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Ninth Edition

# GENERAL CHEMISTRY

Principles and Modern Applications

# Chapter 6: Gases

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# Contents

# Contents

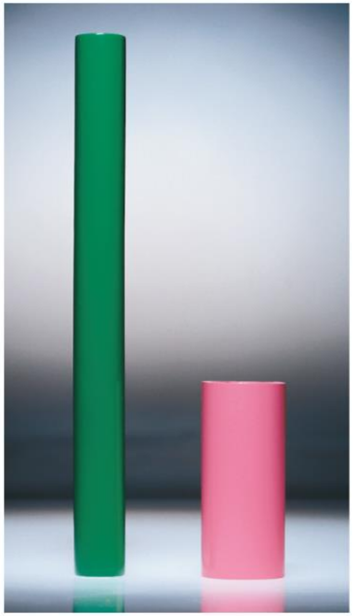
# 6-1 Properties of Gases: Gas Pressure

- The gaseous states of three halogens.

- Most common gases are colorless
  - $H_2$, $O_2$, $N_2$, CO and $CO_2$

# The Concept of Pressure

- The pressure exerted by a solid.
  - Both cylinders have the same mass
  - They have different areas of contact



$$P\ (\text{Pa}) = \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}}$$

# Liquid Pressure

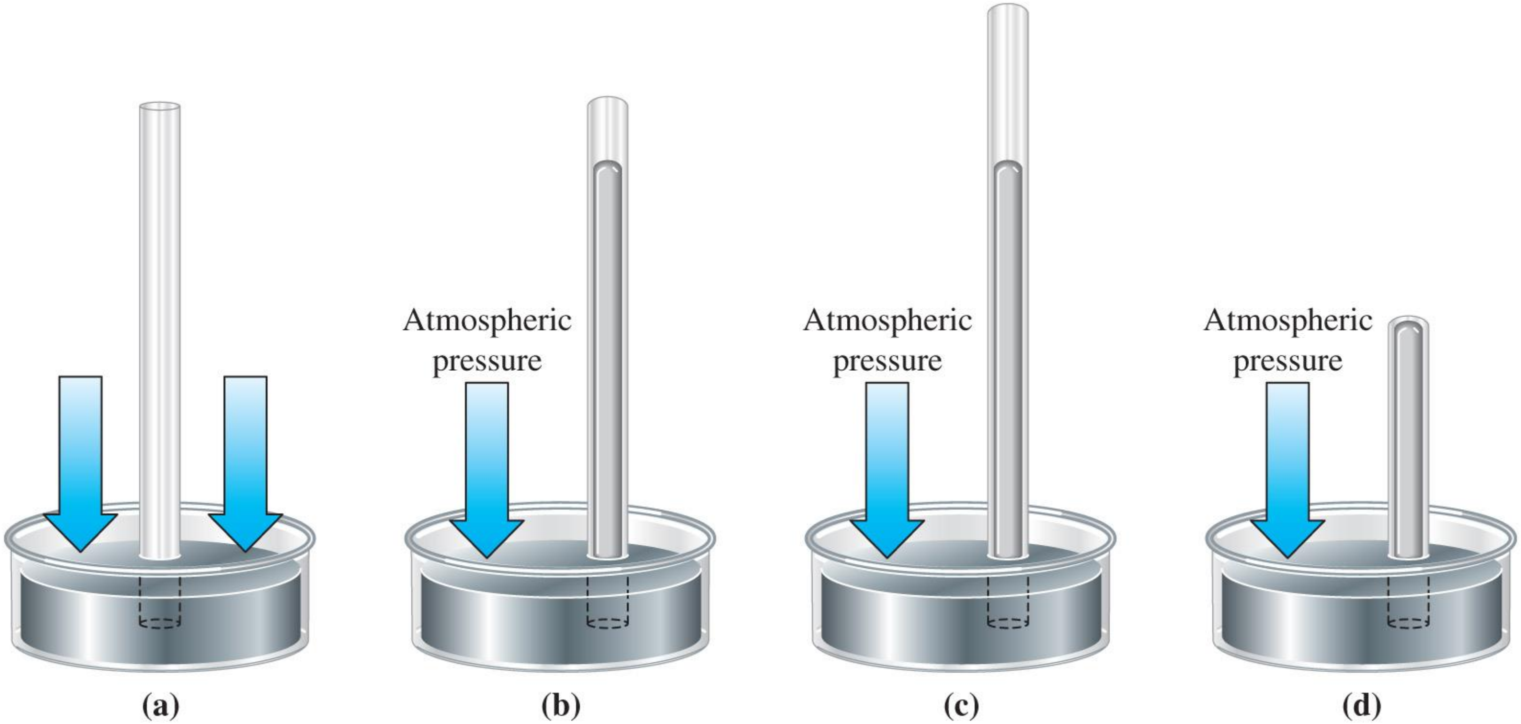
- The pressure exerted by a liquid depends on:
  - The height of the column of liquid.
  - The density of the column of liquid.

$$P = g \cdot h \cdot d$$

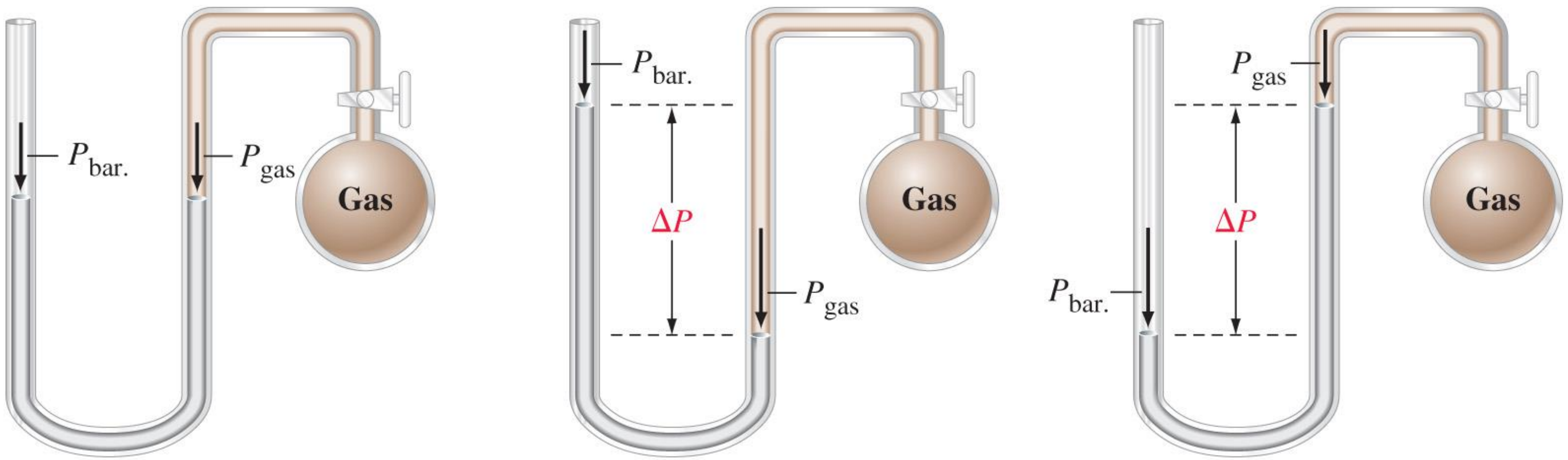
# Barometric Pressure

Standard Atmospheric Pressure

1.00 atm, 760 mm Hg, 760 torr, 101.325 kPa, 1.01325 bar



# Manometers




$P_{gas} = P_{bar.}$

**(a)** Gas pressure equal to barometric pressure

$P_{gas} = P_{bar.} + \Delta P$
$(\Delta P > 0)$

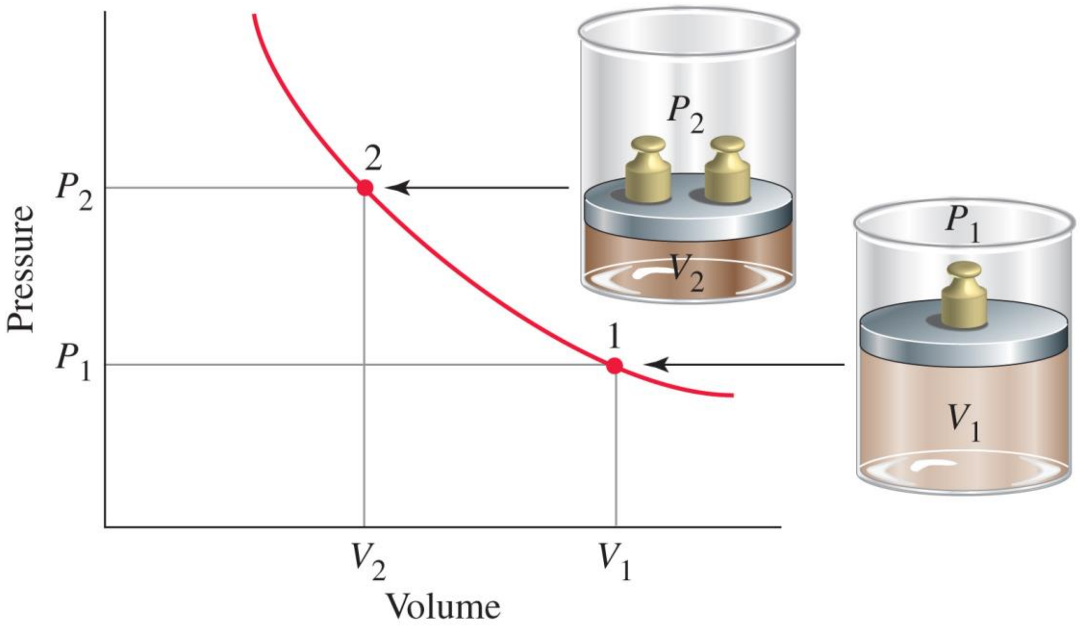
**(b)** Gas pressure greater than barometric pressure

$P_{gas} = P_{bar.} + \Delta P$
$(\Delta P < 0)$

**(c)** Gas pressure less than barometric pressure

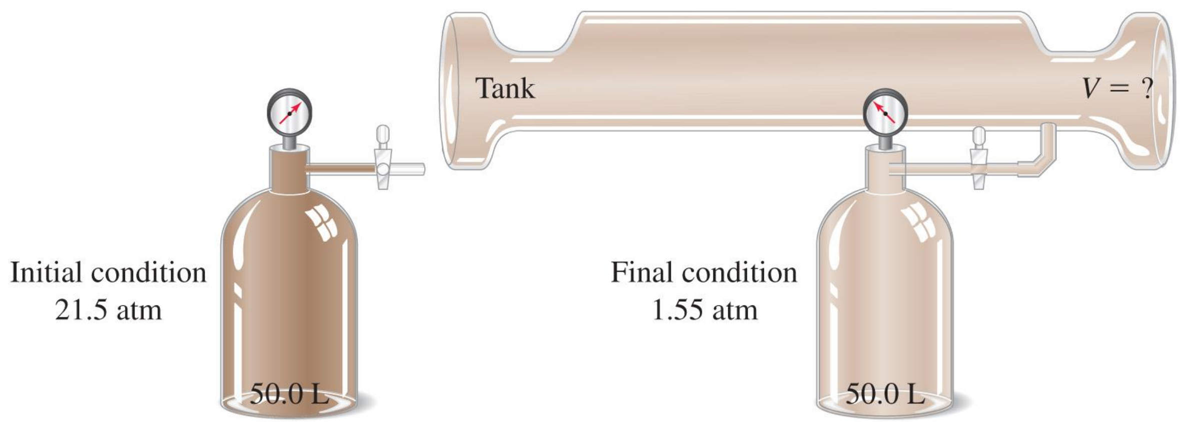
# 6-2 Simple Gas Laws

- Boyle 1662 $$P \propto \frac{1}{V}$$ PV = constant

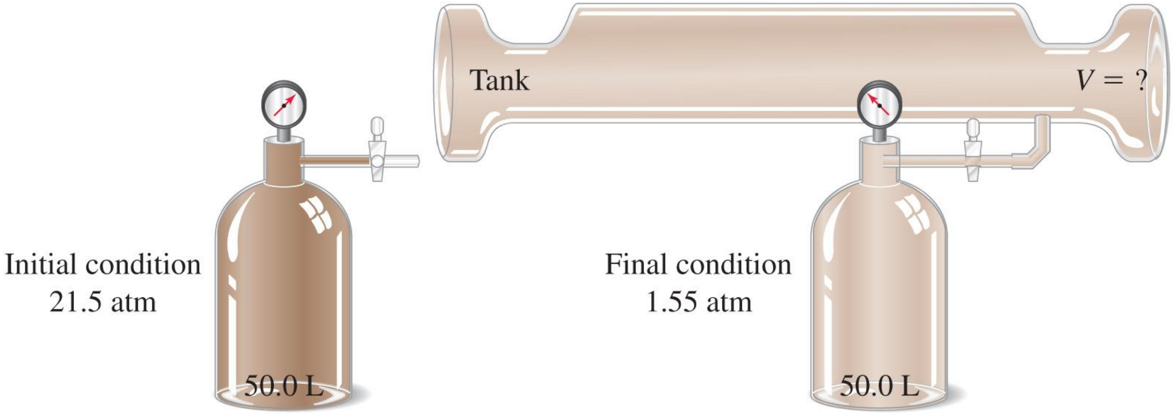


# EXAMPLE 6-4

**Relating Gas Volume and Pressure – Boyle's Law.** The volume of a large irregularly shaped, closed tank can be determined. The tank is first evacuated and then connected to a 50.0 L cylinder of compressed nitrogen gas. The gas pressure in the cylinder, originally at 21.5 atm, falls to 1.55 atm after it is connected to the evacuated tank. What is the volume of the tank?



# EXAMPLE 6-4




$$P_1V_1 = P_2V_2 \qquad V_2 = \frac{P_1V_1}{P_2} = 694\ \text{L} \qquad V_{tank} = 644\ \text{L}$$

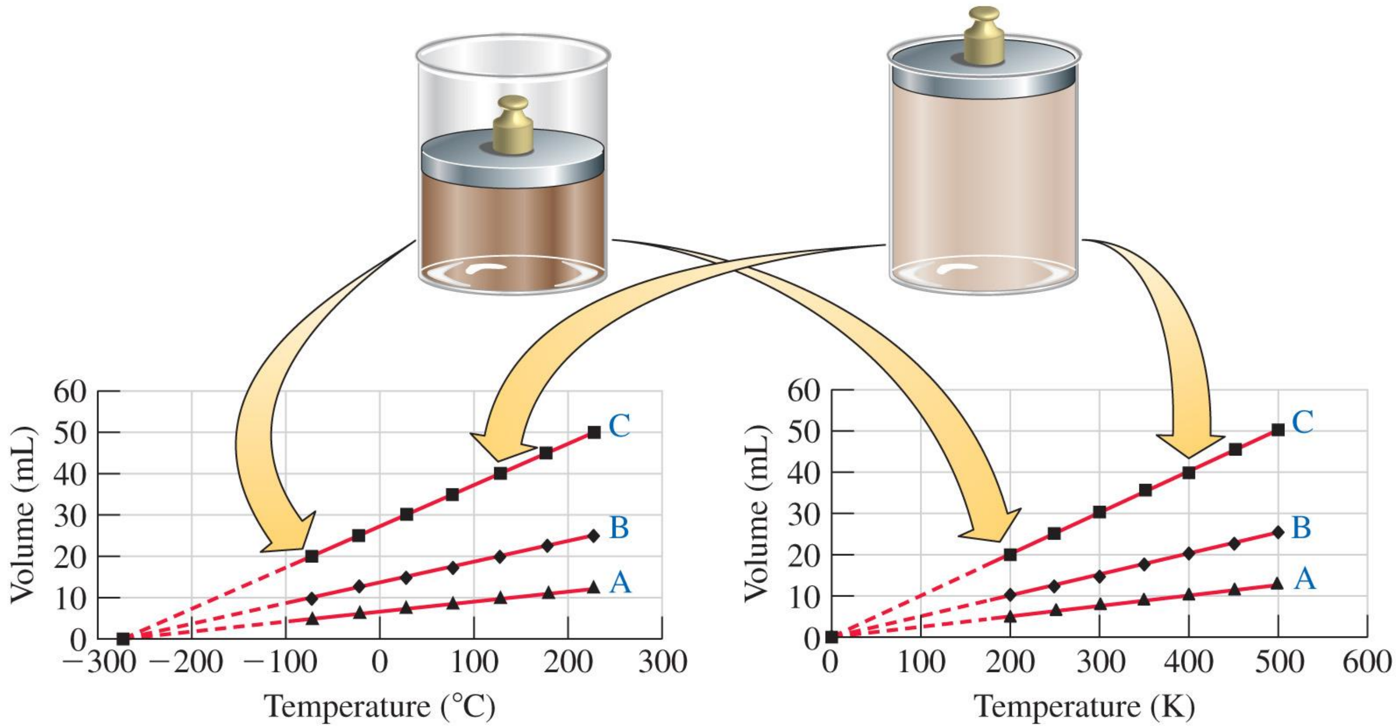
# Charles's Law

Charles 1787

Gay-Lussac 1802

$V \propto T$

$V = b\,T$



# Standard Temperature and Pressure

- Gas properties depend on conditions.
- Define standard conditions of temperature and pressure (STP).

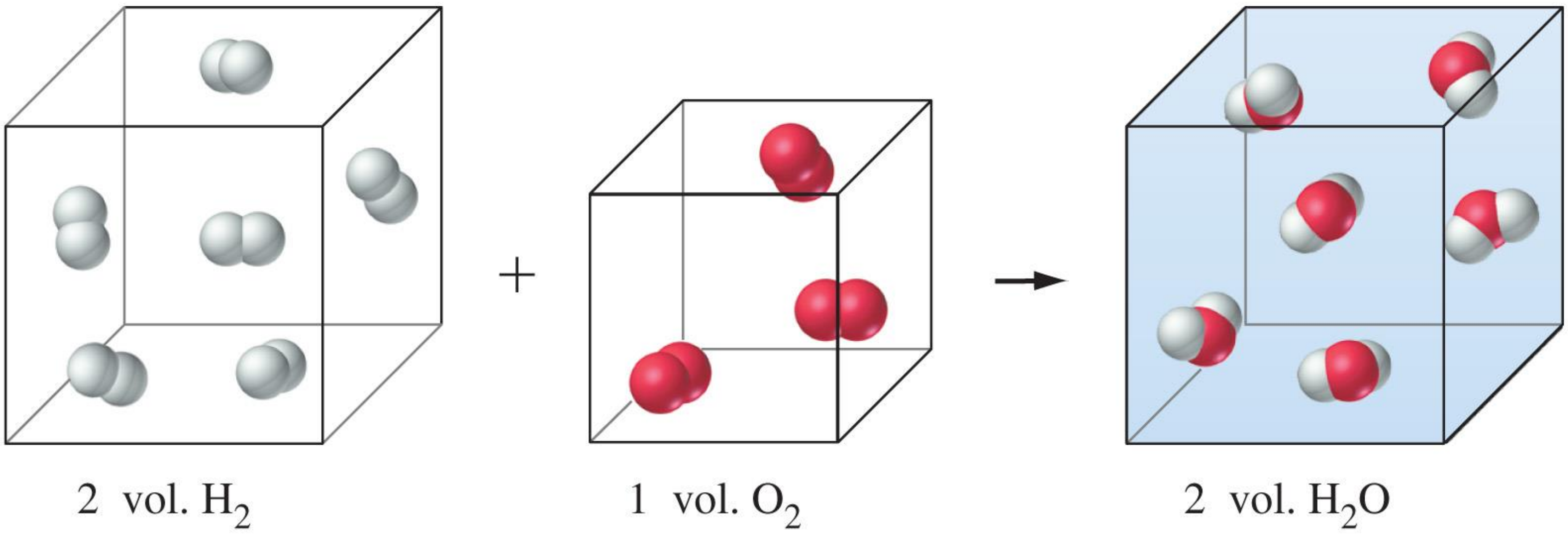
$$P = 1\ \text{atm} = 760\ \text{mm Hg}$$

$$T = 0°\text{C} = 273.15\ \text{K}$$

# Avogadro's Law

- Gay-Lussac 1808
  - Small volumes of gases react in the ratio of small whole numbers.
- Avogadro 1811
  - Equal volumes of gases have equal numbers of molecules *and*
  - Gas molecules may break up when they react.

# Formation of Water



# Avogadro's Law

At an a fixed temperature and pressure:

$$V \propto n \qquad \text{or} \qquad V = c\,n$$

At STP

1 mol gas = 22.4 L gas

# 6-3 Combining the Gas Laws: The Ideal Gas Equation and the General Gas Equation

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

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

$$PV = nRT$$

# The Gas Constant

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

$$= 0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 8.3145 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$$

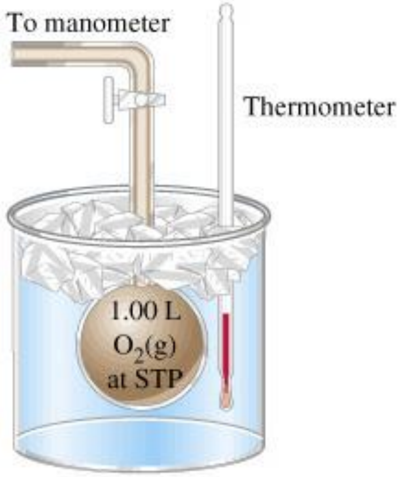
$$= 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

# Using the Gas Law

Collect information
*GIVEN*

# The General Gas Equation

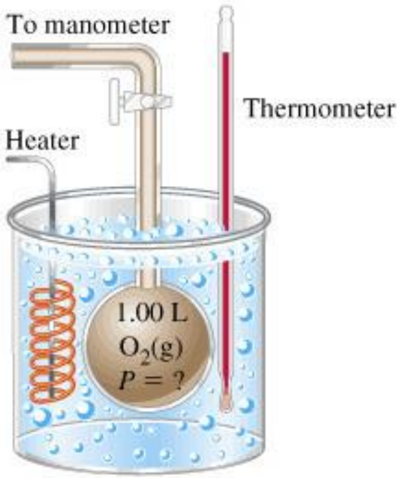
$$R = \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$




(a) Ice bath

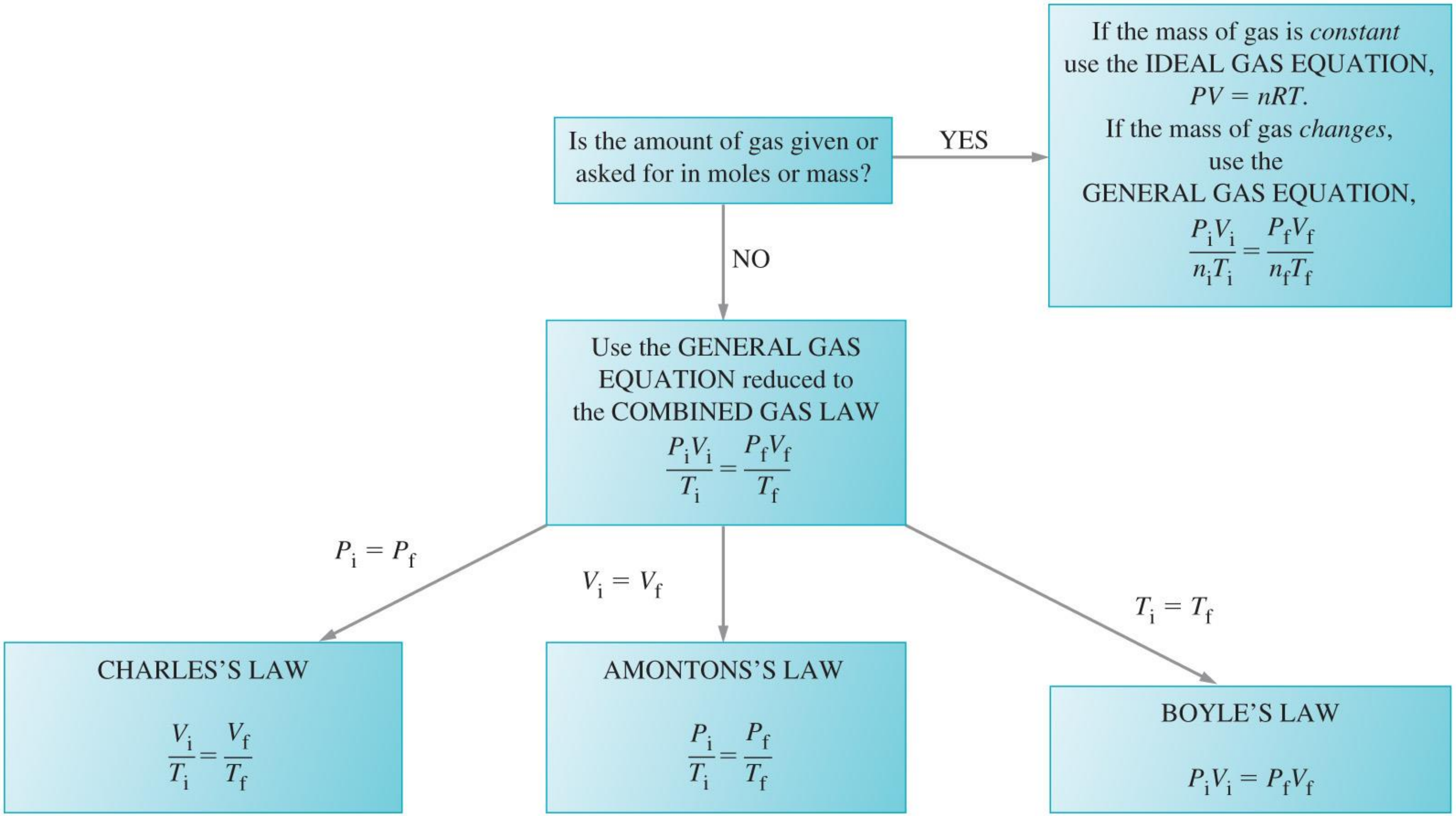
If we hold the amount and volume constant:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$




(b) Boiling water

# Using the Gas Laws



# 6-4 Applications of the Ideal Gas Equation

## Molar Mass Determination

$$PV = nRT \quad \text{and} \quad n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT$$

$$M = \frac{m\,RT}{PV}$$

# EXAMPLE 6-10

**Determining a Molar Mass with the Ideal Gas Equation.** Polypropylene is an important commercial chemical. It is used in the synthesis of other organic chemicals and in plastics production. A glass vessel weighs 40.1305 g when clean, dry and evacuated; it weighs 138.2410 when filled with water at 25°C ($\delta_{water}$ = 0.9970 g cm$^{-3}$) and 40.2959 g when filled with propylene gas at 740.3 mm Hg and 24.0°C. What is the molar mass of polypropylene?

*Strategy:*

Determine $V_{flask}$. Determine $m_{gas}$. Use the Gas Equation.

# EXAMPLE 6-10

*Determine $V_{flask}$:*

$$V_{flask} = m_{H_2O} \div d_{H_2O} = (138.2410\ \text{g} - 40.1305\ \text{g}) \div (0.9970\ \text{g cm}^{-3})$$

$$= 98.41\ \text{cm}^3 = 0.09841\ \text{L}$$

*Determine $m_{gas}$:*

$$m_{gas} = m_{filled} - m_{empty} = (40.2959\ \text{g} - 40.1305\ \text{g})$$

$$= 0.1654\ \text{g}$$

# EXAMPLE 5-6

*Use the Gas Equation:*

$$PV = nRT \qquad PV = \frac{m}{M} RT \qquad M = \frac{m\,RT}{PV}$$

$$M = \frac{(0.6145\ \text{g})(0.08206\ \cancel{\text{L}}\ \cancel{\text{atm}}\ \text{mol}^{-1}\ \cancel{\text{K}}^{-1})(297.2\ \cancel{\text{K}})}{(0.9741\ \cancel{\text{atm}})(0.09841\ \cancel{\text{L}})}$$

$$M = 42.08\ \text{g/mol}$$

# Gas Densities

$$PV = nRT \quad \text{and} \quad d = \frac{m}{V}, \quad n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT$$

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

# 6-5 Gases in Chemical Reactions

- Stoichiometric factors relate gas quantities to quantities of other reactants or products.
- Ideal gas equation relates the amount of a gas to volume, temperature and pressure.
- *Law of combining volumes* can be developed using the gas law.

# EXAMPLE 6-12

**Using the Ideal gas Equation in Reaction Stoichiometry Calculations.** The decomposition of sodium azide, $NaN_3$, at high temperatures produces $N_2(g)$. Together with the necessary devices to initiate the reaction and trap the sodium metal formed, this reaction is used in air-bag safety systems. What volume of $N_2(g)$, measured at 735 mm Hg and 26°C, is produced when 70.0 g $NaN_3$ is decomposed?

$$2\ NaN_3(s) \rightarrow 2\ Na(l) + 3\ N_2(g)$$

# EXAMPLE 6-12

*Determine moles of $N_2$:*

$$n_{N_2} = 70\ \cancel{\text{g NaN}_3} \times \frac{1\ \cancel{\text{mol NaN}_3}}{65.01\ \cancel{\text{g NaN}_3}} \times \frac{3\ \text{mol N}_2}{2\ \cancel{\text{mol NaN}_3}} = 1.62\ \text{mol N}_2$$

*Determine volume of $N_2$:*

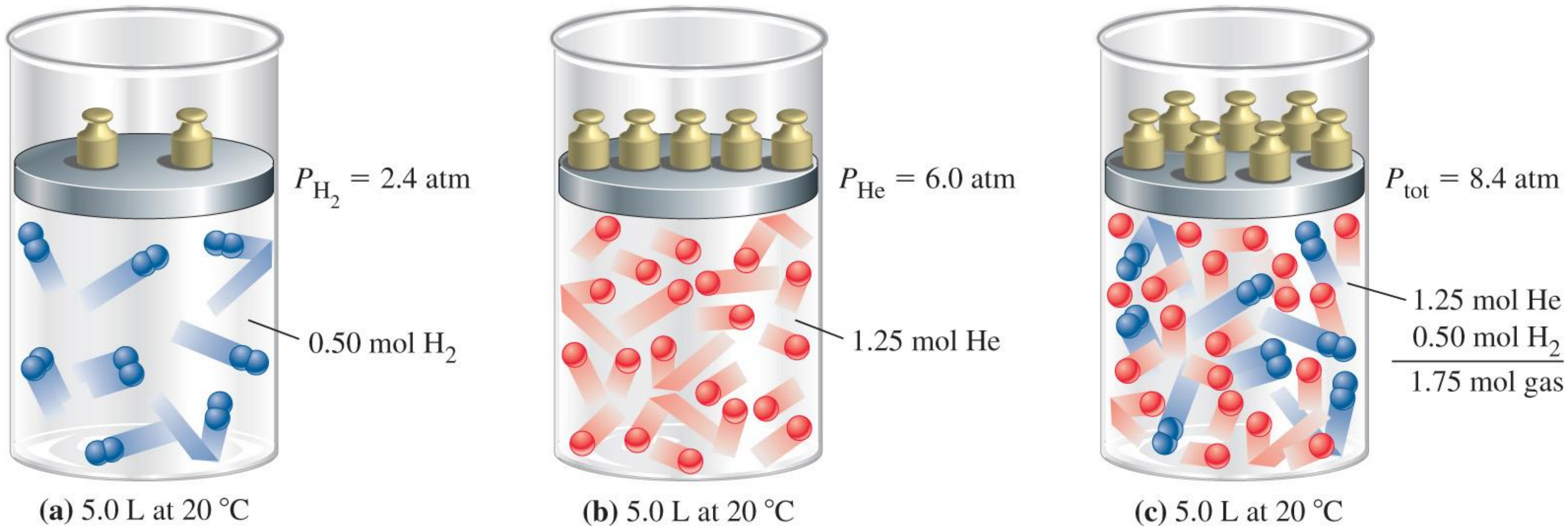
$$V = \frac{nRT}{P} = \frac{(1.62\ \cancel{\text{mol}})(0.08206\ \text{L}\ \cancel{\text{atm}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}})(299\ \cancel{\text{K}})}{\left\{(735\ \cancel{\text{mm Hg}}) \times \dfrac{1.00\ \cancel{\text{atm}}}{760\ \cancel{\text{mm Hg}}}\right\}} = 41.1\ \text{L}$$

# 6-6 Mixtures of Gases

- Gas laws apply to *mixtures* of gases.
- Simplest approach is to use $n_{total}$, but....

- Partial pressure
  - Each component of a gas mixture exerts a pressure that it would exert if it were in the container alone.

# Dalton's Law of Partial Pressure




The total pressure of a mixture of gases is the sum of the partial pressures of the components of the mixture.

# Partial Pressure

$$P_{tot} = P_a + P_b + \ldots$$

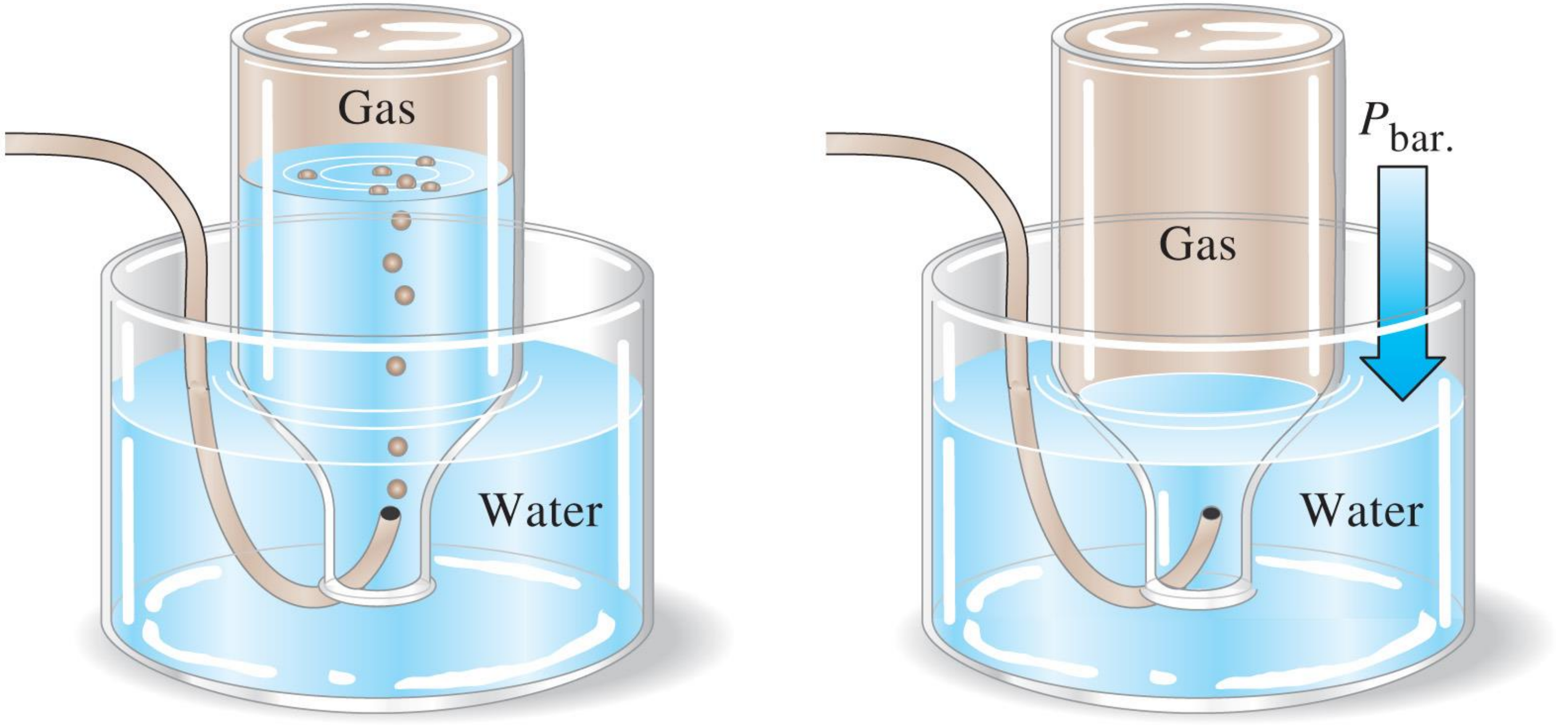
$$V_a = n_a RT/P_{tot} \qquad \text{and} \qquad V_{tot} = V_a + V_b + \ldots$$

$$\frac{V_a}{V_{tot}} = \frac{n_a RT/P_{tot}}{n_{tot} RT/P_{tot}} = \frac{n_a}{n_{tot}}$$

$$\text{Recall} \quad \frac{n_a}{n_{tot}} = \chi_a$$

$$\frac{P_a}{P_{tot}} = \frac{n_a RT/V_{tot}}{n_{tot} RT/V_{tot}} = \frac{n_a}{n_{tot}}$$

# Pneumatic Trough




$$P_{tot} = P_{bar} = P_{gas} + P_{H_2O}$$

# 6-7 Kinetic Molecular Theory

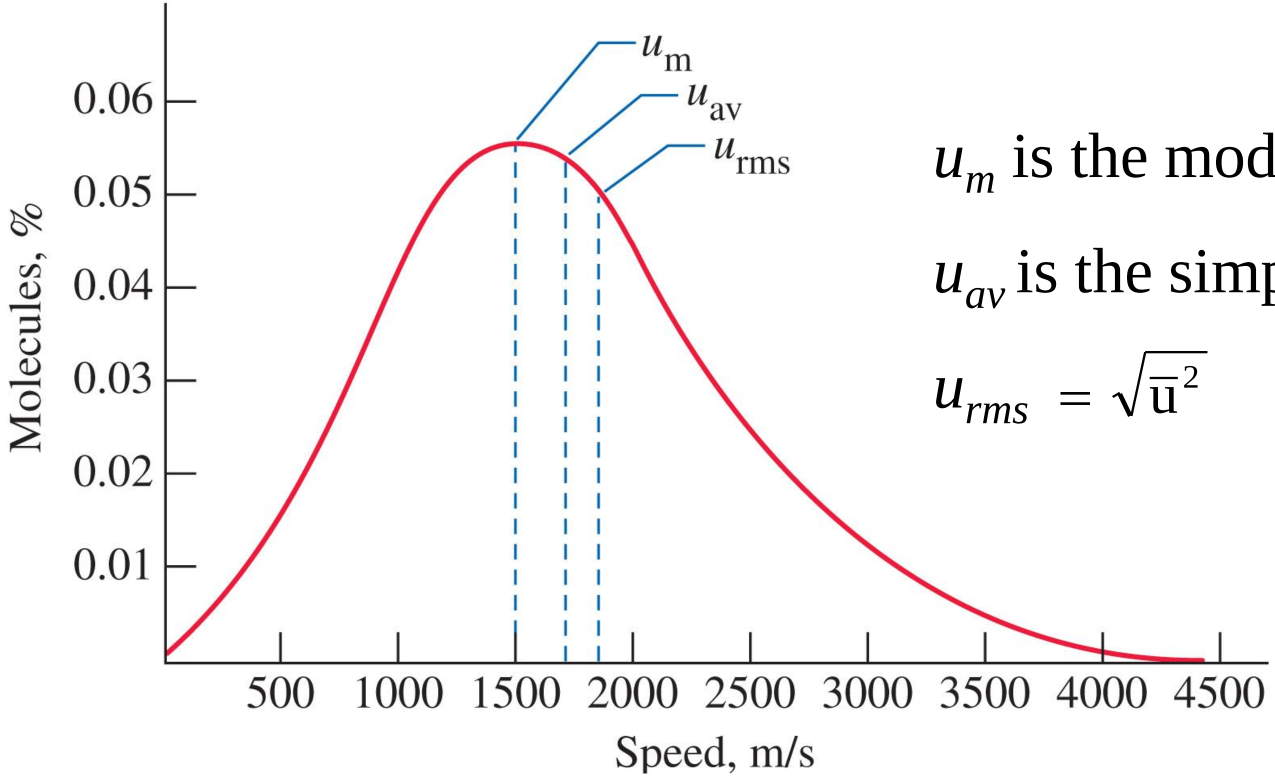
- Particles are point masses in constant, random, straight line motion.
- Particles are separated by great distances.
- Collisions are rapid and elastic.
- No force between particles.
- Total energy remains constant.

# Pressure – Assessing Collision Forces

- Translational kinetic energy, $$e_k = \frac{1}{2}mu^2$$
- Frequency of collisions, $$\nu = u\frac{N}{V}$$
- Impulse or momentum transfer, $$I = mu$$
- Pressure proportional to impulse times frequency $$P \propto \frac{N}{V}mu^2$$

# Pressure and Molecular Speed

- Three dimensional systems lead to: $$P = \frac{1}{3}\frac{N}{V} m \bar{u}^2$$




$u_m$ is the modal speed

$u_{av}$ is the simple average

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

# Pressure

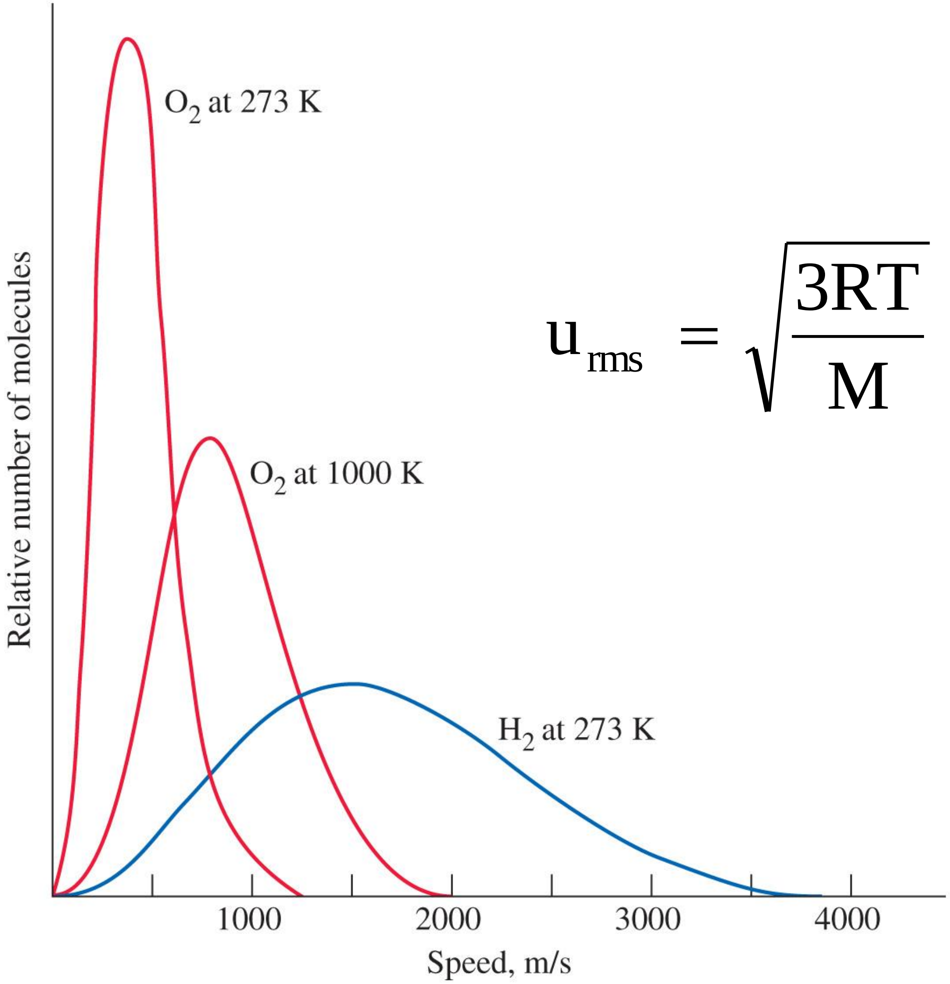
Assume one mole: $$PV = \frac{1}{3} N_A m \overline{u}^2$$

PV=RT so: $$3RT = N_A m \overline{u}^2$$

$N_A m = M$: $$3RT = M \overline{u}^2$$

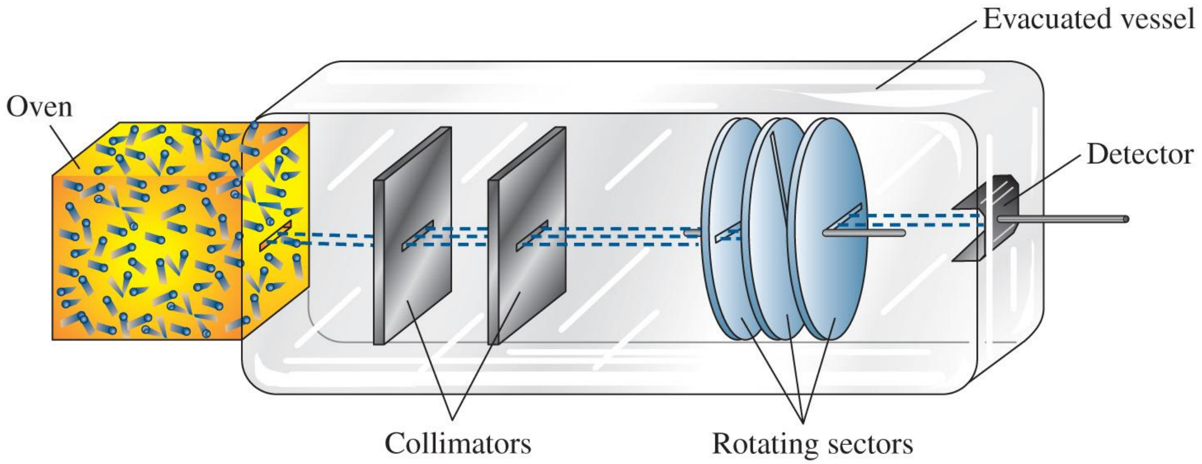
Rearrange: $$u_{rms} = \sqrt{\frac{3RT}{M}}$$

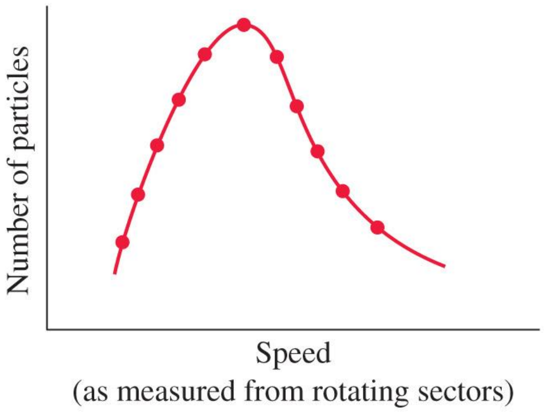
# Distribution of Molecular Speeds




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

# Determining Molecular Speed



# Temperature

Modify:

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

PV=RT so:

$$RT = \frac{2}{3} N_A \overline{e}_k$$

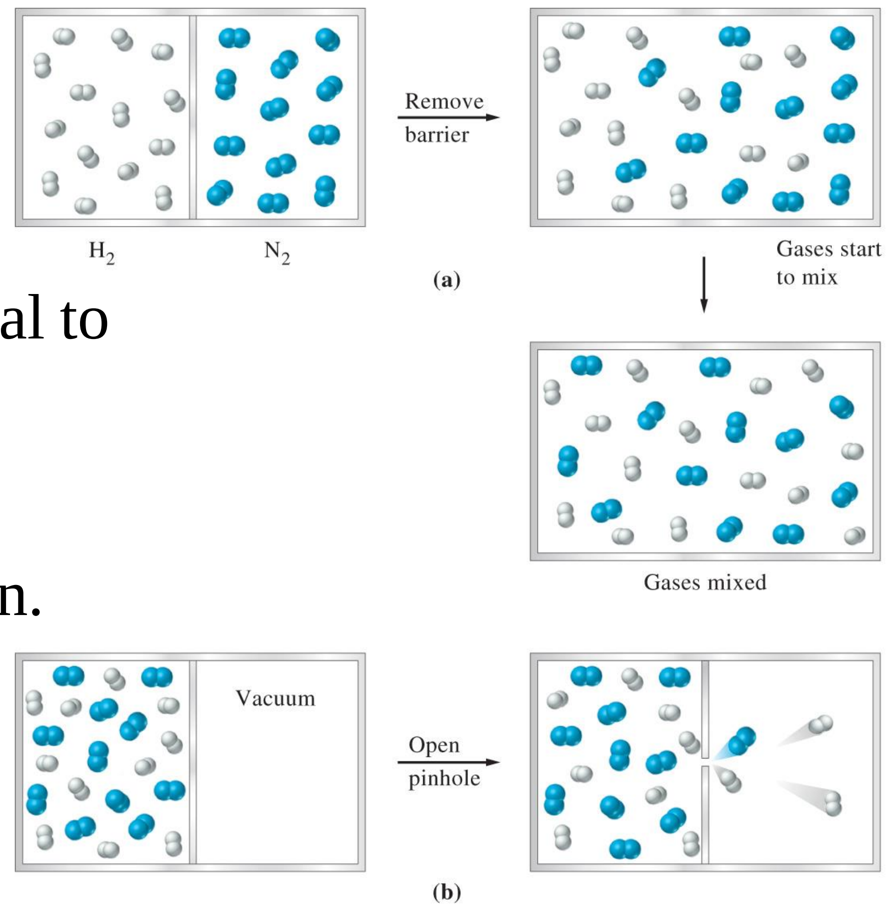
Solve for $\overline{e}_k$:

$$\overline{e}_k = \frac{3}{2} \frac{R}{N_A} (T)$$

Average kinetic energy is directly proportional to temperature!

# 6-8 Gas Properties Relating to the Kinetic-Molecular Theory

- Diffusion
  - Net rate is proportional to molecular speed.
- Effusion
  - A related phenomenon.



# Graham's Law

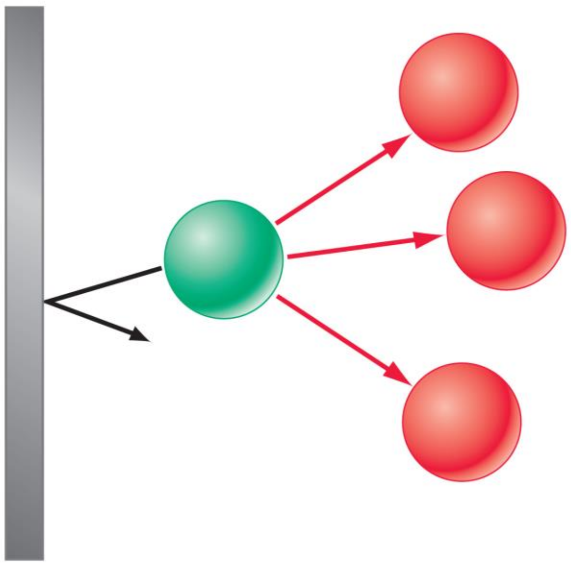
$$\frac{rate\ of\ effusion\ of\ A}{rate\ of\ effusion\ of\ B} = \frac{(u_{rms})_A}{(u_{rms})_B} = \sqrt{\frac{3RT/M_A}{3RT/M_B}} = \sqrt{\frac{M_B}{M_A}}$$

- Only for gases at low pressure (natural escape, not a jet).
- Tiny orifice (no collisions)
- Does not apply to diffusion.

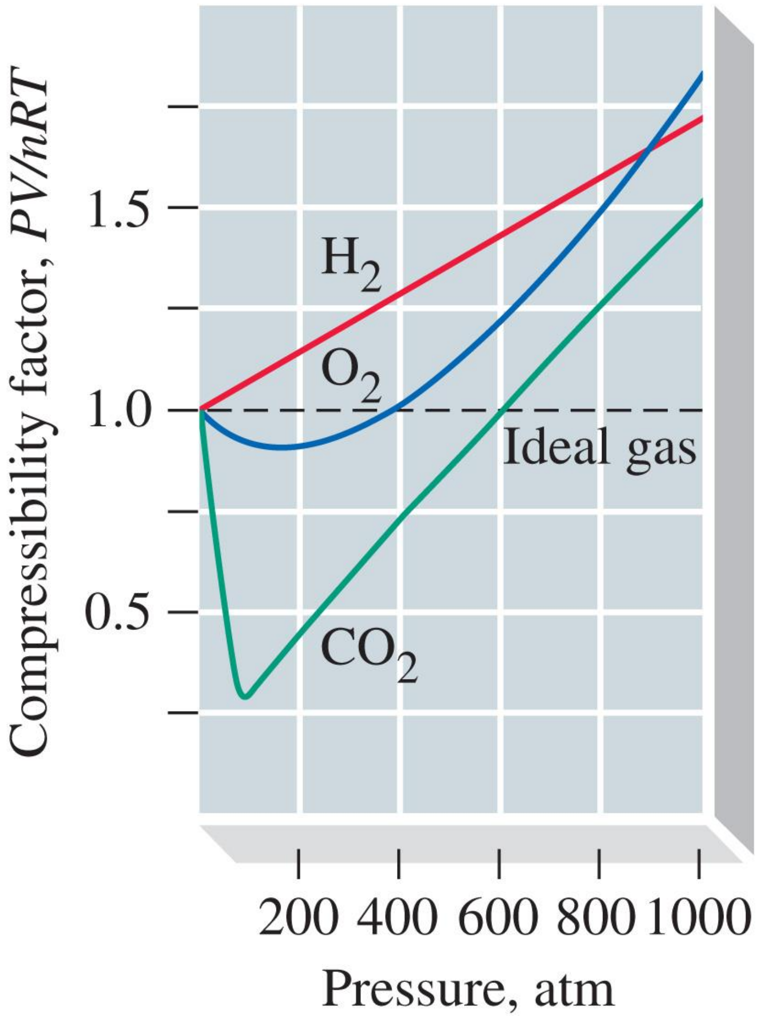
- Ratio used can be:
  - Rate of effusion (as above)
  - Molecular speeds
  - Effusion times
  - Distances traveled by molecules
  - Amounts of gas effused.

# 6-9 Nonideal (Real) Gases

- Compressibility factor PV/nRT = 1
- Deviations occur for real gases.
  - PV/nRT > 1 - molecular volume is significant.
  - PV/nRT < 1 – intermolecular forces of attraction.



# Real Gases



Compressibility factor, PV/nRT
1.5
1.0
0.5
H2
O2
Ideal gas
CO2
200 400 600 800 1000
Pressure, atm

# van der Waals Equation

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

# End of Chapter Questions

- A problem is like a knot in a ball of wool:
  - If you pull hard on any loop:
    - The knot will only tighten.
    - The solution (undoing the knot) will not be achieved.
  - If you pull lightly on one loop and then another:
    - You gradually loosen the knot.
    - As more loops are loosened it becomes easier to undo the subsequent ones.
- Don’t pull too hard on any one piece of information in your problem, it tightens.