
- Temperature is related to the *average* kinetic energy of the molecules.
- Individual molecules can have different speeds.
- The figure shows three different speeds:
  - u_{mp} is the most probable.
  - u_{av} is the average speed of the molecules.
  - u_{rms}, the root-mean-square speed, is the one associated with their average kinetic energy.

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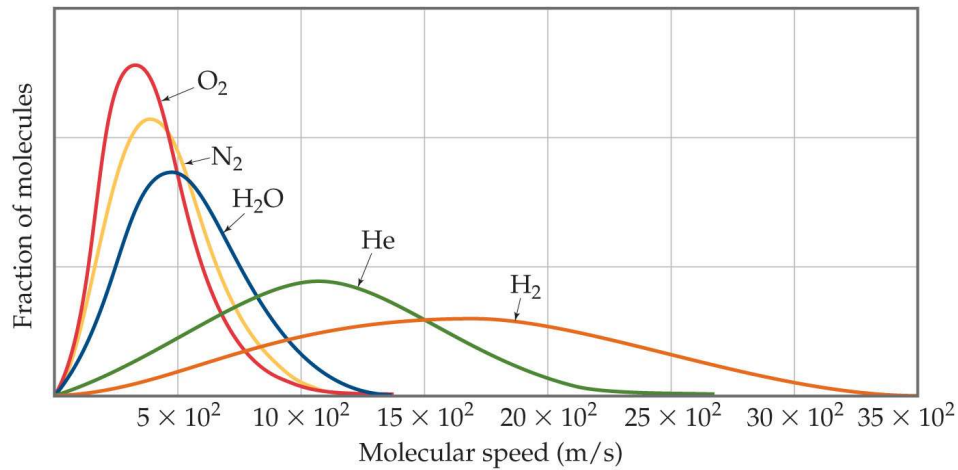
$$u_{RMS} = \sqrt{\frac{3RT}{\mathcal{M}}} \qquad\qquad u_{MP} = \sqrt{\frac{2RT}{\mathcal{M}}}$$

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Effect of an increase in volume (at constant temperature)
- As volume increases at constant temperature, the average kinetic energy of the gas remains constant.
- Therefore, *u is constant*
- However, volume increases, so the gas molecules have to travel further to hit walls of the container.
- Therefore, pressure decreases.

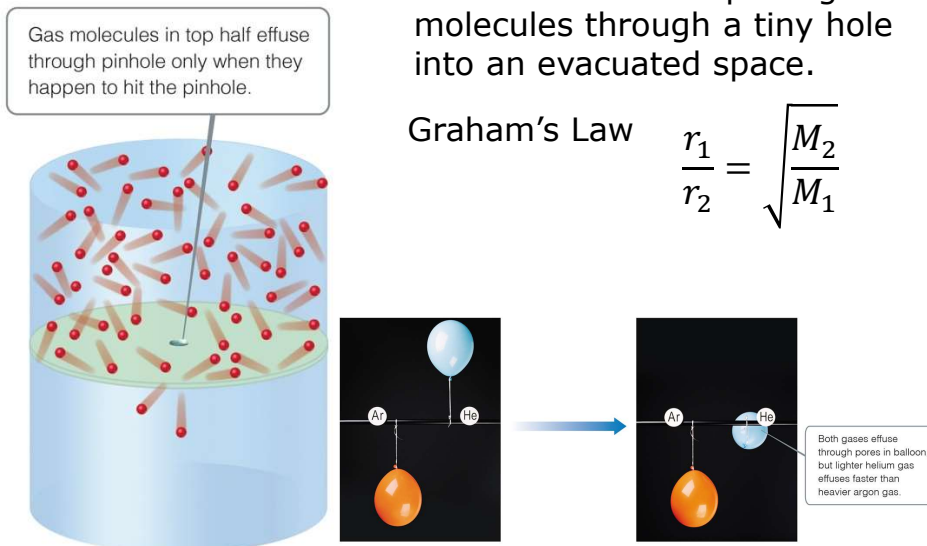### Effect of an increase in temperature (at constant volume)
- If temperature increases (at constant volume), the average kinetic energy of the gas molecules increases.
- There are more collisions with the container walls.
- Therefore, *u* increases.
- The change in momentum in each collision increases (molecules strike harder).
- Therefore, pressure increases.

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Effusion

Effusion is the escape of gas molecules through a tiny hole into an evacuated space.

Graham's Law $$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Gas molecules in top half effuse through pinhole only when they happen to hit the pinhole.

Both gases effuse through pores in balloon, but lighter helium gas effuses faster than heavier argon gas.
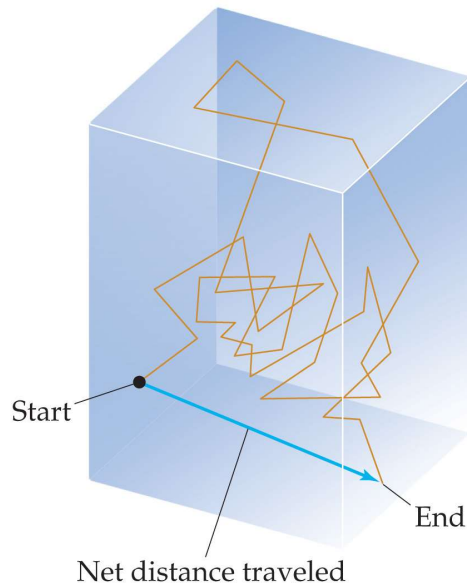
Example

An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is only 0.355 times that of oxygen gas at the same temperature. What is the unknown gas?
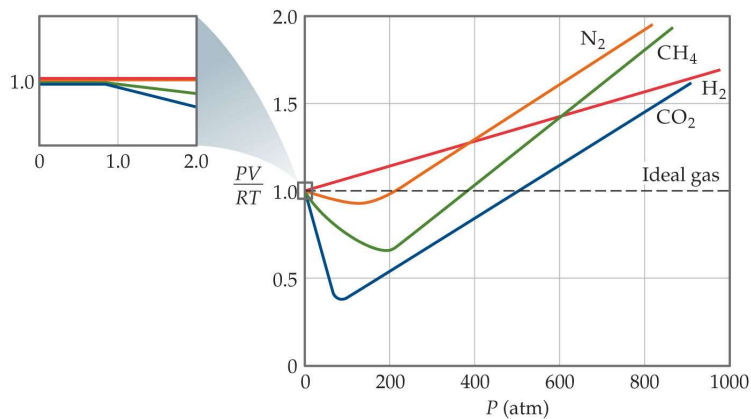
Diffusion

Diffusion is the spread of one substance throughout a space or throughout a second substance.

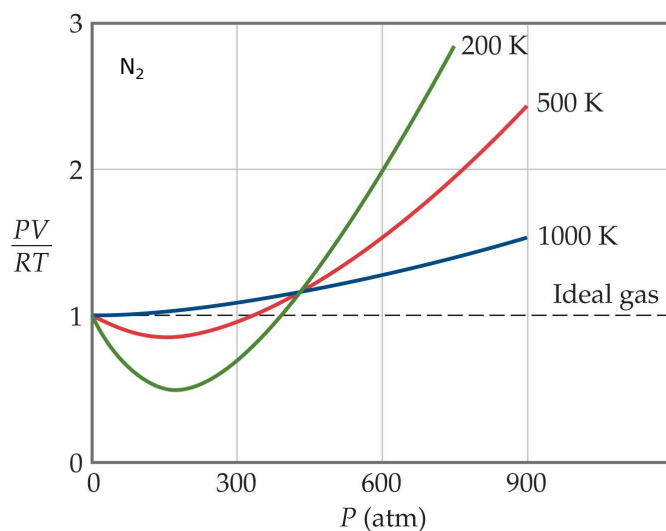- The average distance travelled by a gas molecule between collisions is called the **mean free path**.

Start

End

Net distance traveled

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Real Gases

$\frac{PV}{RT}$

2.0

1.5

1.0

0.5

0

0   200   400   600   800   1000

P (atm)

N$_2$

CH$_4$

H$_2$

CO$_2$

Ideal gas

1.0

0   1.0   2.0

The behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.
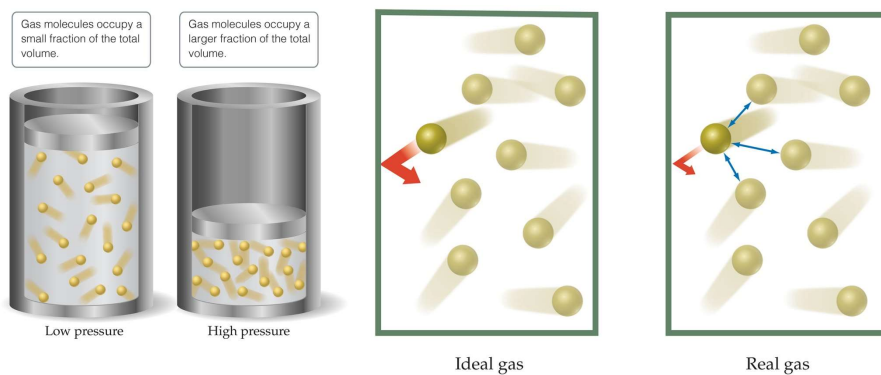
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Real Gases

Even the same gas will show different behavior under high pressure at different temperatures.

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Deviations from Ideal Behavior

The assumptions made in the kinetic-molecular model (negligible volume of gas molecules themselves, no attractive forces between gas molecules, etc.) break down at high pressure and/or low temperature.

- Large molar mass and polar molecules tend to deviate from ideal behavior.

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Corrections for Nonideal Behavior

- The ideal-gas equation can be adjusted to take these deviations from ideal behavior into account.
- The corrected ideal-gas equation is known as the van der Waals equation.

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

where a and b are empirical constants that differ for each gas.

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The van der Waals Equation

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

TABLE 10.3 Van der Waals Constants for Gas Molecules

Substance	a (L^2-atm/mol^2)	b (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
F_2	1.06	0.0290
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
NH_3	4.17	0.0371
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383

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Example

Use the van der Waals equation to estimate the pressure exerted by 1.000 mol Cl_2 in 22.41 L at 0.0 °C. Compare to an ideal gas.

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