

Lecture 25-27

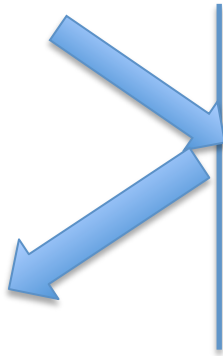
Gases

Characteristics of Gases

- Unlike liquids and solids, gases
 - Expand to fill their containers.
 - Are highly compressible.
 - Have extremely low densities.

Pressure of a gas

- Force per unit area exerted by the gas.
 - How? By colliding with the surface of the vessel



$$F = ma = \Delta mv$$

$$F/A = P$$

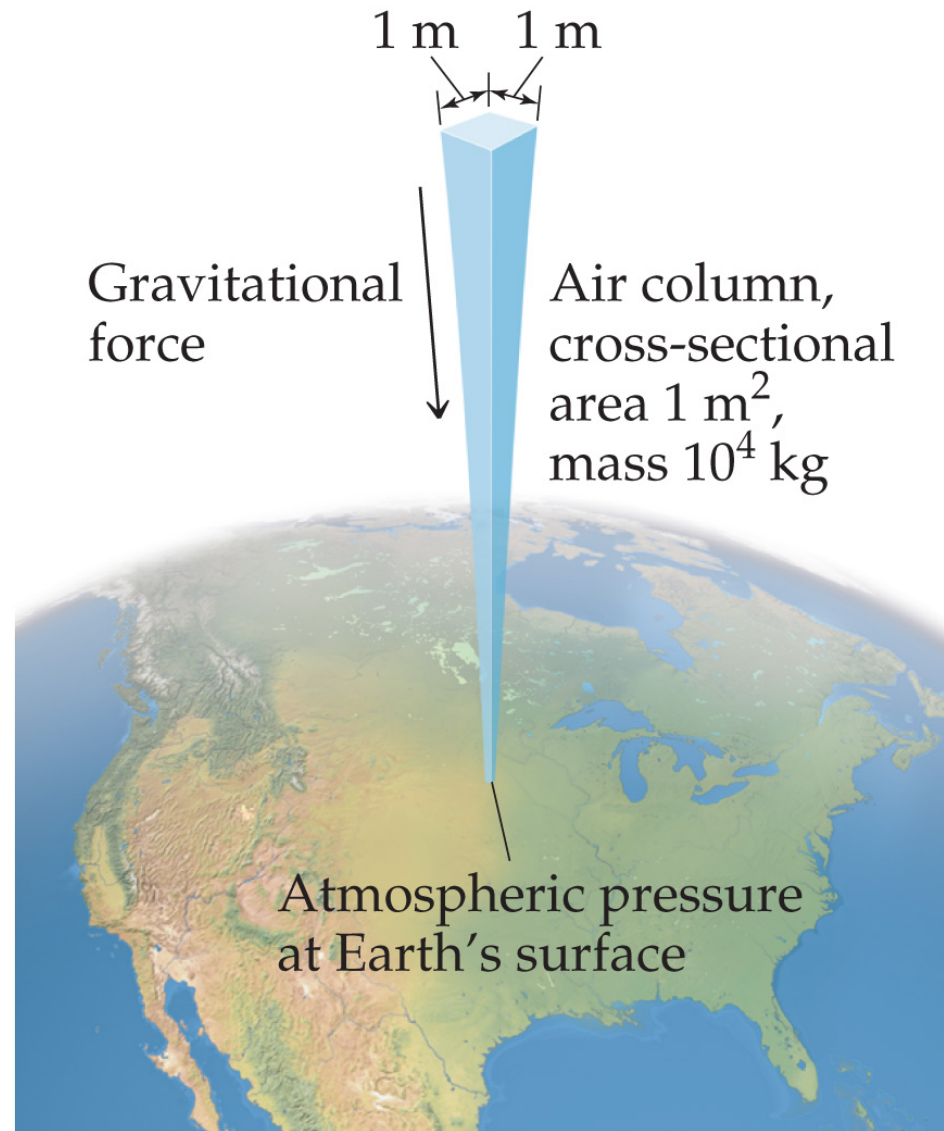
SI units: Nm^{-2} Pascals, Pa.

Pressure

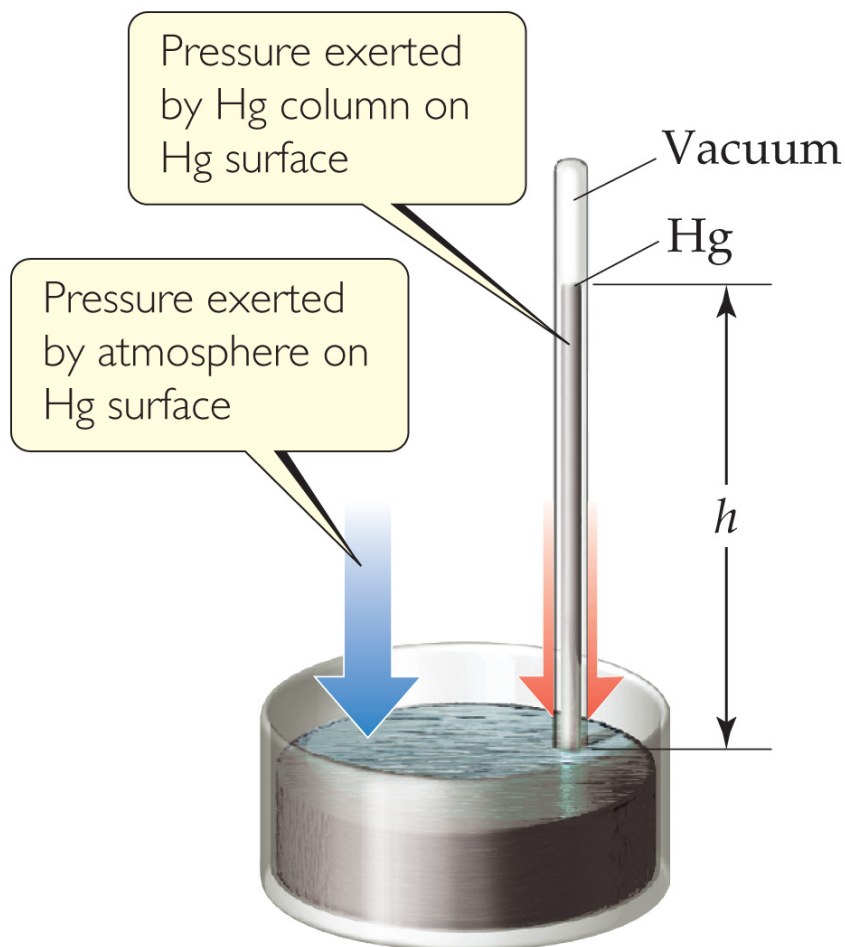
- **Pressure** is the amount of force applied to an area:

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

- **Atmospheric pressure** is the weight of air per unit of area.

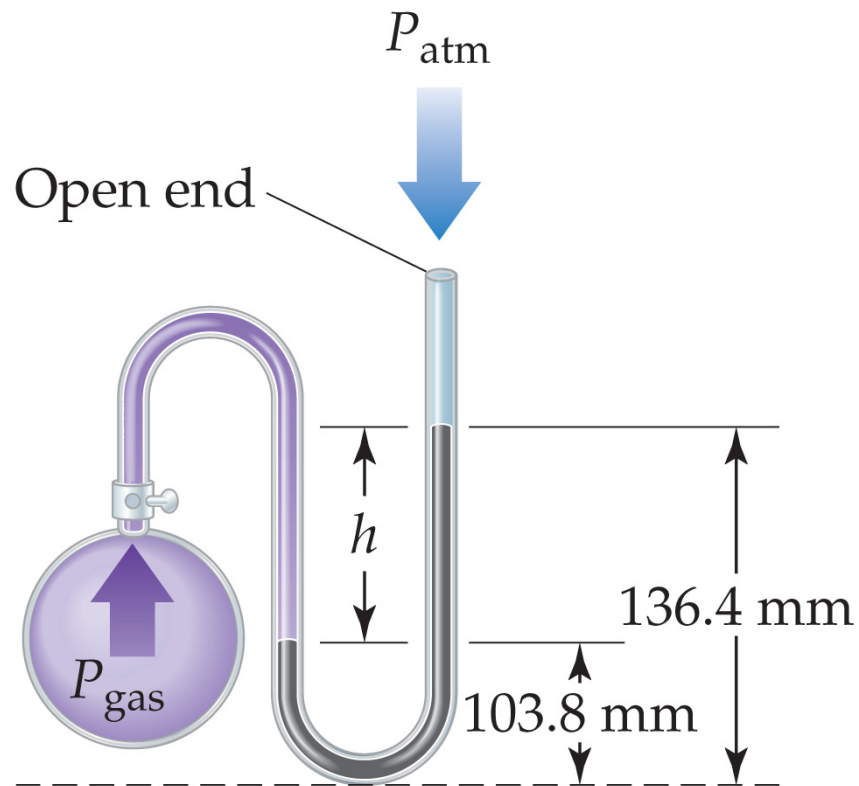


Units of Pressure



- mmHg or torr
 - These units are literally the difference in the heights measured in mm (h) of two connected columns of mercury.
- Atmosphere
 - 1.00 atm = 760 torr

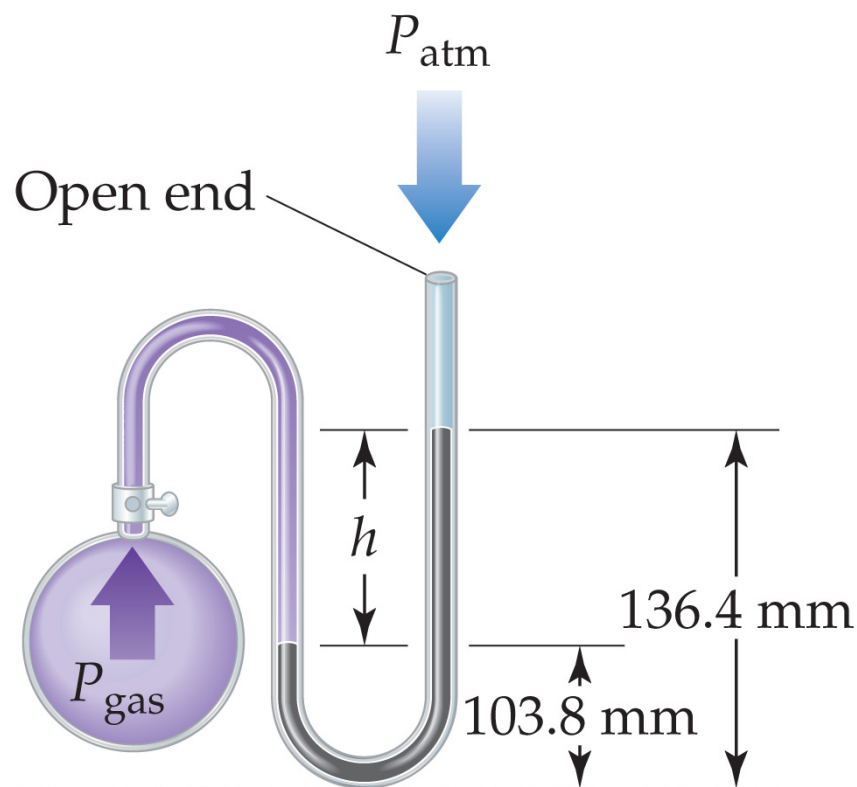
Manometer



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

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

Manometer



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

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Example: What is the pressure in atmospheres of the gas in the figure?

$$\begin{aligned} P_{\text{gas}} &= 760 \text{ mm} + (136.4 - 103.8) \\ &= 760 \text{ mm} + 32.6 \text{ mm} = 792.6 \text{ mm} \end{aligned}$$

$$\begin{aligned} 792 \text{ mm} (1 \text{ atm} / 760 \text{ mm}) &= \\ 1.04 \text{ atm} \end{aligned}$$

Standard Pressure

- Normal atmospheric pressure at sea level is referred to as **standard pressure**.
- It is equal to
 - 1.00 atm
 - 760 torr (760 mmHg)
 - 101.325 kPa

Avogadro's Law

- The volume of a gas at constant temperature and pressure is directly proportional to the number of moles of the gas.
- Mathematically, this means $V = kn$



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

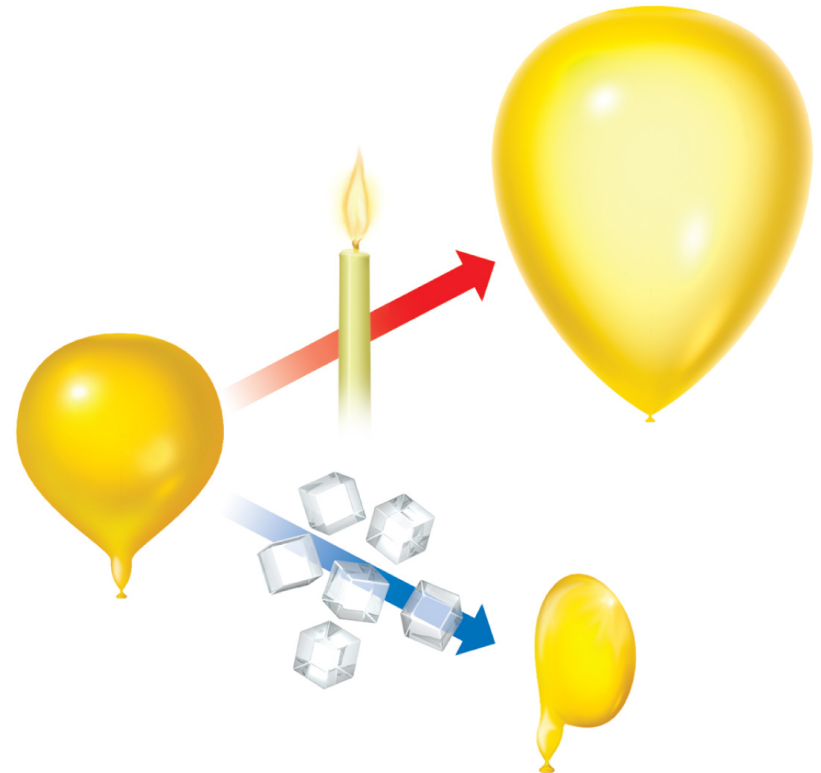
Number of
gas molecules 6.02×10^{23}

6.02×10^{23}

6.02×10^{23}

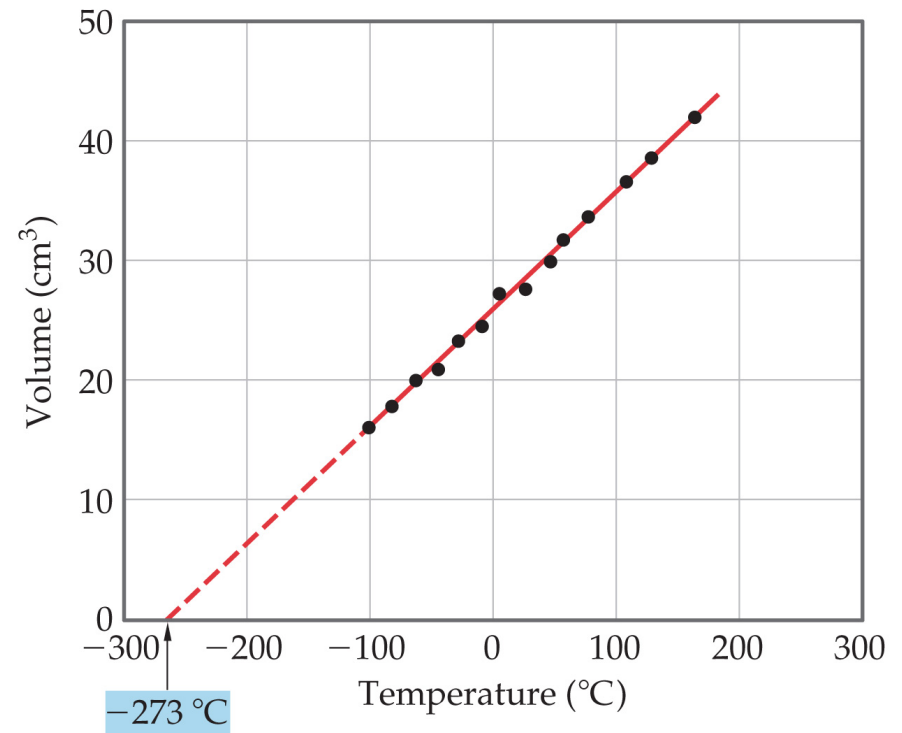
Charles's Law

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



Charles' s Law

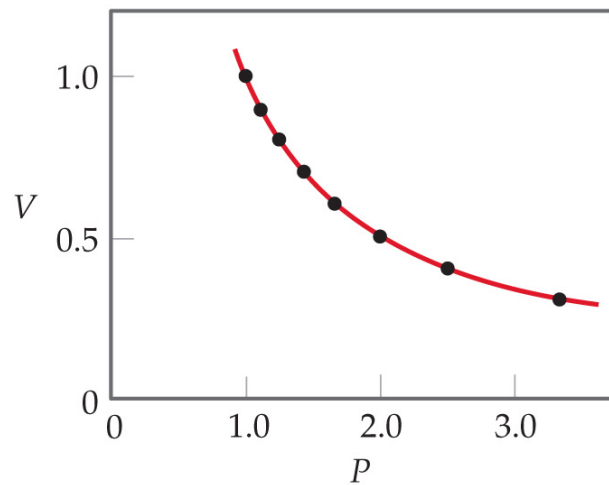
- So, $\frac{V}{T} = k$
- A plot of V versus T will be a straight line.



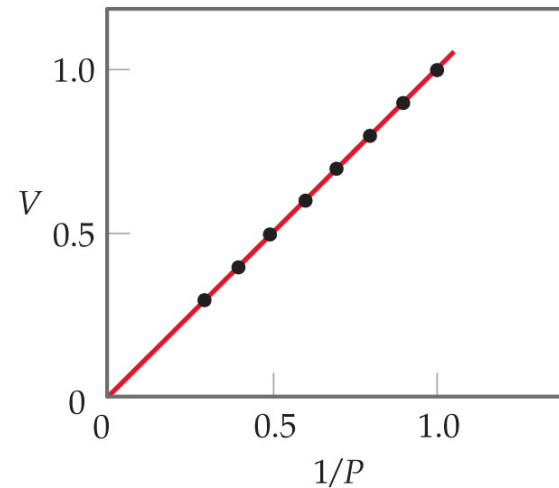
Boyle's Law

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

P and V are Inversely Proportional



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Since $PV = k$
A plot of V versus P results in a curve.

$$V = k (1/P)$$

This means a plot of V versus $1/P$ will be a straight line.

Ideal-Gas Equation

- So far we've seen that

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

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

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

- Combining these, we get

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

Ideal-Gas Equation

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

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

then becomes

$$V = R \frac{nT}{P}$$

or

$$PV = nRT$$

A gas law problem

- 2.0 liters of an ideal gas is heated from 50° C to 150 °C under a constant pressure of 1 atm. What happens to the volume?
- n is constant, P is constant:
- $PV=nRT \quad V_{\text{init}}/T_{\text{init}} = nR/P = K = V_{\text{final}}/T_{\text{final}}$
- $2.0\text{atm}/323\text{K} = V_{\text{final}}/423\text{K}$
- $2.0\text{atm}(423\text{K})/323\text{K} = 2.6 \text{ liters}$

Gas law problem

- To what must the pressure be increased (at 423 K) to reduce the volume back to its original value (2.0 L)?
- Now T and n are constant:
- $PV=nRT$ $PV=K$
- $1\text{atm}(2.6\text{L})=P_{\text{final}}(2.0\text{L})$
- $1\text{atm}(2.6\text{L})/2.0\text{L} = 1.31 \text{ atm.}$

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.
- In other words,

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

Gases

- 3 samples of gases
- 1 liter O₂ at 2 atm pressure
- 2 liter N₂ at 1 atm pressure
- 2 liter He at 2 atm pressure
- What's the final pressure if all are put in a 3 L container, assume T constant.

Partial pressures

- $P_i V_i = nRT = P_f V_f$
- $P_i V_i / V_f = P_f$

Oxygen: $2 \text{ atm}(1 \text{ L})/3 \text{ L} = 2/3 \text{ atm}$

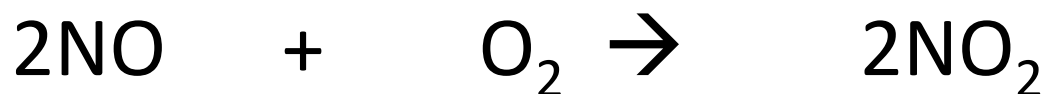
Nitrogen: $1 \text{ atm}(2 \text{ L})/3 \text{ L} = 2/3 \text{ atm}$

Helium: $2(2 \text{ L})/3 \text{ L} = 4/3 \text{ atm}$

TOTAL $8/3 \text{ atm.}$

Partial pressures

- 2 gases mix and react. Open valve, gases form as much product as possible. What is the final pressure? Assume T constant.

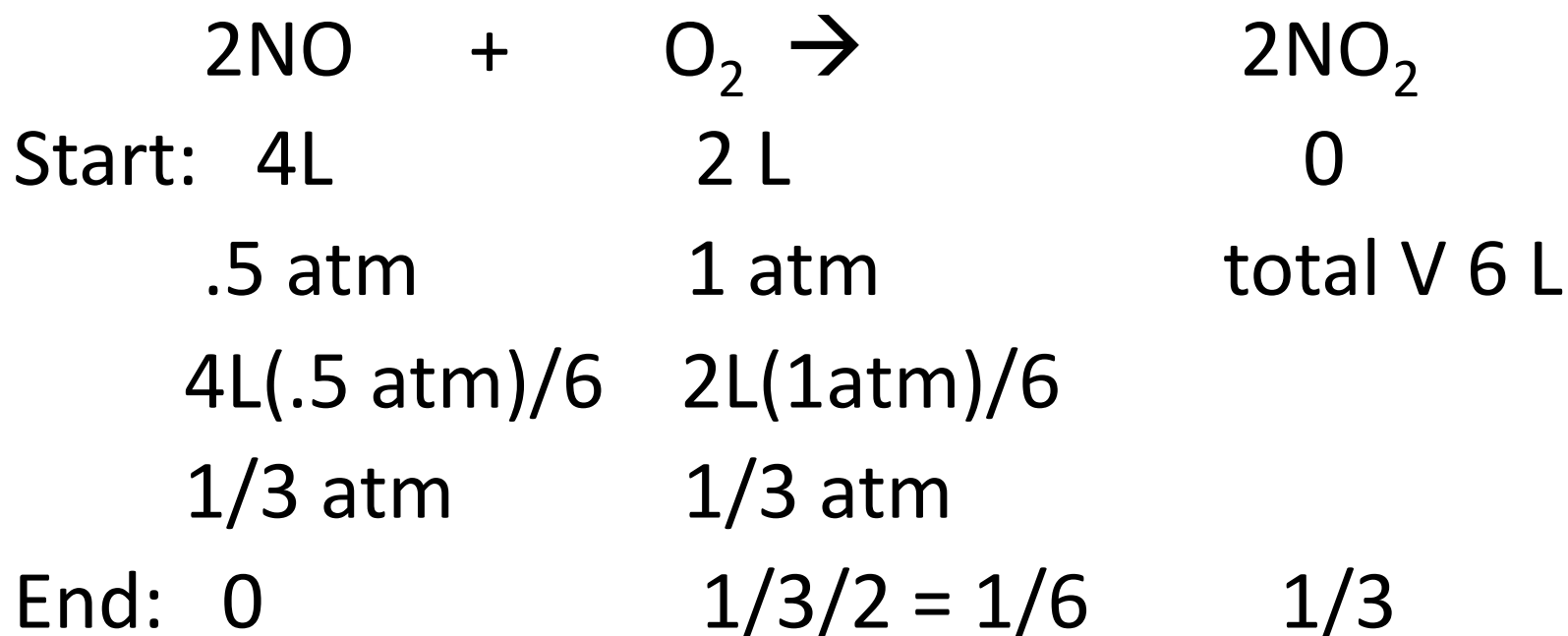


4L 2 L ?

.5 atm 1 atm total V 6 L

$4\text{L}(.5 \text{ atm})/6$ $2\text{L}(1\text{atm})/6$

$1/3 \text{ atm}$ $1/3 \text{ atm}$



Total: $1/6 \text{ atm} + 1/3 \text{ atm} = 1/2 \text{ atm}.$

Partial pressures

- Mixture of 40g each of He and O₂ at 2 atm.
- What is the partial pressure of each?

$$PV = nRT \quad P = nRT/V \quad P/n = RT/V$$

$$P_{\text{He}}/P_{\text{tot}} = n_{\text{He}}RTV^{-1}/n_{\text{tot}}RTV^{-1} = n_{\text{He}}/n_{\text{tot}}$$

$$P_{\text{He}} = n_{\text{He}}/n_{\text{tot}}(P_{\text{tot}})$$

$$\text{Moles He} = 40 \text{ g}/4 \text{ g mol}^{-1} = 10 \text{ mole}$$

$$\text{Moles Oxygen: } 40 \text{ g}/32 \text{ g mol}^{-1} = 5/4 \text{ mole}$$

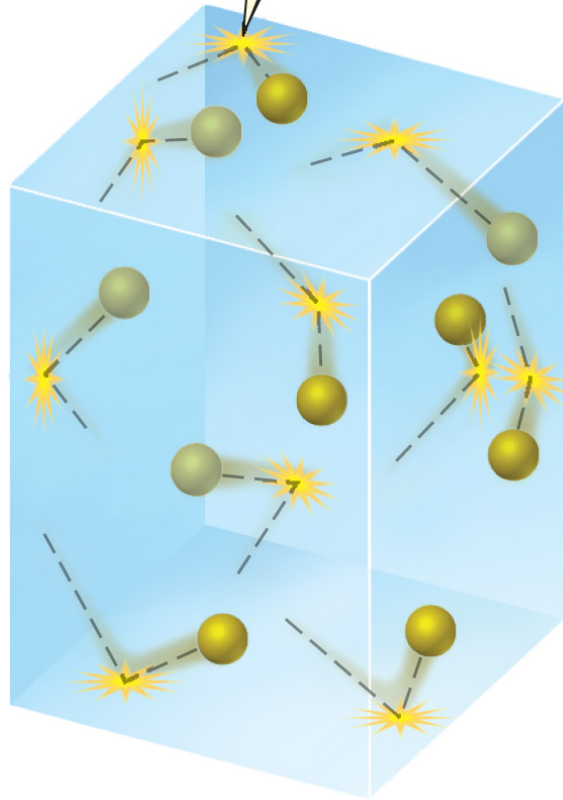
$$n_{\text{tot}} = 11.25 \text{ moles}$$

$$P_{\text{He}} = 10/11.25(2\text{atm})$$

$$P_{\text{O}_2} = 1.25 \text{ mole}/11.25 \text{ mole}(2 \text{ atm}) =$$

Kinetic-Molecular Theory

Pressure inside container comes from collisions of gas molecules with container walls



This is a model that aids in our understanding of what happens to gas particles as environmental conditions change.

Main Tenets of Kinetic-Molecular Theory

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

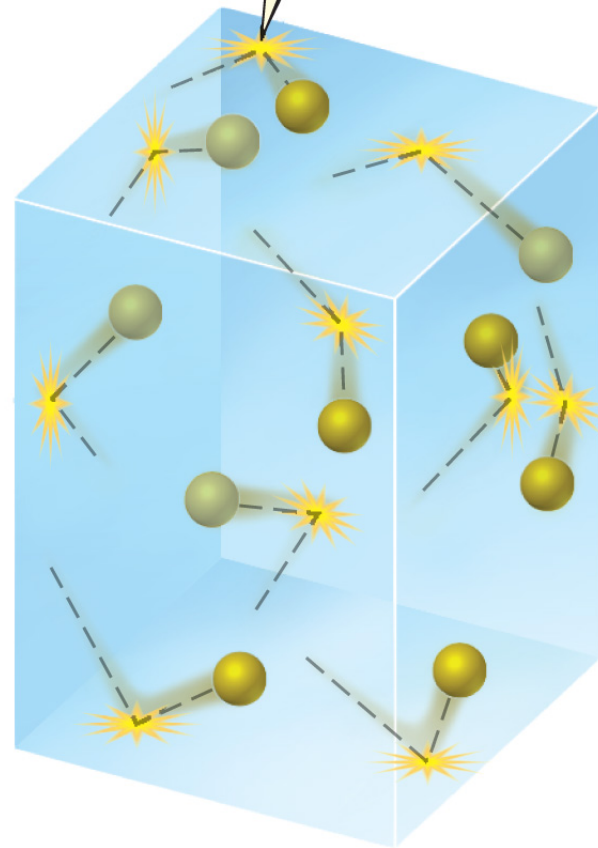
Main Tenets of Kinetic-Molecular Theory

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

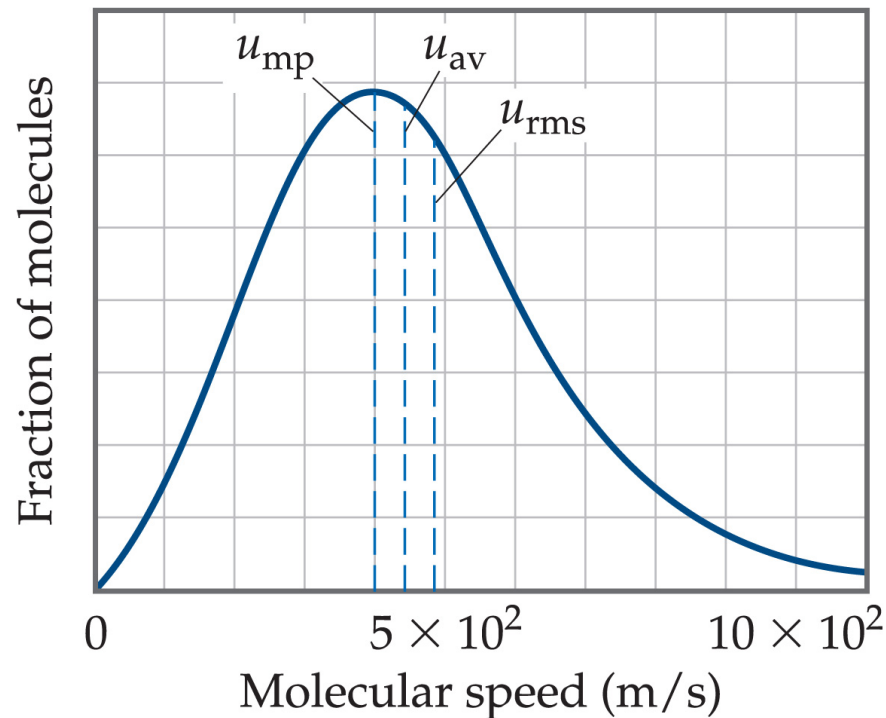
Main Tenets of Kinetic-Molecular Theory

Attractive and repulsive forces between gas molecules are negligible.

Pressure inside container comes from collisions of gas molecules with container walls



Main Tenets of Kinetic-Molecular Theory

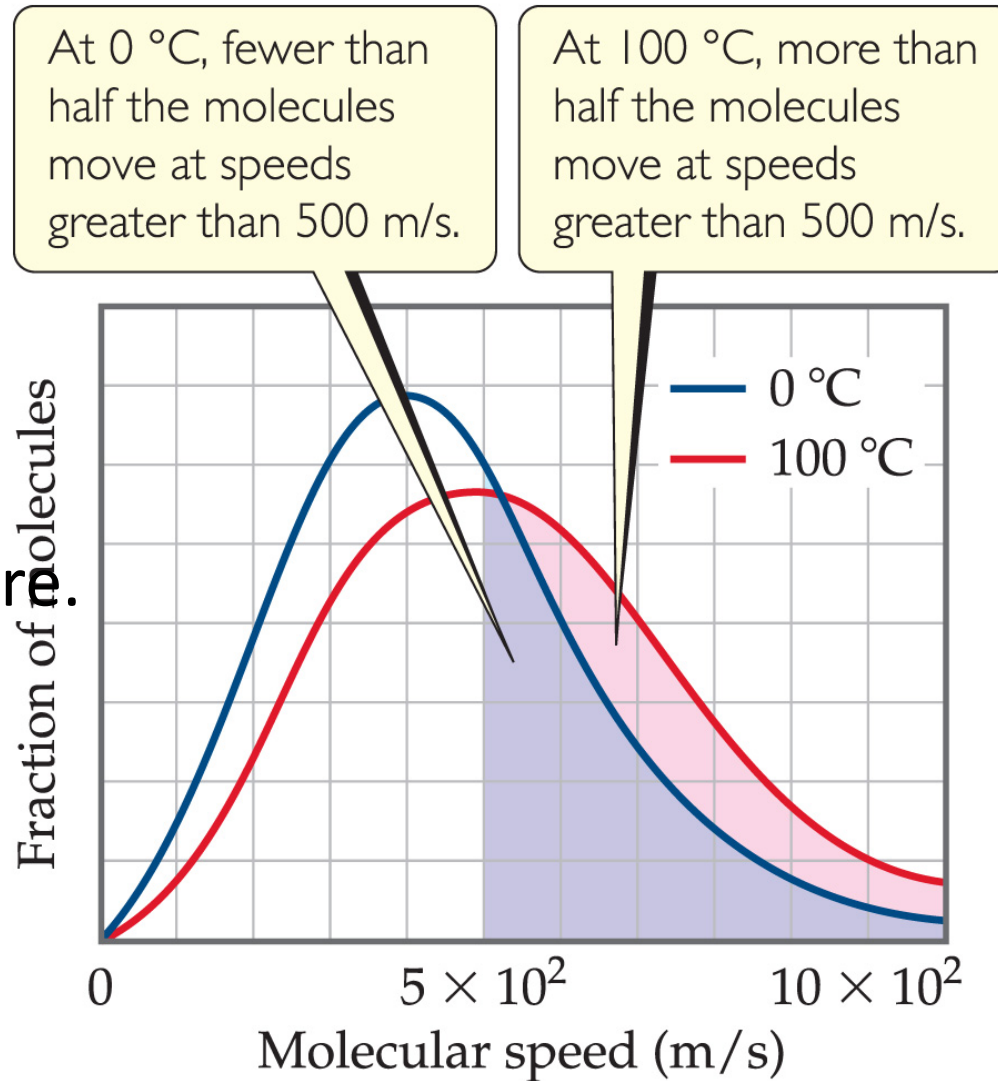


(b)

Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant.

Main Tenets of Kinetic-Molecular Theory

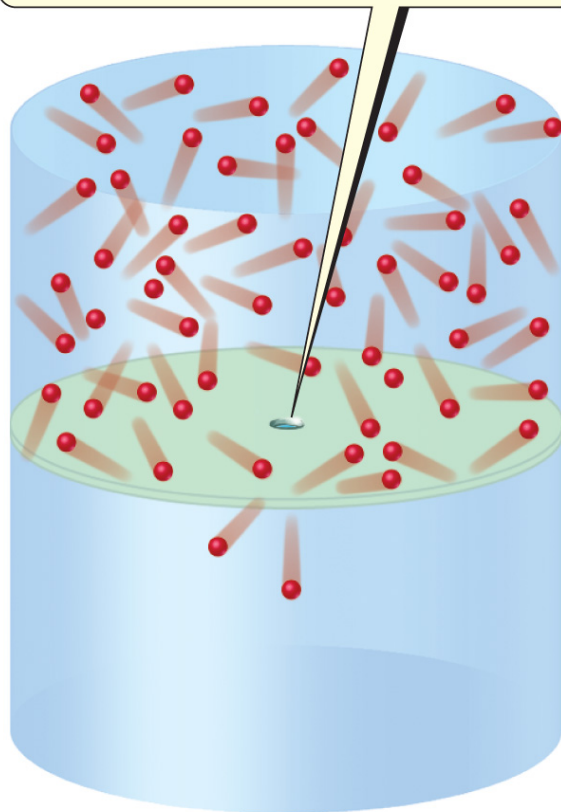
The average kinetic energy of the molecules is proportional to the absolute temperature.



(a)

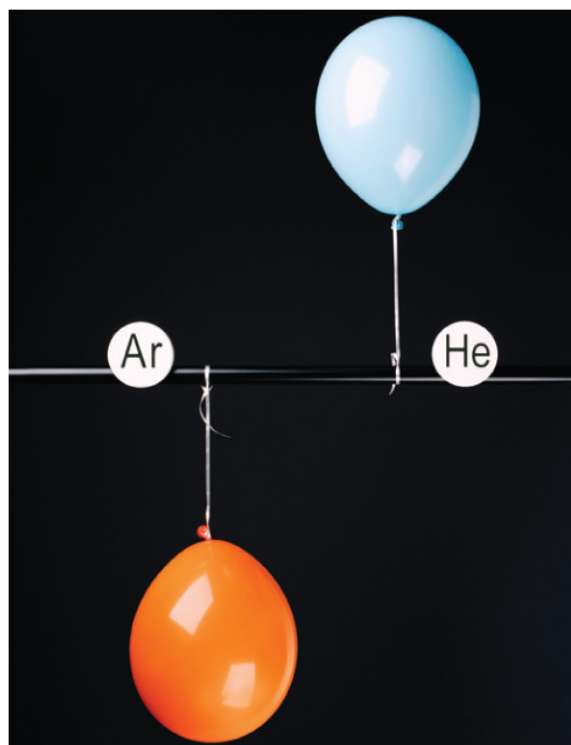
Effusion

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

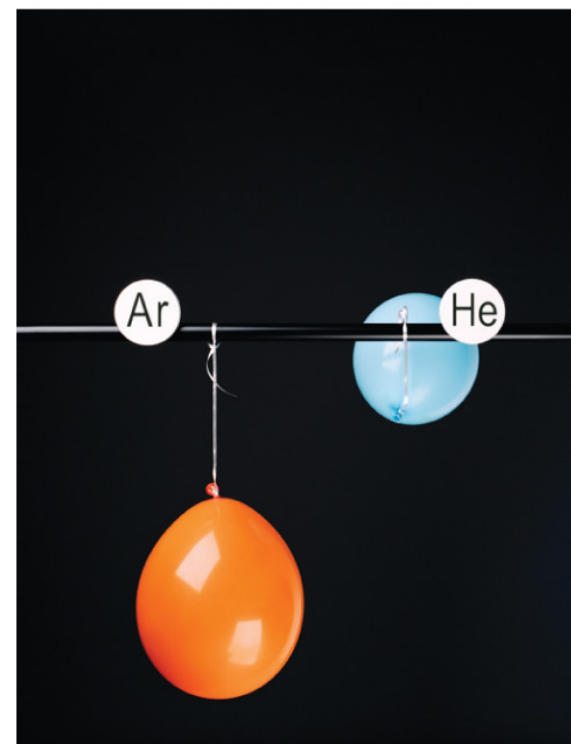


Effusion is the escape of gas molecules through a tiny hole into an evacuated space.

Effusion



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

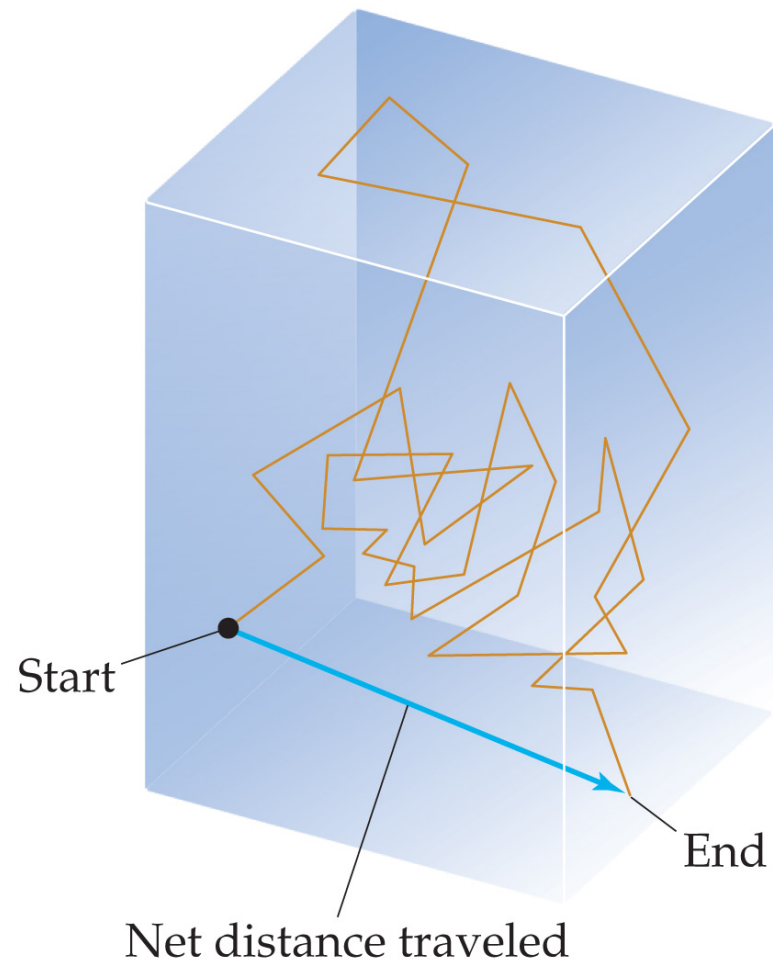


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The difference in the rates of effusion for helium and nitrogen, for example, explains why a helium balloon would deflate faster.

Diffusion

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



Graham's Law

$$KE_1 = KE_2$$

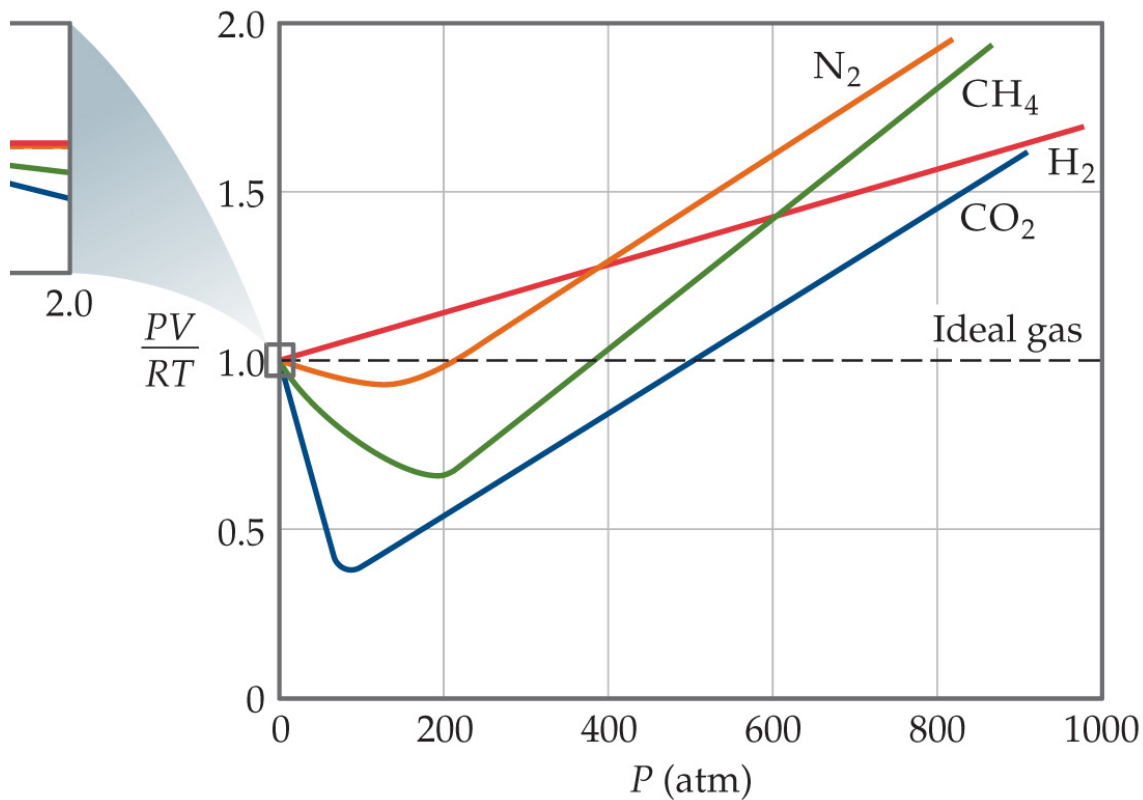
$$1/2 m_1 v_1^2 = 1/2 m_2 v_2^2$$

$$\frac{m_1}{m_2} = \frac{v_2^2}{v_1^2}$$

$$\frac{\text{Diffusion rate 1}}{\text{Diffusion rate 2}} = \frac{m_2^{1/2}}{m_1^{1/2}} \quad \text{compare H}_2 \text{ and O}_2:$$
$$\text{rate H}_2 / \text{rate O}_2 = (32)^{1/2} / 2^{1/2} = 4$$

Hydrogen effuses or diffuses 4 times faster than oxygen

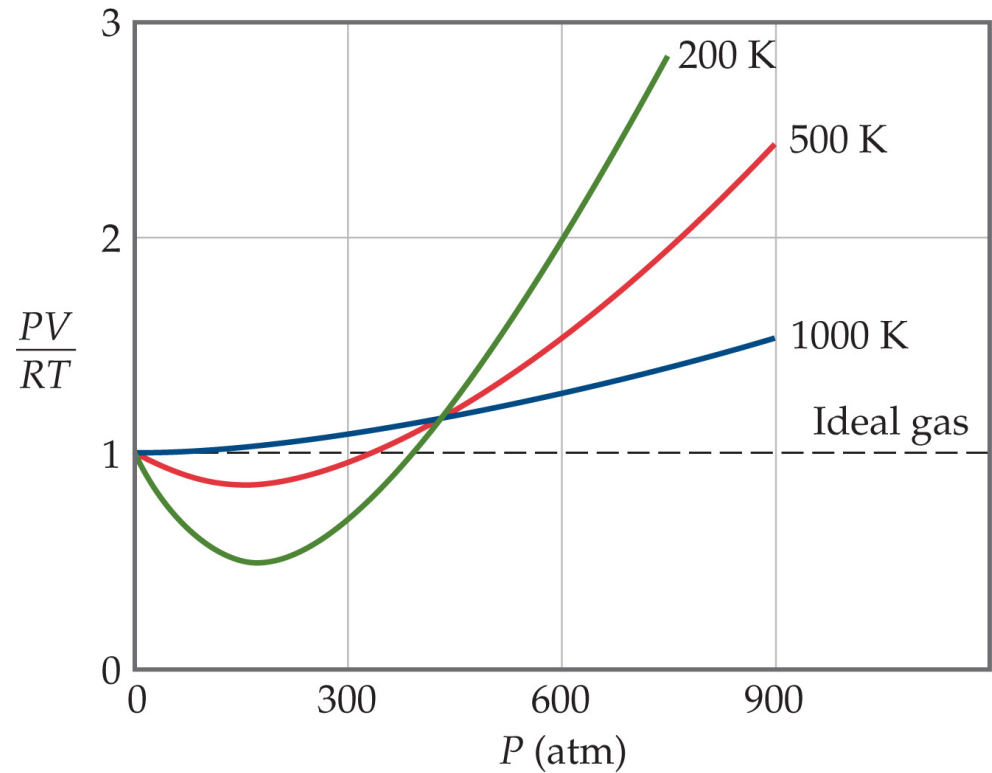
Real Gases



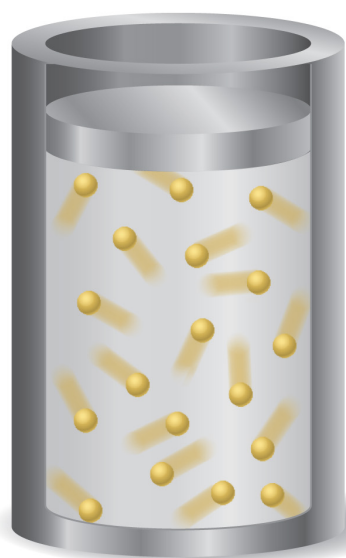
In the real world, the behavior of gases only conforms to the ideal-gas equation at relatively high temperature and low pressure.

Real Gases

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

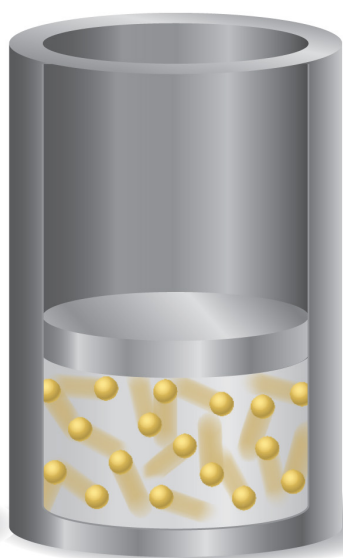


Deviations from Ideal Behavior

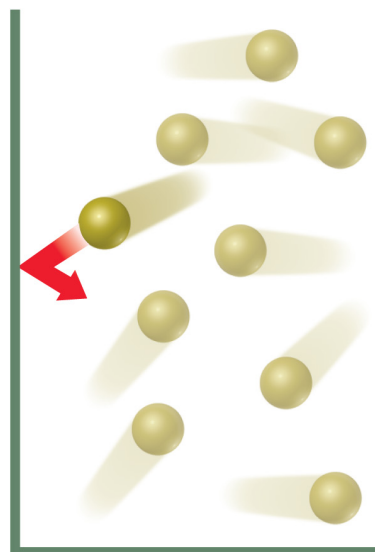


Low pressure

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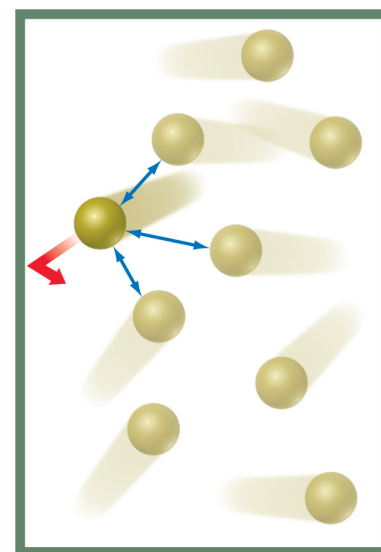


High pressure



Ideal gas

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Real gas

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.

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**.

Non ideal gases

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

- Van der Waals equation
- a corrects for attraction of gas atoms/molecules
- b corrects for the fact that molecules have size.

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	$a(\text{L}^2\text{-atm/mol}^2)$	$b (\text{L/mol})$
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
Cl ₂	6.49	0.0562
H ₂ O	5.46	0.0305

