

Chapter 9

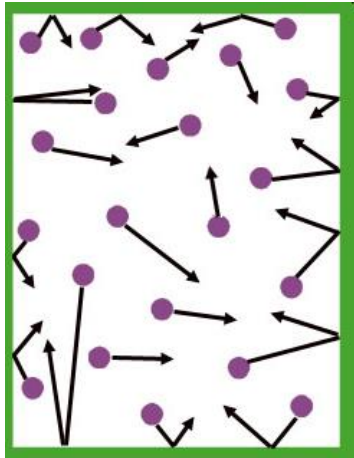
Gases



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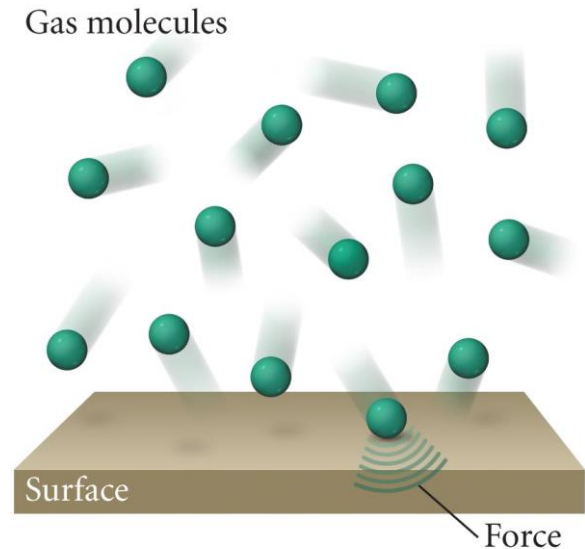
Simple Questions



1. How can we inflate ball?
2. Which one needs more air, big or small balls?
3. Why inflated ball is hard?
4. What's the pressure?
5. What happens if you press the ball (reduce the volume)?
6. What happens if you warm the ball (increase temperature)?
7. So pressure depends on () and () and ()

Gases Pushing: Pressure

- Gas molecules are constantly in motion
- As they move and strike a surface, they push on that surface
 - ✓ push = force
- If we could measure the total amount of force exerted by gas molecules hitting the entire surface at any one instant, we would know the **pressure** the gas is exerting
 - ✓ **pressure** = force per unit area



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

The Pressure of a Gas

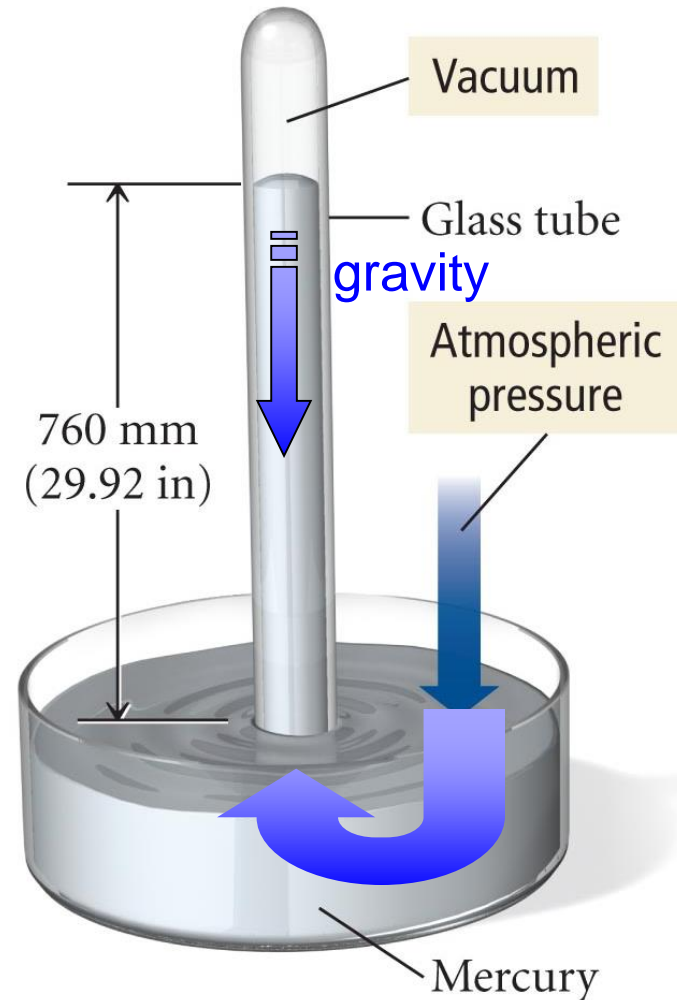
- Gas pressure is a result of the constant movement of the gas molecules and their collisions with the surfaces around them
- The pressure of a gas depends on several factors
 - ✓ number of gas particles in a given volume (n)
 - ✓ volume of the container (V)
 - ✓ average speed of the gas particles (T)



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Measuring Air Pressure

- We measure air pressure with a **barometer**
- Column of mercury supported by air pressure
- Force of the air on the surface of the mercury counter balances the force of gravity on the column of mercury



Common Units of Pressure

Unit	Average Air Pressure at Sea Level
pascal (Pa), $1\text{Pa} = 1 \frac{\text{N}}{\text{m}^2}$	101,325
kilopascal (kPa)	101.325
atmosphere (atm)	1 (exactly)
millimeters of mercury (mmHg)	760 (exactly)
inches of mercury (inHg)	29.92
torr (torr)	760 (exactly)
pounds per square inch (psi, lbs./in ²)	14.7

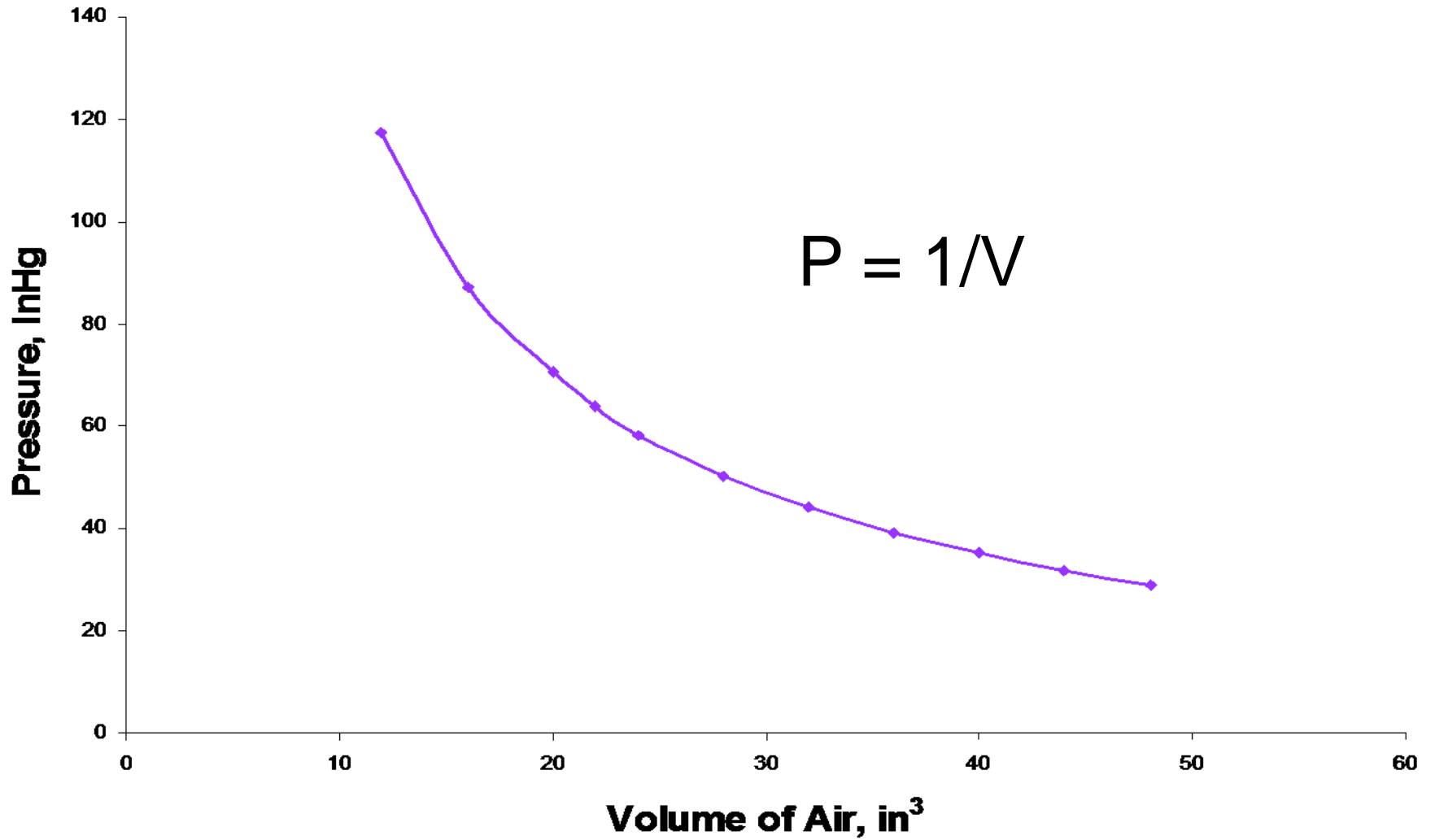
A high-performance bicycle tire has a pressure of 132 psi. What is the pressure in mmHg?

Boyle's Law

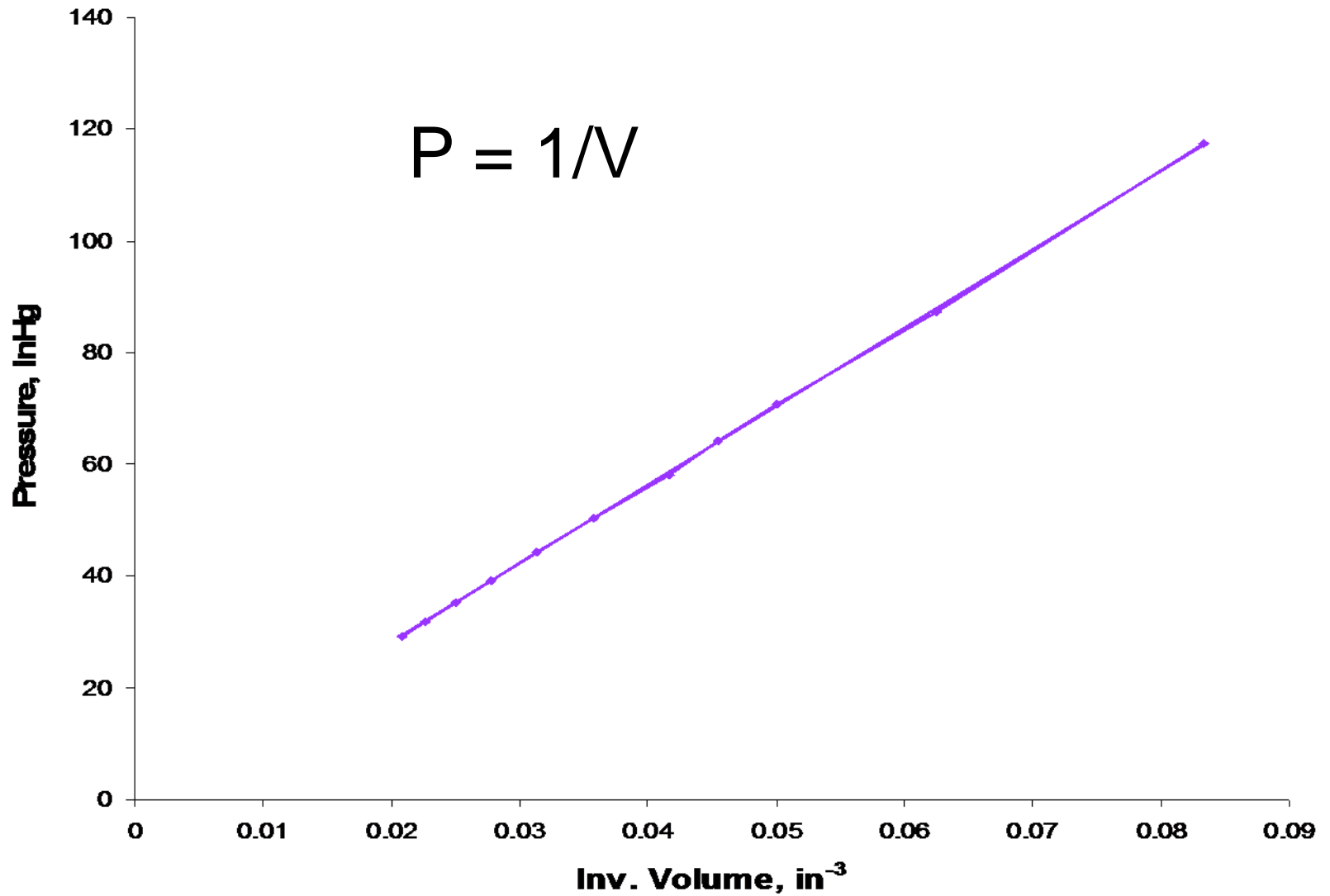
Robert Boyle (1627–1691)

- Pressure of a gas is inversely proportional to its volume
 - ✓ constant T and amount of gas
 - ✓ graph P vs V is curve
 - ✓ graph P vs 1/V is straight line
- As P increases, V decreases by the same factor
- $P \times V = \text{constant}$
- $P_1 \times V_1 = P_2 \times V_2$

Boyle's Expt.

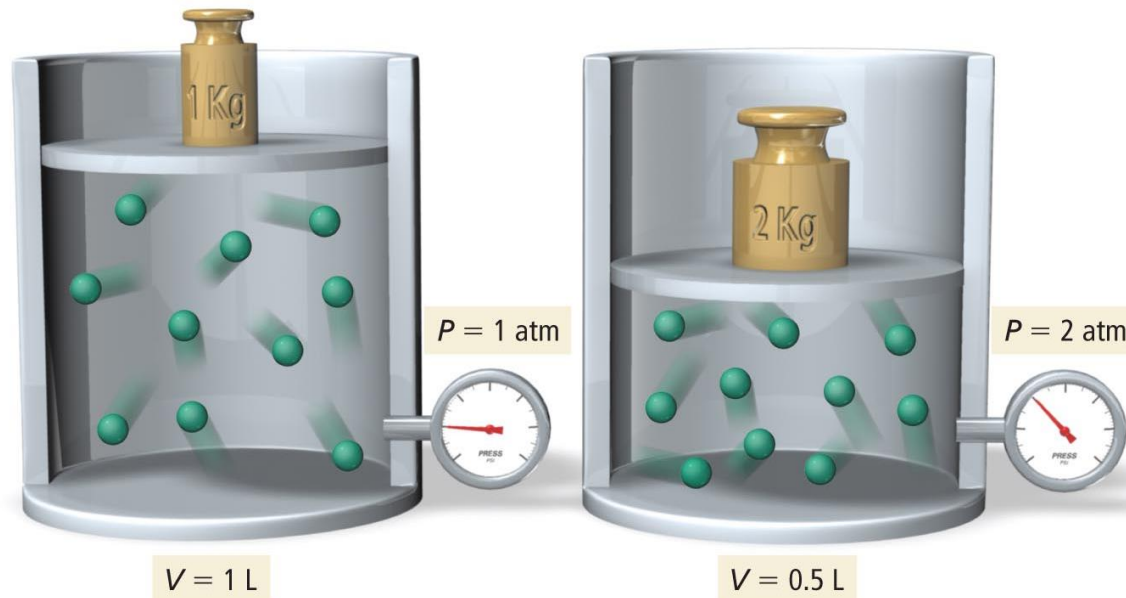


Inverse Volume vs Pressure of Air, Boyle's Expt.



Boyle's Law: A Molecular View

- Pressure is caused by the molecules striking the sides of the container
- When you **decrease the volume** of the container with the same number of molecules in the container, more molecules will hit the wall at the same instant
- This results in **increasing the pressure**



A cylinder with a movable piston has a volume of 7.25 L at 4.52 atm. What is the volume at 1.21 atm?

Charles's Law

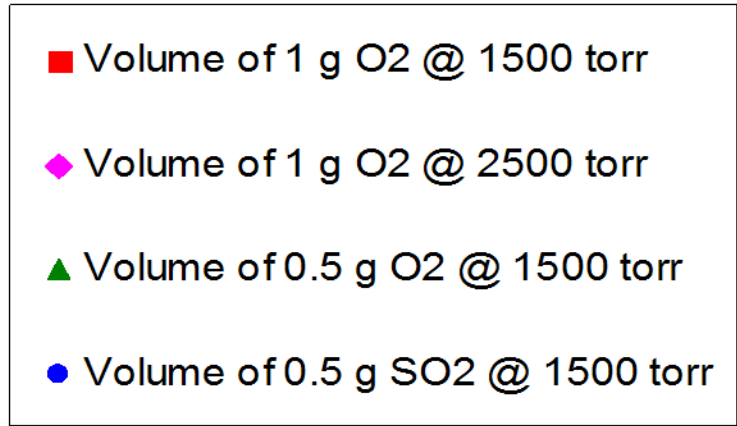
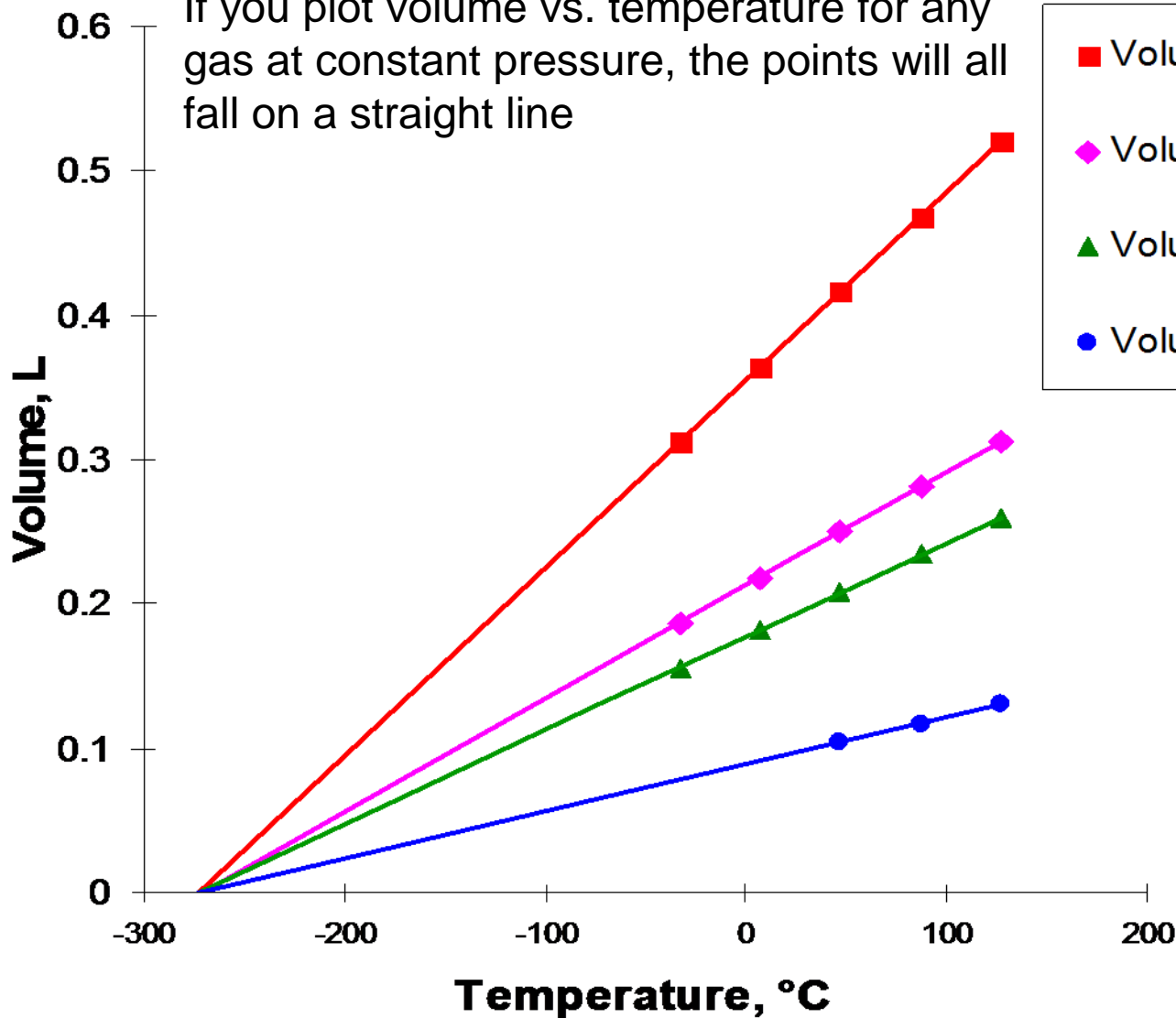
Jacques Charles (1746–1823)

- Volume is directly proportional to temperature
- $V \propto T$
 - ✓ constant P and amount of gas
 - ✓ graph of V vs. T is straight line
- As T increases, V also increases
- Kelvin $T = \text{Celsius } T + 273$
- $V = \text{constant} \times T$
 - ✓ if T measured in Kelvin

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

Charles's Law & Absolute Zero

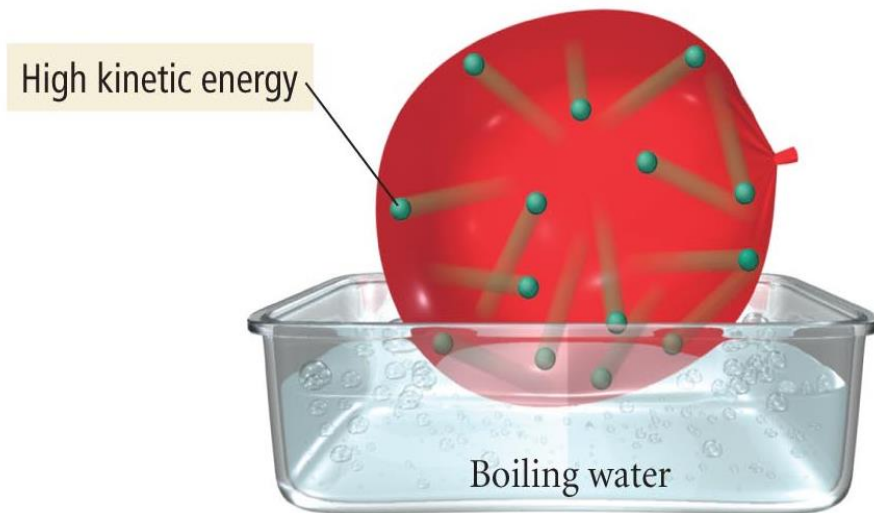
If you plot volume vs. temperature for any gas at constant pressure, the points will all fall on a straight line



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

Charles's Law – A Molecular View

- The pressure of gas inside and outside the balloon are the same
- At high temperatures, the gas molecules are moving faster, so they hit the sides of the balloon harder and often – causing the volume to become larger



A gas has a volume of 2.57 L at 0.00 °C. What was the temperature at 2.80 L?

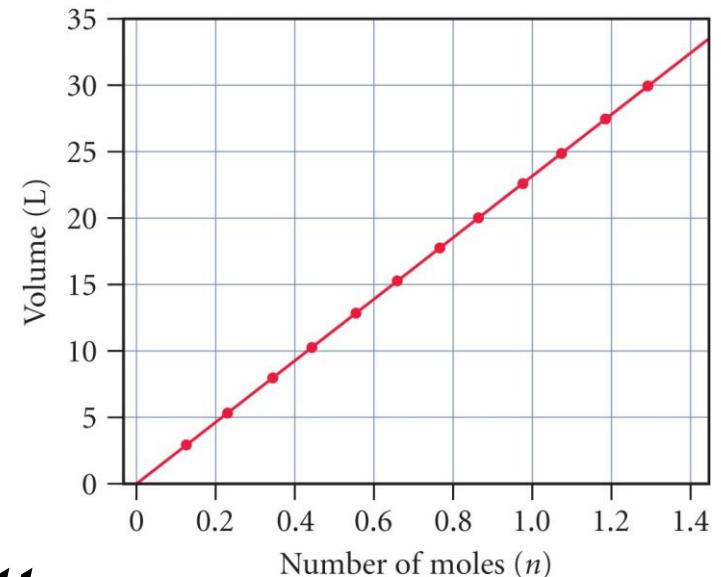
Avogadro's Law

- Volume directly proportional to the number of gas molecules
 - ✓ $V = \text{constant} \times n$
 - ✓ constant P and T
 - ✓ more gas molecules = larger volume
- Count number of gas molecules by **moles**
- Equal volumes of gases contain equal numbers of molecules
 - ✓ *the nature of gas doesn't matter*

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

Avogadro's Law

As amount of gas increases, volume increases.



0.225 mol sample of He has a volume of 4.65 L. How many moles must be added to give 6.48 L?

If 1.00 mole of a gas occupies 22.4 L at STP, what volume would 0.750 moles occupy?

STP: Standard temperature and pressure (0 °C and 1 atm)

Ideal Gas Law

$$\frac{(P) \cdot (V)}{(n) \cdot (T)} = R \quad \text{or} \quad PV = nRT$$

P: pressure (atm)

V: volume (L)

N: # of moles

R: 0.082 (atm·L)/(mole·K)

T: temperature (K)

How many moles of gas are in a basketball with total pressure 24.3 psi, volume of 3.24 L at 25°C?

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

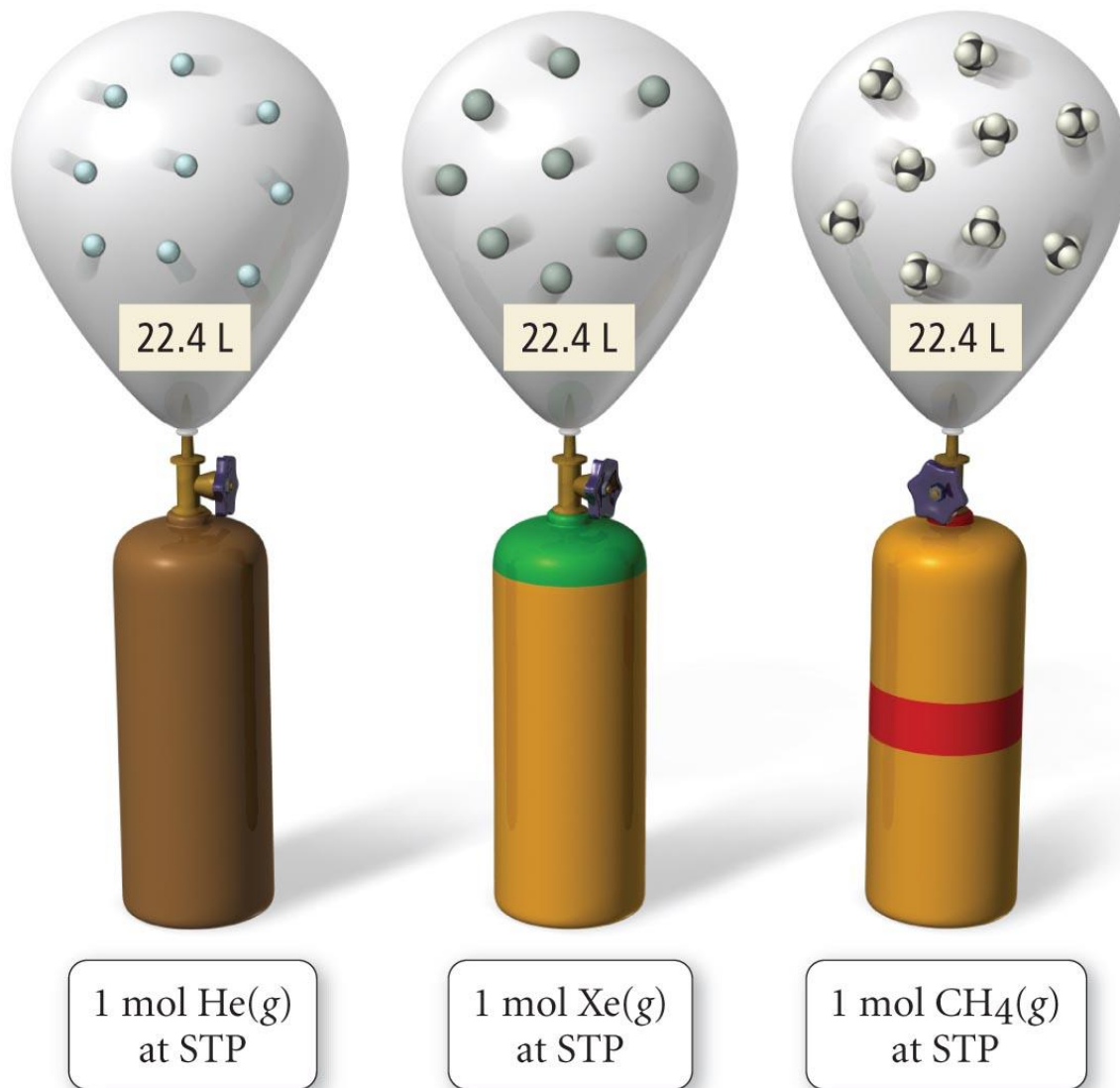
- Standard pressure = 1 atm
- Standard temperature = 273 K
0 °C

Practice – A gas occupies 10.0 L at 44.1 psi and 27 °C. What volume will it occupy at standard conditions?

Molar Volume

- Solving the ideal gas equation for the volume of 1 mol of gas at STP gives 22.4 L
6.022 x 10²³ molecules of gas
- We call the volume of 1 mole of gas at STP the **molar volume**
- it is important to recognize that one mole measures of different gases have different masses, even though they have the same volume

Molar Volume



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How many liters of O₂ @ STP can be made from the decomposition of 100.0 g of PbO₂?



(PbO₂ = 239.2, O₂ = 32.00)

Density at Standard Conditions

- 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

$$\text{Density} = \frac{\text{Molar Mass, g}}{22.4 \text{ L}}$$

Calculate the density of $\text{N}_2(g)$ at STP

Gas Density

$$\text{mass} \times \frac{1 \text{ mol}}{\text{molar mass}} = \text{moles} \quad \therefore \quad \text{moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{density} = \frac{\text{mass in grams}}{\text{volume in liters}}$$

$$P \times V = n \times R \times T$$

$$P \times V = \frac{\text{mass}}{\text{molar mass}} \times R \times T$$

$$\frac{\text{mass}}{V} = \text{density} = \frac{P \times (\text{molar mass})}{R \times T}$$

- Density is directly proportional to molar mass

Calculate the density of N_2 at 125°C and 755 mmHg

What is the molar mass of a gas if 12.0 g occupies 197 L at 3.80×10^2 torr and 127°C ?

Composition of Dry Air

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

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

The partial pressure of each gas in a mixture can be calculated using the ideal gas law

for two gases, A and B, mixed together

$$P_A = \frac{n_A \times R \times T}{V} \quad P_B = \frac{n_B \times R \times T}{V}$$

the temperature and volume of everything in the mixture are the same

$$n_{\text{total}} = n_A + n_B$$

$$P_{\text{total}} = P_A + P_B = \frac{n_{\text{total}} \times R \times T}{V}$$

Find the partial pressure of neon in a mixture with total pressure 3.9 atm, volume 8.7 L, temperature 598 K, and 0.17 moles Xe.

Mole Fraction

The ratio of the moles of a single component to the total number of moles in the mixture is called the **mole fraction, χ**

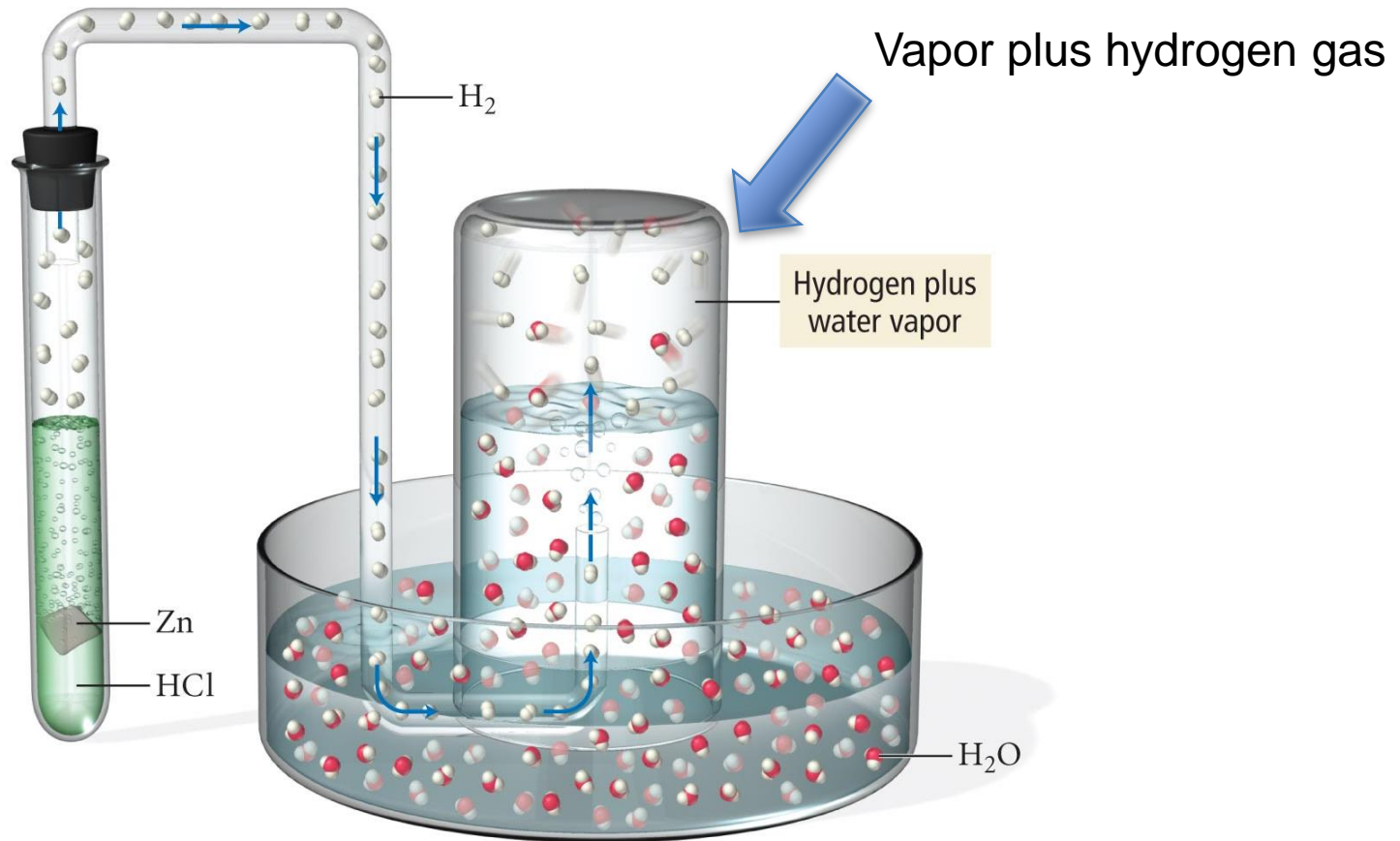
$$\chi_A = \frac{n_A}{n_{\text{total}}}$$

The partial pressure of a gas is equal to the mole fraction of that gas times the total pressure

$$P_A = \chi_A \cdot P_{\text{total}}$$

Find the mole fractions and partial pressures in a 12.5 L tank with 24.2 g He and 4.32 g O₂ at 298 K

Collecting Gas by Water Displacement



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- 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

Vapor Pressure of Water

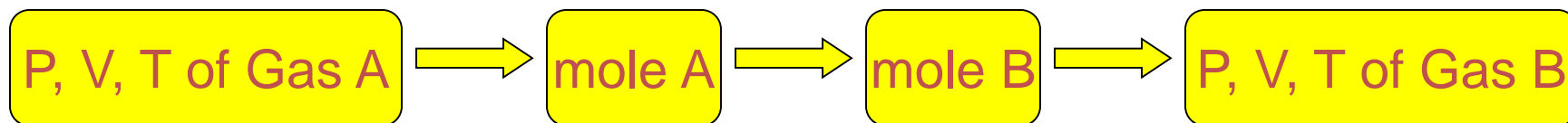
TABLE 5.4 Vapor Pressure of Water versus Temperature

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		

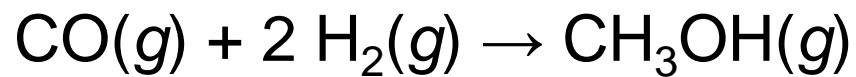
1.02 L of O_2 collected over water at 293 K with a total pressure of 755.2 mmHg. Find mass O_2 .

Reactions Involving Gases

- The principles of reaction stoichiometry from Chapter 4 can be combined with the gas laws for reactions involving gases
- In reactions of gases, the amount of a gas is often given as a volume
 - ✓ instead of moles
 - ✓ as we've seen, you must state pressure and temperature
- The ideal gas law allows us to convert from the volume of the gas to moles; then we can use the coefficients in the equation as a mole ratio
- When gases are at STP, use $1 \text{ mol} = 22.4 \text{ L}$



What volume of H_2 is needed to make 35.7 g of CH_3OH at 738 mmHg and 355 K?



Kinetic Molecular Theory

- The size of a gas particle is negligibly small but not zero.
- The average kinetic energy of the gas particles is directly proportional to the temperature (K)
- The collision of one particle with another is completely elastic (no loss of energy).



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Kinetic Energy (KE) and Molecular Velocities

- Average kinetic energy depends on the **mass** and **velocity**

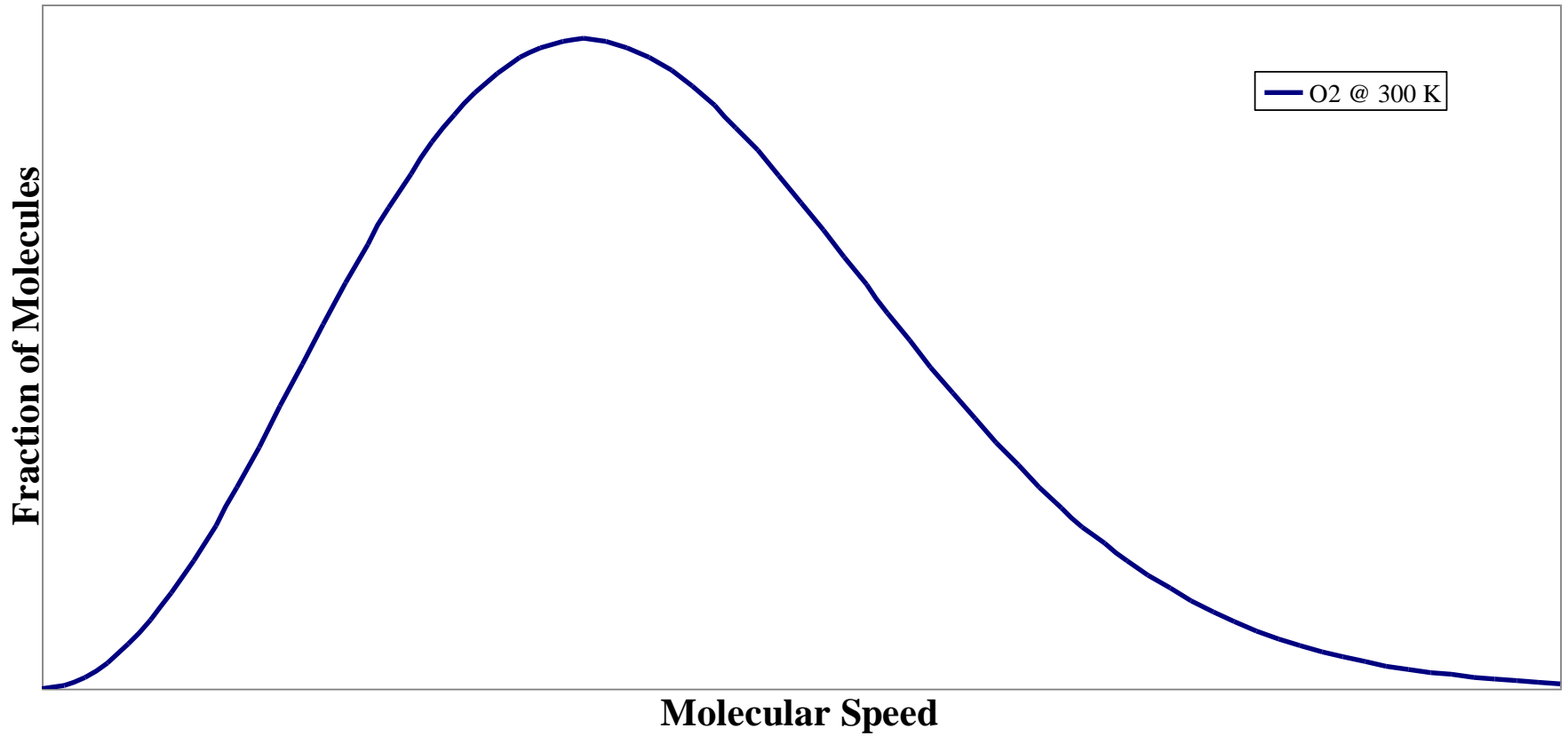
$$KE = \frac{1}{2}mv^2$$

- Gases in the same container have the same average kinetic energy at constant T
- 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

Boltzmann Distribution

Distribution Function



Molecular Velocities

- u_{rms} : average molecular velocity

N_A is Avogadro's number

m : mass of individual gas molecule

$N_A \cdot \text{mass} = \text{molar mass in kg/mol}$

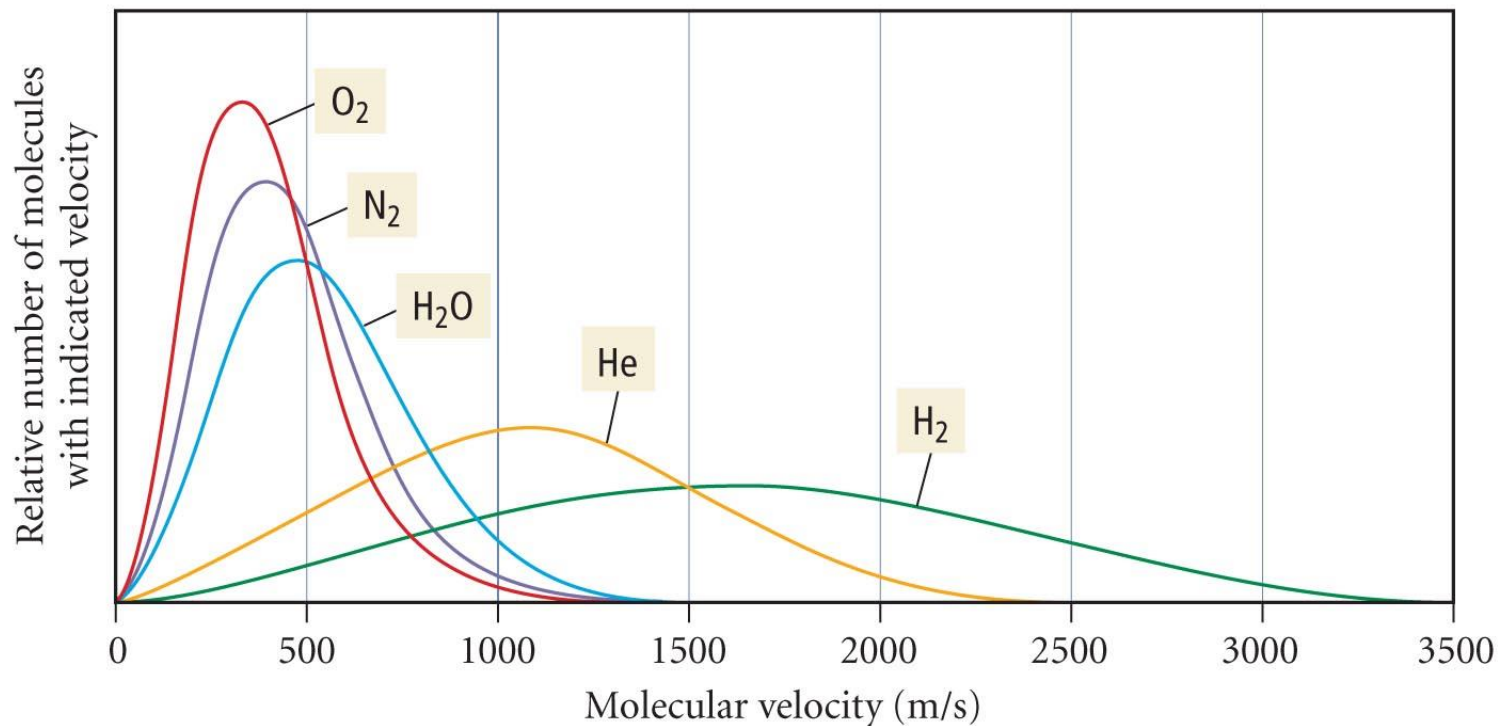
R is the gas constant in energy units, 8.314 J/mol·K

$$u_{\text{rms}} = \sqrt{\frac{3RT}{N_A \cdot m}} = \sqrt{\frac{3RT}{MM}}$$

- As temperature increases, the average velocity increases
- As the molar mass increases, the average velocity decreases

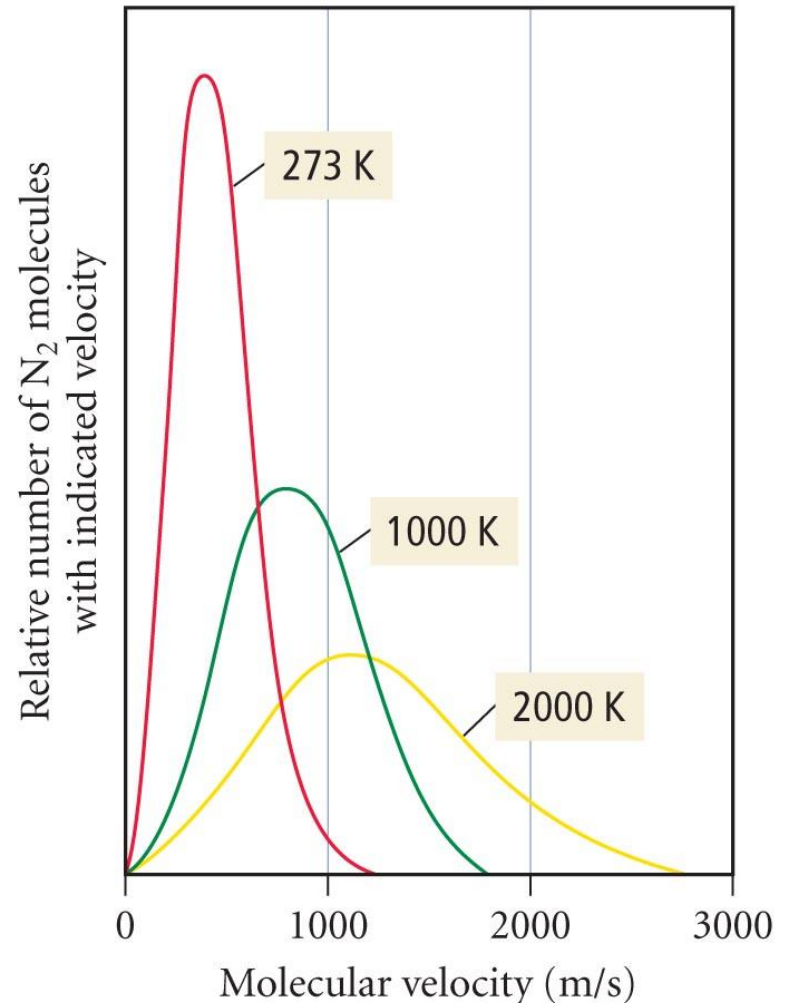
Molecular Speed vs. Molar Mass

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



Temperature vs. Molecular Speed

- As the absolute temperature increases, the average velocity increases
the distribution function “spreads out,” resulting in more molecules with faster speeds



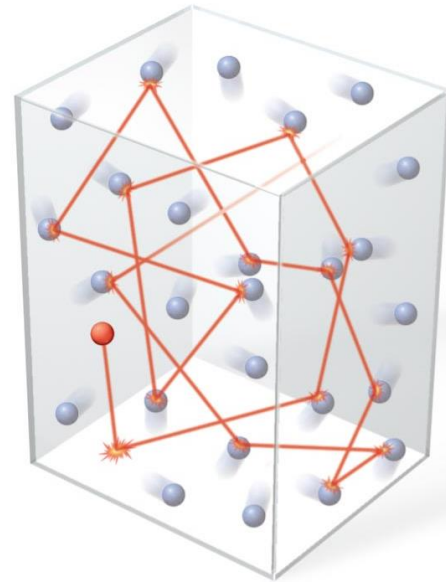
Calculate the average velocity of O₂ at 25 °C

$$u_{\text{rms}} = \sqrt{\frac{3RT}{N_A \cdot m}} = \sqrt{\frac{3RT}{MM}}$$

Mean Free Path

- The average distance a molecule travels between collisions is called the **mean free path**
- Mean free path decreases as the pressure increases

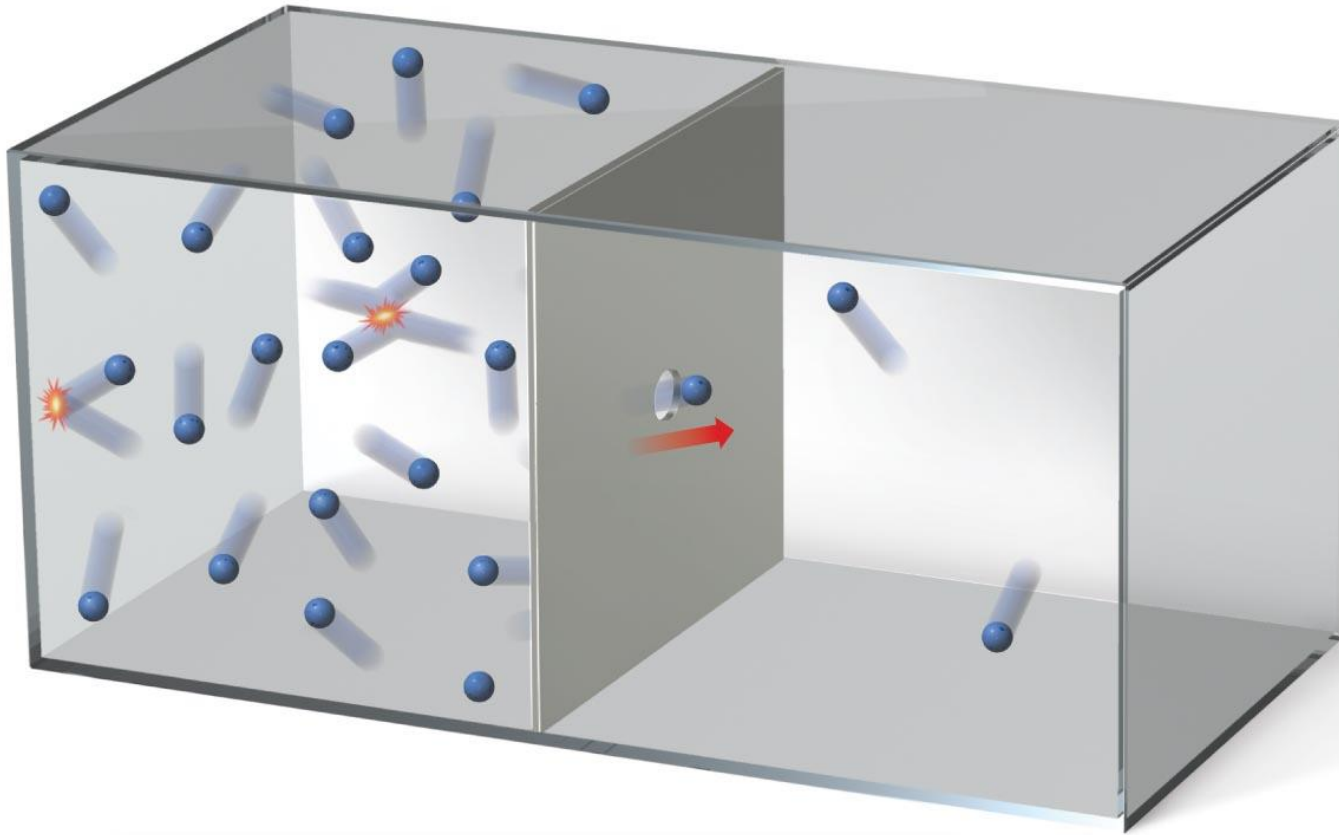
The average distance between collisions is the mean free path.



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**

Effusion



Gas escapes from container into a vacuum through a small hole

Ideal vs. 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

van der Waals' Equation

For ideal gas:
 $PV = nRT$

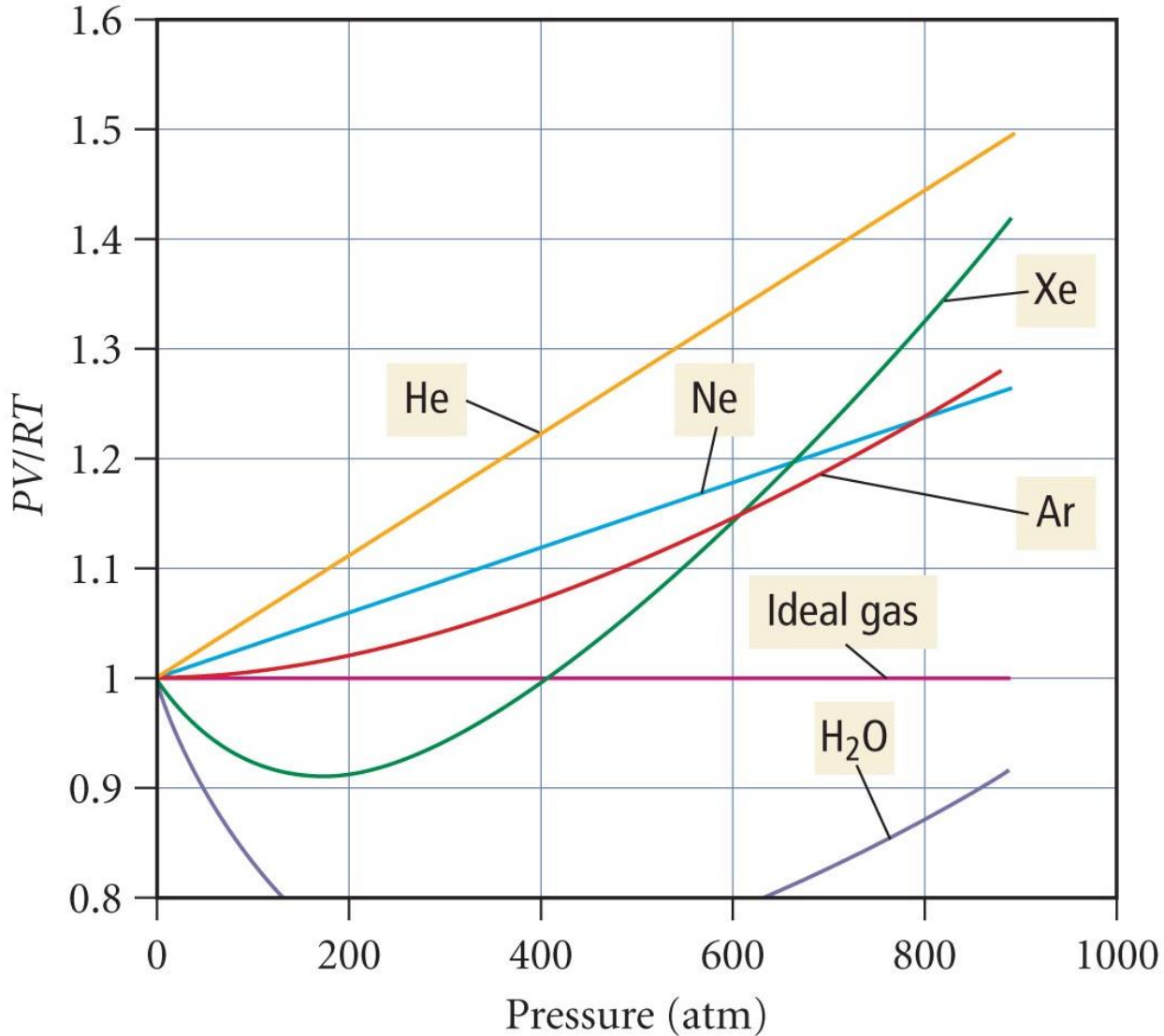
For real gas:

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

TABLE 5.5 Van der Waals Constants for Common Gases

Gas	a (L ² · 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 ₂ O	5.46	0.0305
CH ₄	2.25	0.0428
CO ₂	3.59	0.0427
CCl ₄	20.4	0.1383

PV/RT Plots



Homework

TBA