Ch. 10: Gases

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Chem 200: General Chemistry I

I. Chapter Outline

I.   Introduction

II.   Kinetic Molecular Theory of Gases

III.   Gas Pressure

IV.   Gas Laws

V.   Gas Law Problems

VI.   Dalton's Law of Partial Pressures

VII.   Gas Molecular Velocities

VIII.   Real Gases

I. The Unique Gas Phase

- Physical properties of a gas are nearly <u>independent</u> of its chemical identity!

- Gas behavior is markedly different than solid or liquid behavior.

- Gas behavior can be explained using a particulate view – *i.e.* by thinking of gases as composed of particles in constant motion.

II. Kinetic-Molecular Theory

- Why do gas laws work well for <u>all</u> gases?
- The kinetic molecular theory of gases was proposed which consists of 3 postulates.
  1) Gas particles are negligibly small, and any sample has a huge # of particles. The volume of each particle is so small that we assume they have mass but no volume.
  2) The average kinetic energy (not velocity) of a particle is proportional to the kelvin temperature
  3) Gas particles collide in perfectly elastic collisions w/ themselves and container walls and they move in straight lines between collisions, neither attracting nor repelling one another.

II. Imagining a Sample of Gas
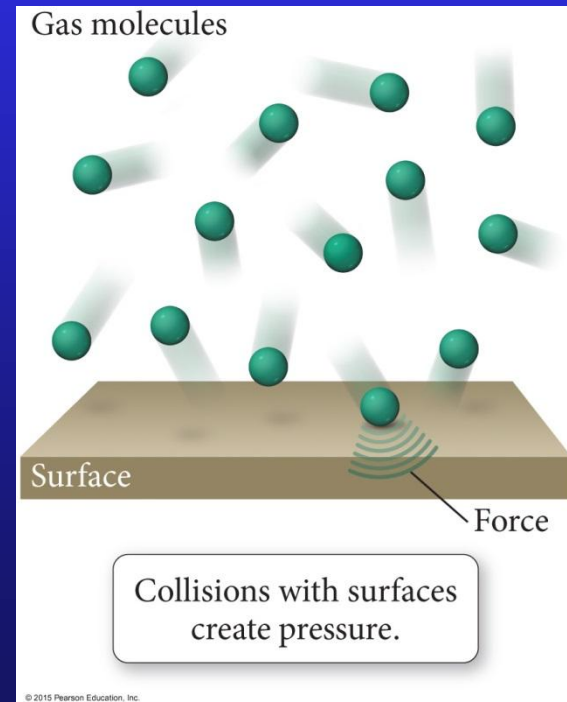

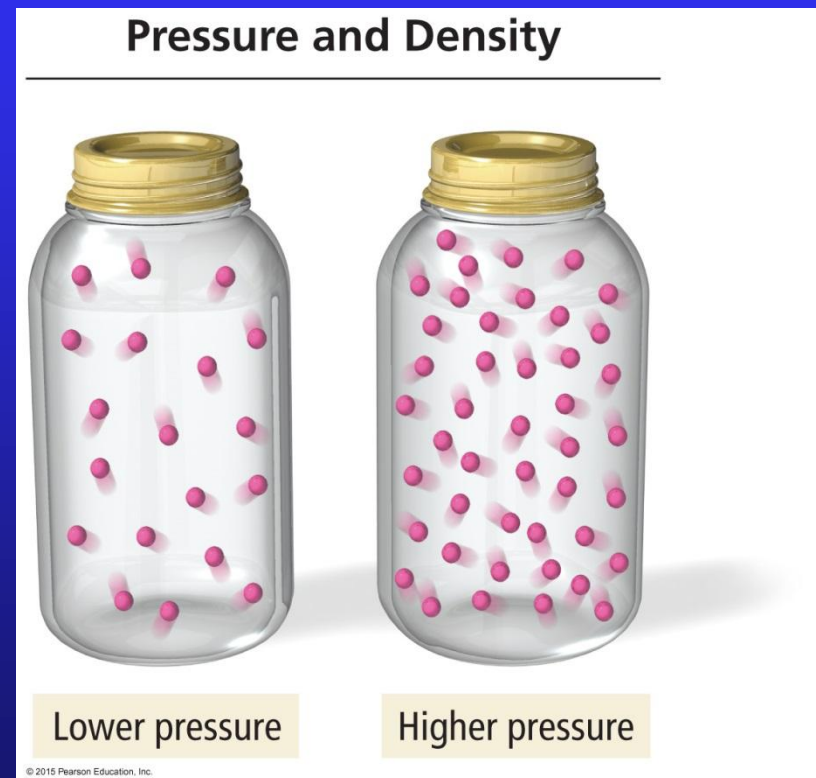Kinetic Molecular Theory

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Elastic collision   Inelastic collision

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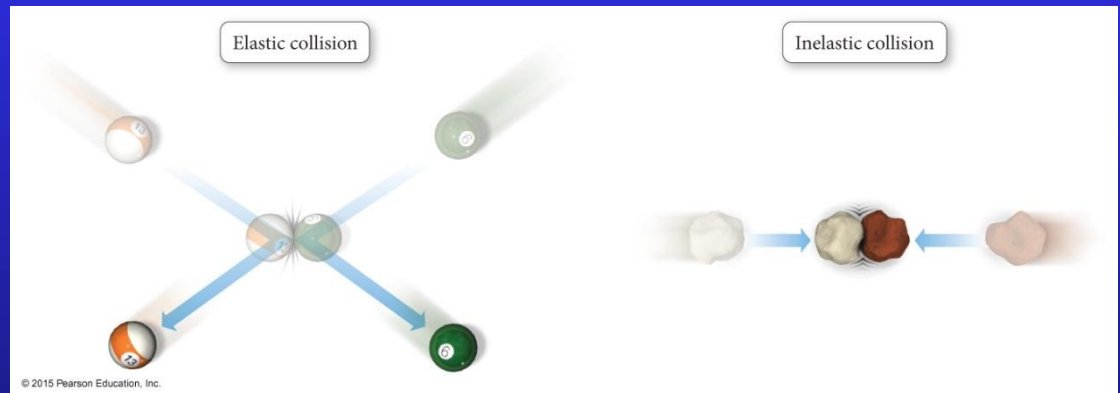
III. Pressure

- Collisions exert a force!
- Pressure is simply a force exerted over a surface area.

$$P = \frac{force}{area}$$

Gas molecules

Surface

Force

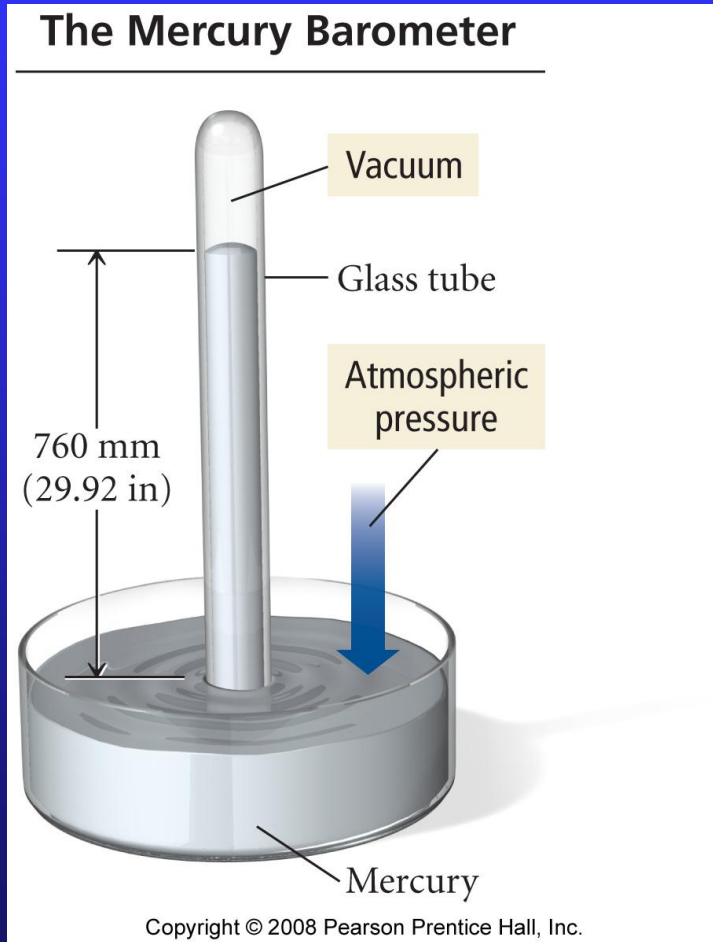Collisions with surfaces create pressure.

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III. Gas Pressure

- If gases are comprised of particles, then pressure must depend on the number of gas particles in a certain volume.

Pressure and Density

Lower pressure

Higher pressure

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III. Atmospheric Pressure

The Mercury Barometer

Vacuum

Glass tube

Atmospheric pressure

760 mm (29.92 in)

Mercury

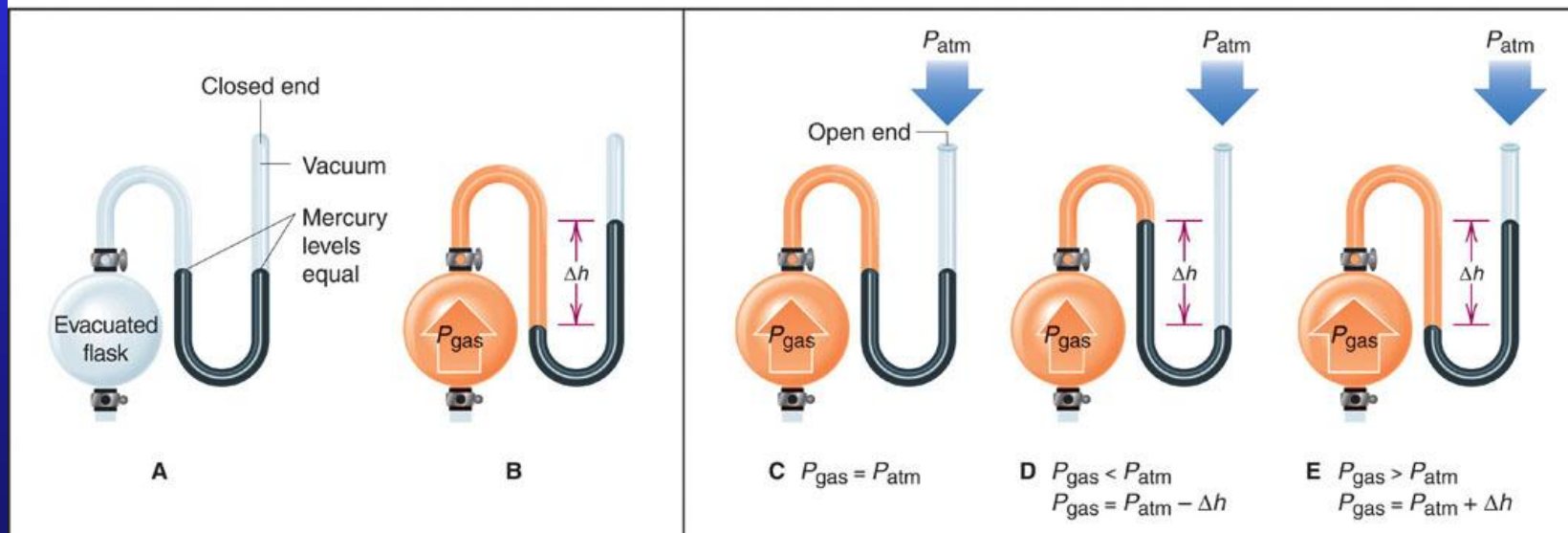Copyright © 2008 Pearson Prentice Hall, Inc.

- P_{atm} is simply the weight of the earth's atmosphere pulled down by gravity.

- Barometers are used to monitor daily changes in P_{atm}.

- Torricelli barometer was invented in 1643.

III. Manometers

- In the lab, we use <u>manometers</u> to measure pressures of gas samples.

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A

B

C $P_{gas} = P_{atm}$

D $P_{gas} < P_{atm}$
$P_{gas} = P_{atm} - \Delta h$

E $P_{gas} > P_{atm}$
$P_{gas} = P_{atm} + \Delta h$
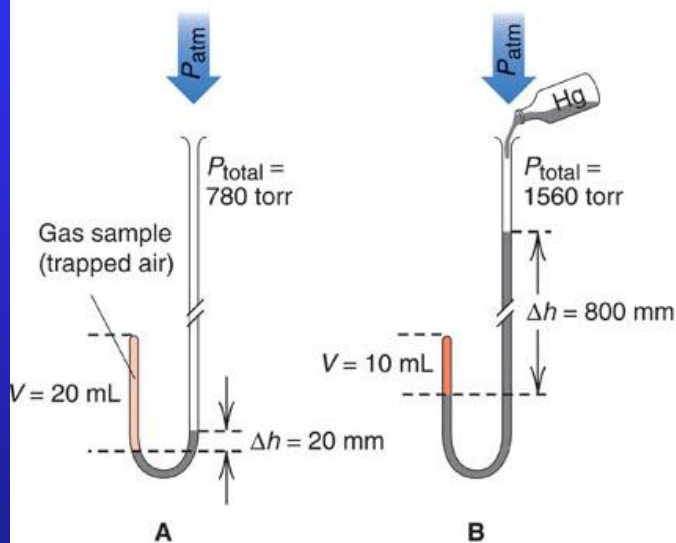
III. Units of Pressure

- For historic reasons, we have units such as torr and mmHg. (Why?)

- The derived SI unit for pressure is N/m^2, known as the pascal (Pa).

- Note that 1 atm = 760 mm Hg = 760 torr = 101.325 kPa.

IV. Gas Laws

- A sample of gas can be physically described by its pressure (P), temperature (T), volume (V), and amount of moles (n).

- If you know any 3 of these variables, you know the 4th.

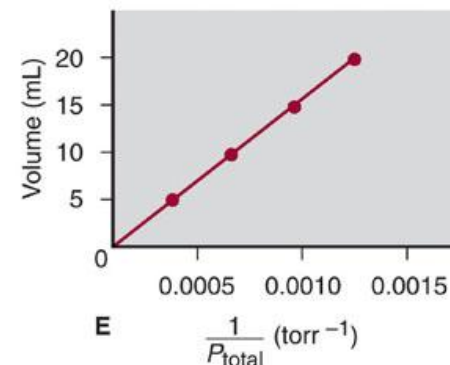- We look at the history of how the ideal gas law was formulated.
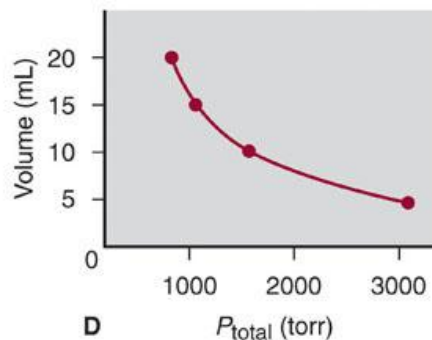
IV. Volume and Pressure – Boyle's Law

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- The volume of a gas is inversely related to pressure, *i.e.* if P increases, V decreases.

IV. Explaining Boyle's Law

Volume versus Pressure: A Molecular View

$P = 1$ atm

$V = 1$ L

$P = 2$ atm

$V = 0.5$ L
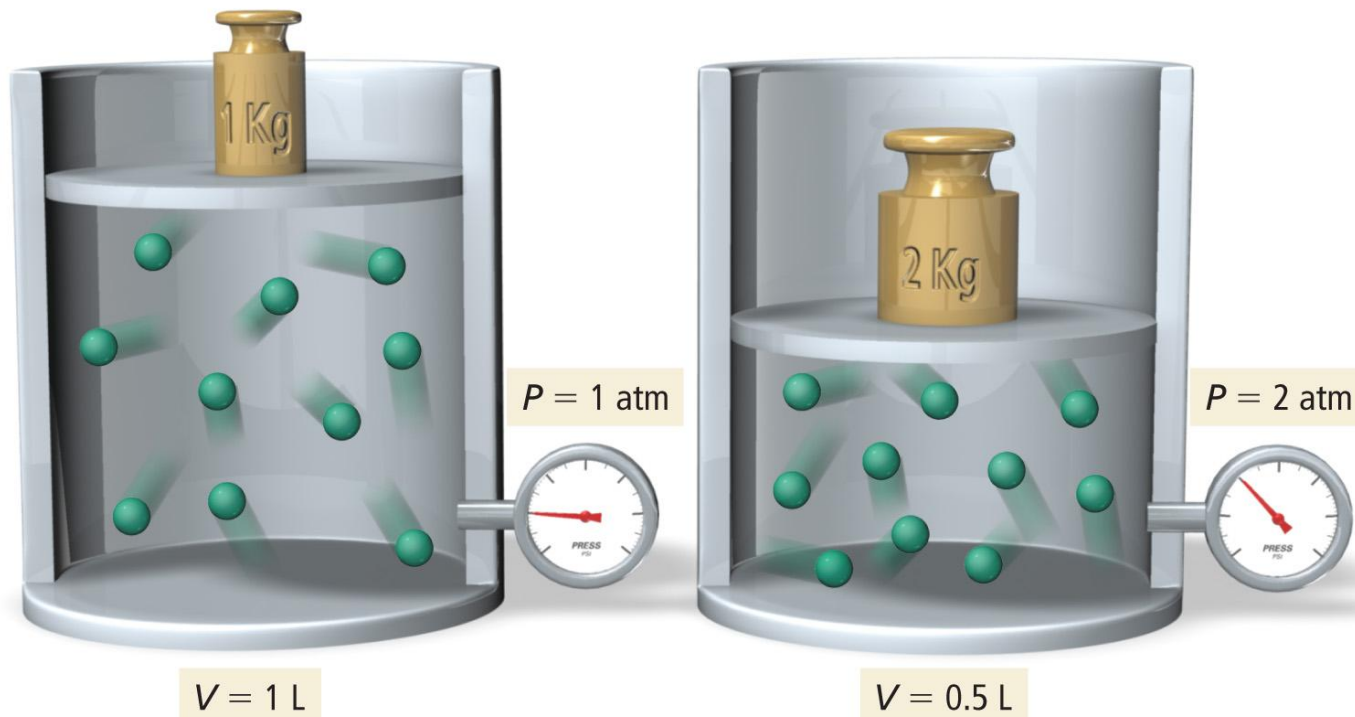
IV. Volume and Temperature – Charles's Law
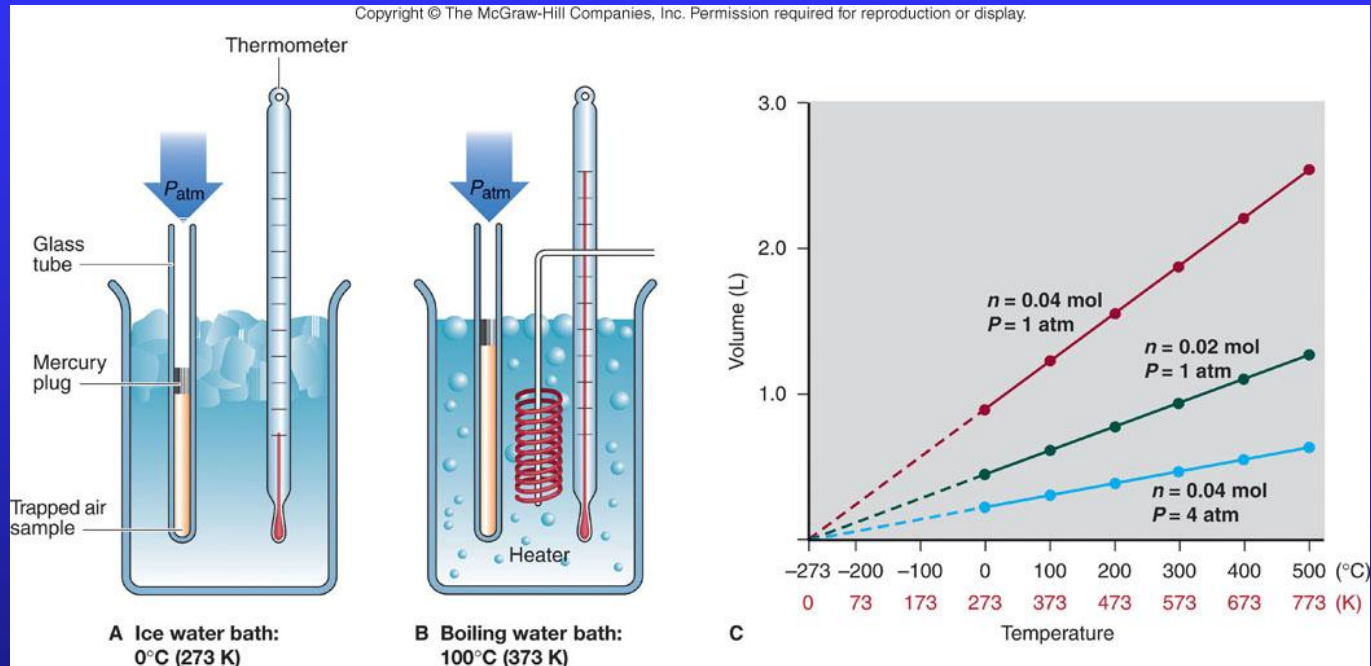
- The volume of a gas is directly related to its temperature, *i.e.* if T is increased, V will increase.

IV. Explaining Charles's Law

Volume versus Temperature: A Molecular View

Low kinetic energy

High kinetic energy

Ice water

Boiling water
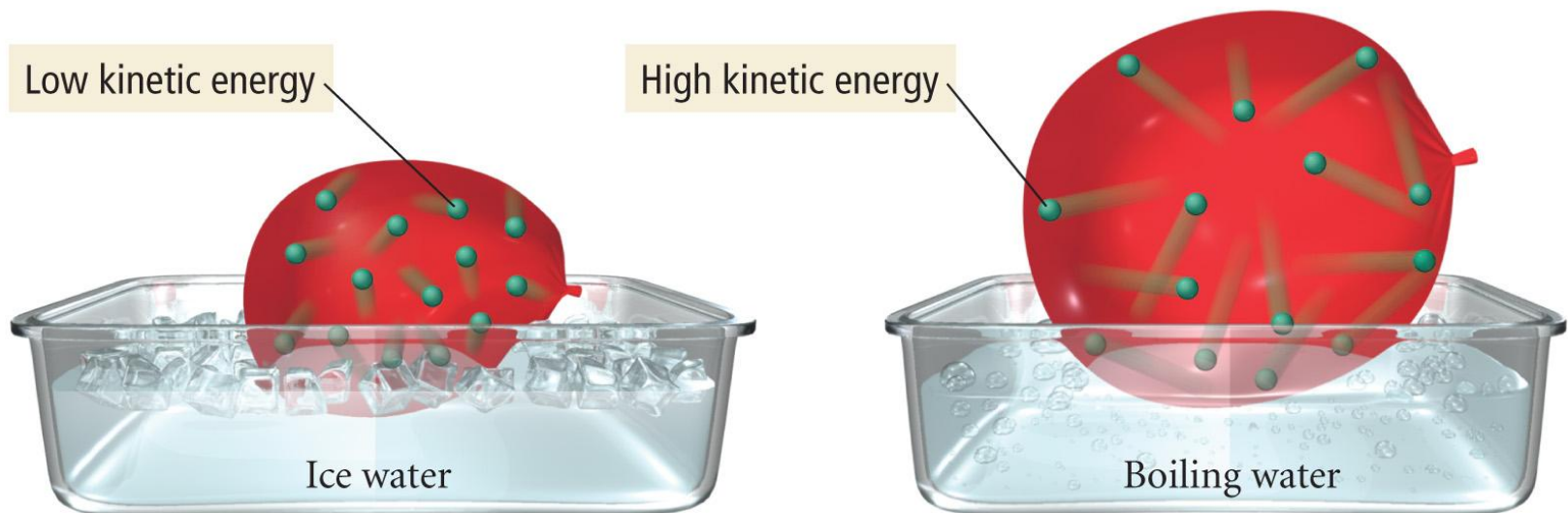
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IV. The Combined Gas Law

- Boyle's and Charles's Laws can be combined into a convenient form.

$$V \propto \frac{1}{P} \quad \text{and} \quad V \propto T$$

$$\therefore \quad V \propto \frac{T}{P}$$

$$\text{or} \quad V = \text{constant} \quad \times \frac{T}{P}$$

$$\frac{PV}{T} = \text{constant}$$

$$\text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

IV. Volume and Moles – Avogadro's Law

Avogadro's Law

As amount of gas increases, volume increases.

Volume (L) vs. Number of moles (n)

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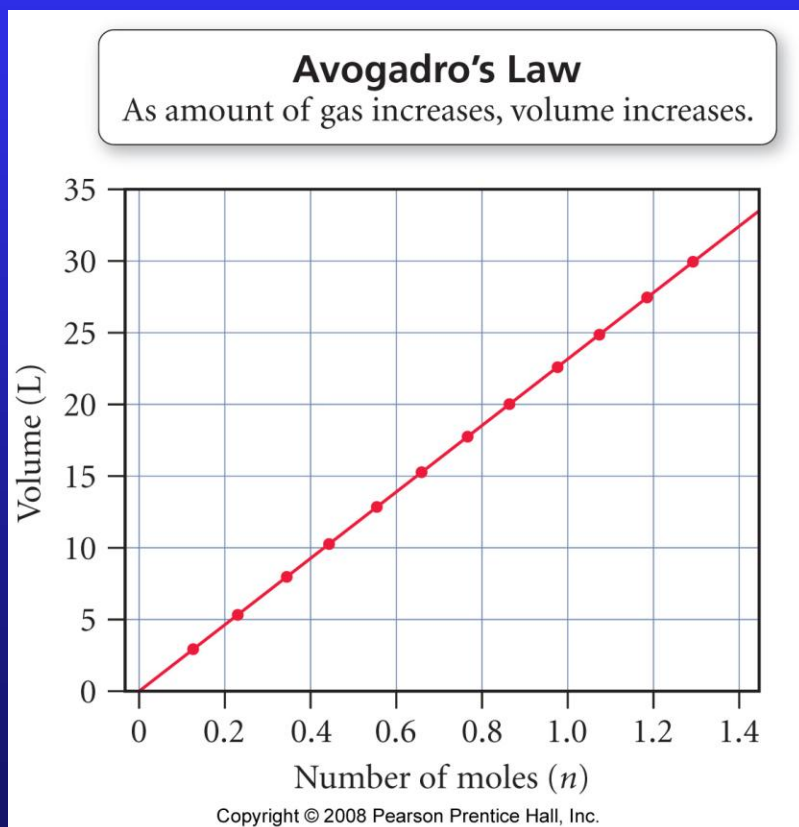
- The pressure of a gas is directly related to the number of moles of gas, *i.e.* if n increases, V will increase.

IV. Explaining Avogadro's Law

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$P_{gas} = P_{atm}$

n increases
fixed T

More molecules increase collisions:
$P_{gas} > P_{atm}$

V increases

V increases until
$P_{gas} = P_{atm}$
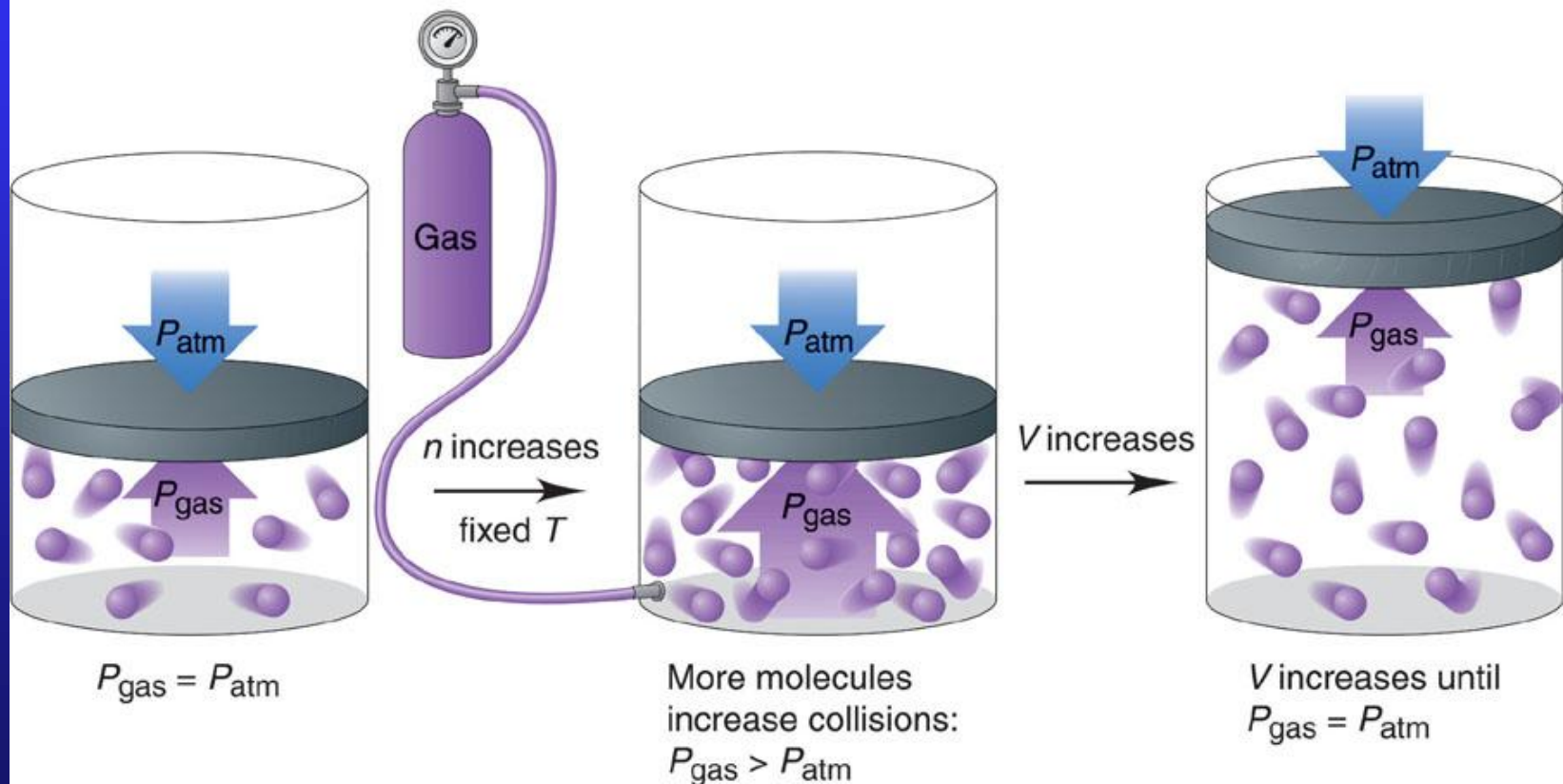
IV. The Ideal Gas Law

- The ideal gas law is a combination of the combined gas law and Avogadro's Law.

$$V \propto \frac{T}{P} \quad \text{and} \quad V \propto n$$

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

$$\text{or} \quad V = \text{constant} \times \frac{nT}{P}$$

$$PV = n(\text{constant})T$$

$R = 0.082058 \text{ L·atm/K·mole}$

IV. Molar Volume and STP

- <u>Molar volume</u> is the volume occupied by 1 mole of a substance.

- For gases, <u>standard temperature and pressure (STP)</u> means 0 °C and 1.00 atm.

22.4 L   22.4 L   22.4 L

1 mol He(g) at STP   1 mol Xe(g) at STP   1 mol CH4(g) at STP

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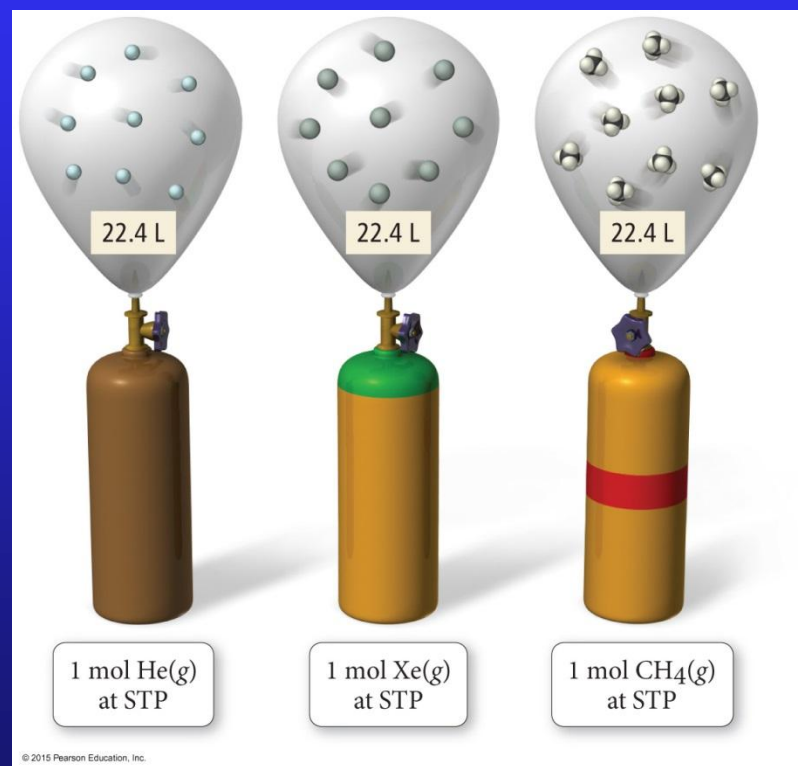
V. Gas Law Problems

- There are many variations on gas law problems.

- A few things to keep in mind:

  1) Temperature must be in K

  2) If problem involves a set of initial and final conditions, use combined gas law.

  3) If problem only gives information for one set of conditions, use ideal gas law.

V. Sample Problem 10.1

- What's the final pressure of a sample of N_2 with a volume of 952 m^3 at 745 torr and 25 °C if it's heated to 62 °C with a final volume of 1150 m^3?

V. Sample Problem 10.2

- What volume, in mL, does a 0.245 g sample of N_2 occupy at 21 °C and 750 torr?

V. Sample Problem 10.3

- A sample of N_2 has a volume of 880 mL and a pressure of 740 torr. What pressure will change the volume to 870 mL at the same temperature?

V. Other Uses of Ideal Gas Law

- The ideal gas law can be used to find other physical values of a gas that are not as obvious.

  - gas density, d = mass/volume

  - gas molar mass, MW = mass/mole

  - stoichiometry, via moles and a balanced equation

V. Sample Problem 10.4

- Find the density of $CO_{2(g)}$ at 0 °C and 380 torr.

V. Sample Problem 10.5

- An unknown noble gas was allowed to flow into a 300.0 mL glass bulb until the P = 685 torr. Initially, the glass bulb weighed 32.50 g, but now it weighs 33.94 g. If the temperature is 27.0 °C, what's the identity of the gas?

V. Sample Problem 10.6

- How many mL of $HCl_{(g)}$ forms at STP when 0.117 kg of NaCl reacts with excess H_2SO_4?

$$H_2SO_{4(aq)} + 2NaCl_{(s)} \rightarrow Na_2SO_{4(aq)} + 2HCl_{(g)}$$

VI. Partial Pressures

- Each gas in a mixture behaves like it's the only gas there; they don't interact.
- <u>Dalton's Law of Partial Pressures</u> states that the total pressure of a mixture of unreacting gases is the sum of all individual pressures.
- Each individual pressure is a <u>partial pressure</u>.
  - $P_{total} = P_1 + P_2 + P_3 + P_4 + \ldots$

VI. Partial Pressures in Air

TABLE 11.2 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

VI. An O_2/N_2 Gas Mixture

- Let's say we have O_2 and N_2 as a gas mixture. Then $P_{total} = P_{O2} + P_{N2}$. Applying the ideal gas law…

$$PV = nRT$$

$$P_{O_2}V = n_{O_2}RT$$

$$P_{O_2} = \frac{n_{O_2}RT}{V}$$

$$PV = nRT$$

$$P_{N_2}V = n_{N_2}RT$$

$$P_{N_2} = \frac{n_{N_2}RT}{V}$$

VI. An O_2/N_2 Gas Mixture

- Now we add the individual pressures to find the total pressure.

- Note that the total pressure is related to the total moles.

$$P_{total} = P_{O_2} + P_{N_2}$$

$$P_{total} = \frac{n_{O_2} RT}{V} + \frac{n_{N_2} RT}{V}$$

$$P_{total} = (n_{O_2} + n_{N_2}) \frac{RT}{V}$$

$$P_{total} = \frac{n_{total} RT}{V}$$

VI. An O_2/N_2 Gas Mixture

- What happens if we divide P_{O_2} by P_{total}?
- A new quantity which we call the <u>mole fraction</u> appears.

$$\frac{P_{O_2}}{P_{total}} = \frac{n_{O_2}(RT/V)}{n_{total}(RT/V)}$$

$$\frac{P_{O_2}}{P_{total}} = \frac{n_{O_2}}{n_{total}}$$

$$P_{O_2} = \left(\frac{n_{O_2}}{n_{total}}\right) P_{total}$$

VI. Mole Fraction

- We define a new unit of concentration, the <u>mole fraction (X)</u>.
- Partial pressures are directly related to the mole fraction.
- For the O_2/N_2 mixture, for N_2 specifically, we have…

$$X_{N_2} = \frac{n_{N_2}}{n_{total}} = \frac{n_{N_2}}{n_{N_2} + n_{O_2}}$$

$$\text{and } P_{N_2} = X_{N_2} P_{total}$$

VI. Sample Problem 10.7

- A gas mixture contains 5.50 g He, 15.0 g Ne, and 35.0 g Kr at 25 °C. If the total pressure is 4.00 atm, calculate the partial pressures of each gas.

VI. Collecting Gas Over Water

Collecting a Gas over Water

- H_2
- Hydrogen plus water vapor
- Zn
- HCl
- H_2O

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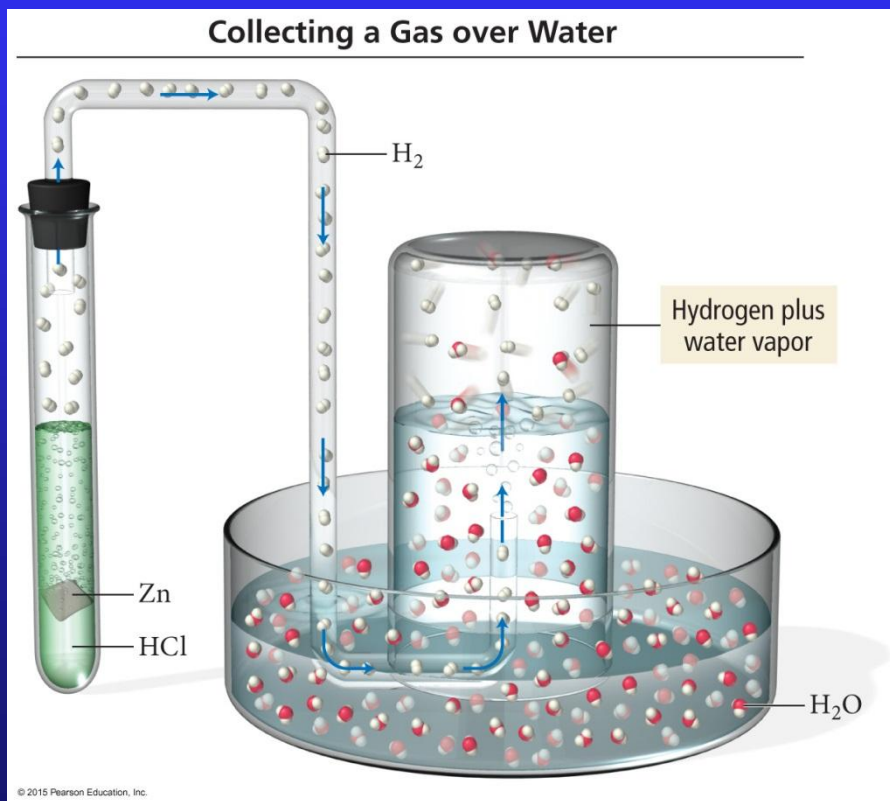
- Gas collection over water is a partial pressure situation.
- The partial pressure of water is equal to its <u>vapor pressure</u>.
- $P_{total} = P_{gas} + P_{H2O}$

VI. Vapor Pressures of Water

TABLE 11.3 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		

VI. Sample Problem 10.8

- A student uses the reaction below to make H_2 gas, which is collected over water. If 154.4 mL of gas at a pressure of 742 mmHg and a temperature of 25 °C are collected, how many mg of molecular hydrogen was captured?

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$

VII. Gas Molecular Velocities

- According to K-M theory, at the same temperature, two particles with different masses have the same KE.

- How can this be?

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

- In a gas mixture at a certain temp., lighter particles move faster (on avg.) than heavier ones.

VII. Average Molecular Speed

- To get to an average molecular speed, we can go through average KE.

$$KE_{avg} = \frac{1}{2}m\overline{u^2}$$

- Here, $\overline{u^2}$ is the average of the squares of the velocities.
- If we take the square root, we get the root mean square velocity, u_{rms}.

VII. Root Mean Square Velocity

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

- The root mean square velocity is a special type of average.
- Although not equal to average velocity, it is close and conceptually similar.
- We derive a formula that will allow us to calculate u_{rms}.

VII. Deriving u_{rms}

$$KE_{avg} = \frac{1}{2} N_A m \overline{u^2} = \frac{3}{2} RT$$

$$\frac{1}{2} N_A m \overline{u^2} = \frac{3}{2} RT$$

$$\overline{u^2} = \frac{3/2 \, RT}{1/2 \, N_A m}$$

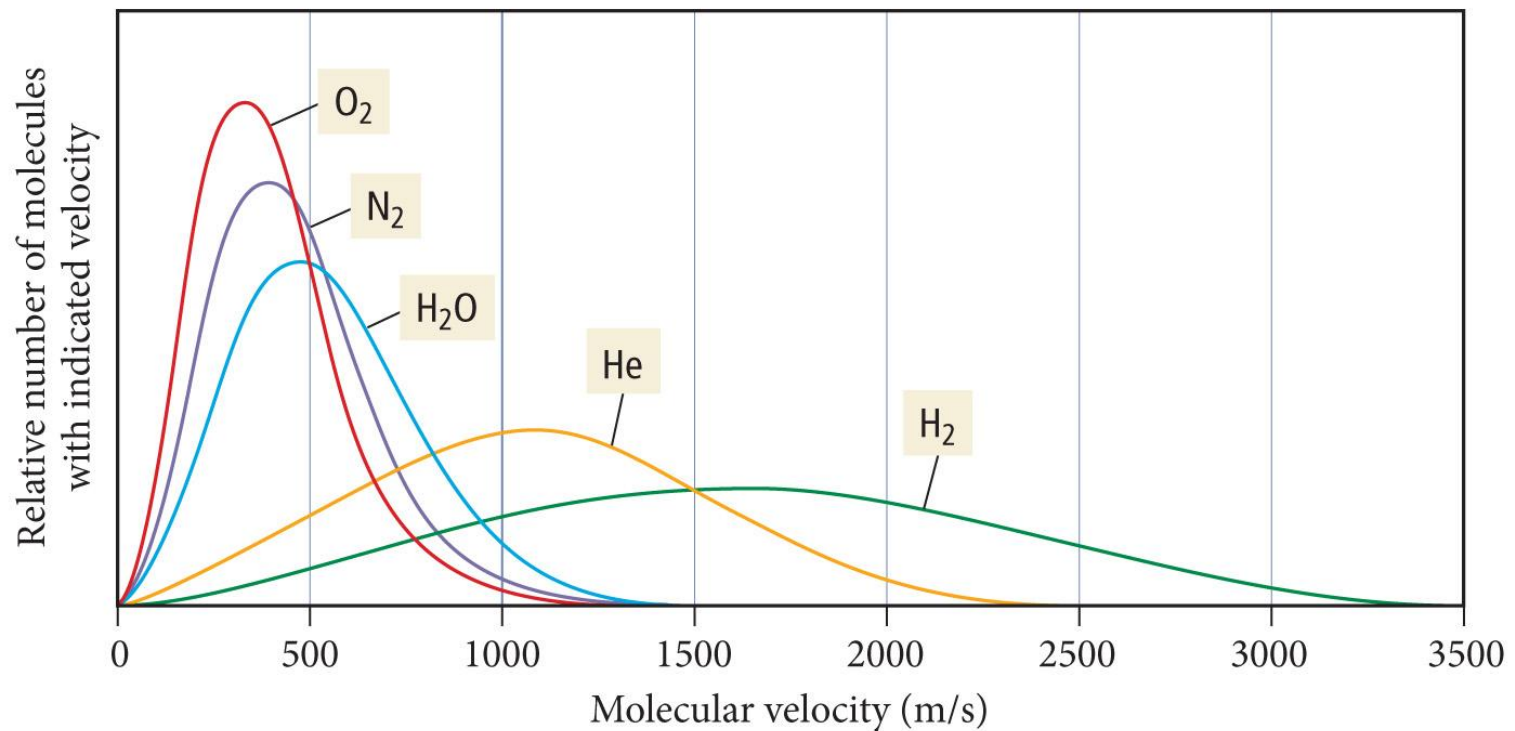$$\overline{u^2} = \frac{3RT}{N_A m}$$

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

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

M is the molar mass in kg/mole!

VII. Molar Mass and Velocity

Variation of Velocity Distribution with Molar Mass

O$_2$

N$_2$

H$_2$O

He

H$_2$

Relative number of molecules with indicated velocity

Molecular velocity (m/s)

0   500   1000   1500   2000   2500   3000   3500

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VII. Temperature and Velocity

Variation of Velocity Distribution with Temperature

273 K

1000 K

2000 K

Relative number of N₂ molecules with indicated velocity

Molecular velocity (m/s)

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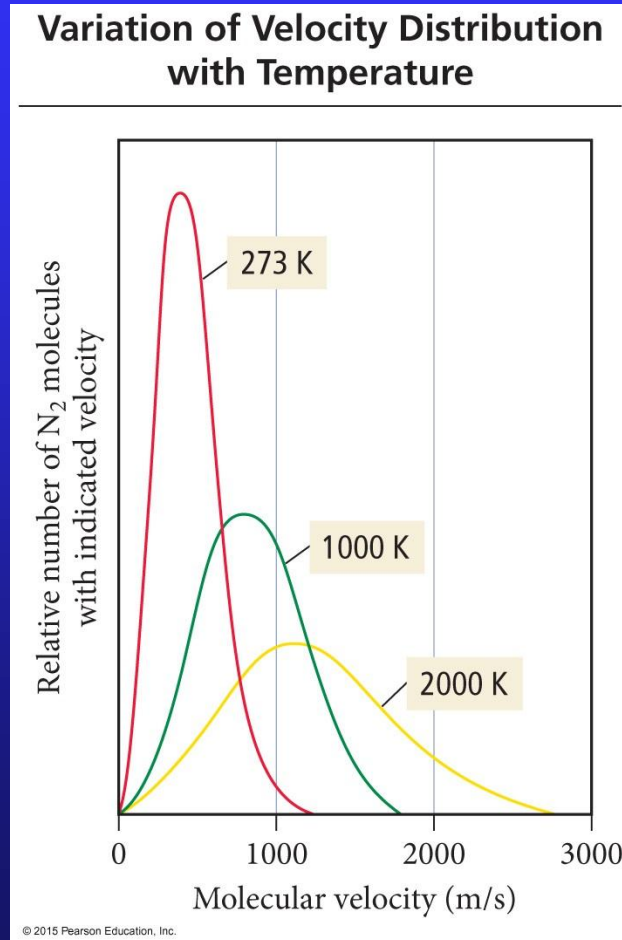
VII. Sample Problem 10.9

- Calculate the root mean square velocity of gaseous xenon atoms at 25 °C.

VII. Mean Free Path

- Gas particles move fast.

- So why does it take a while for a smell to diffuse?

- Average distance travelled between collisions is the mean free path.

Typical Gas Molecule Path

The average distance between collisions is the mean free path.

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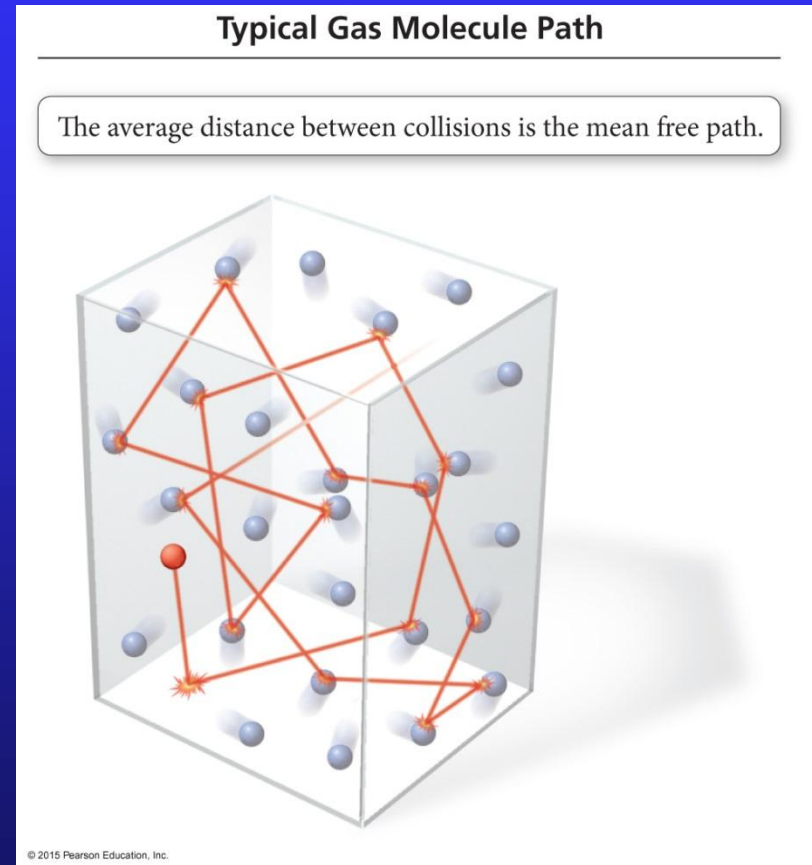
VII. Diffusion

- <u>Diffusion</u> is the movement of molecules in response to a concentration gradient.
  - Atoms/molecules move from high concentration to low concentration.
- For gases, rate of diffusion depends on the root mean square velocity.
- Thus, the first molecules you smell are the ones with least mass.

VII. Effusion

- <u>Effusion</u> is related to diffusion; it is when a gas escapes into a vacuum through a small hole.

- Effusion is related to root mean square velocity; heavier molecules effuse more slowly.

Effusion

Gas escapes from container into a vacuum through a small hole.

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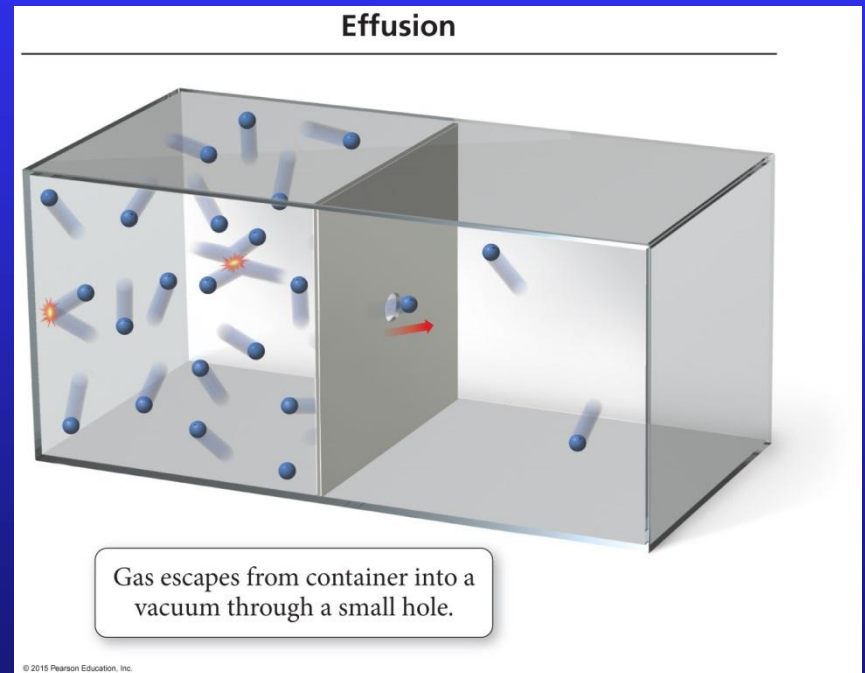
VII. Graham's Law of Effusion

- How much gas effuses over time is inversely related to the square root of the molar mass.

- The ratio of effusion *rates* (amount/time) of 2 gases is given by Graham's law of effusion.
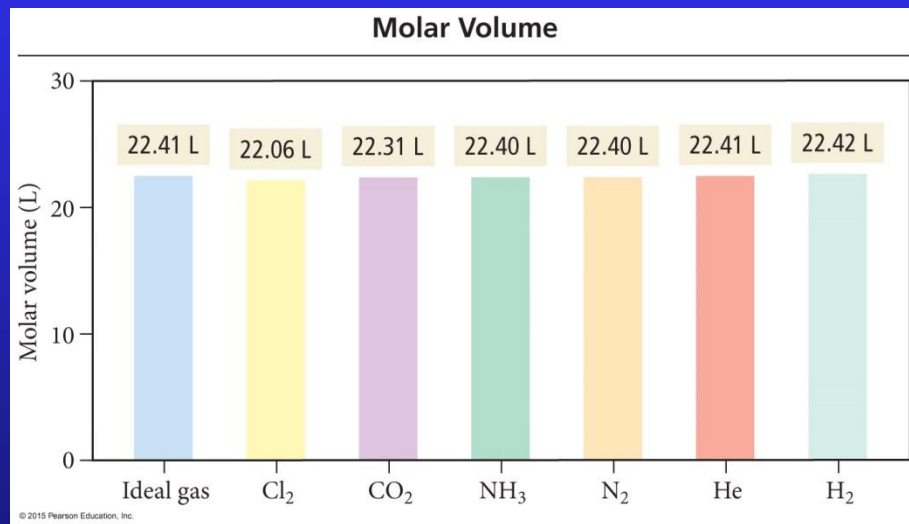
$$\frac{Effusion\ rate\ gas\ A}{Effusion\ rate\ gas\ B} = \sqrt{\frac{M_B}{M_A}}$$

VII. Sample Problem 10.10

- A sample of Xe takes 75 seconds to effuse out of a container while a sample of an unknown diatomic gas takes 37 seconds to effuse out under the same conditions. What is the identity of the unknown diatomic gas?

VIII. Real Gases Close To Ideal

- One mole of an ideal gas occupies 22.41 L at STP.

- Gases behave ideally when:
  - Volume of gas particles is small relative to space between them.
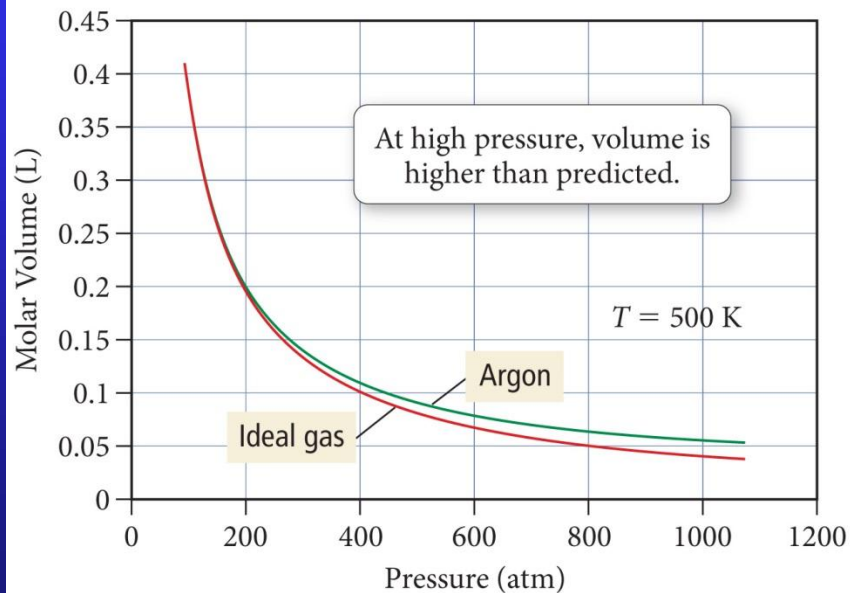 - Intermolecular forces are insignificant.

Molar Volume

| | 22.41 L | 22.06 L | 22.31 L | 22.40 L | 22.40 L | 22.41 L | 22.42 L |

Ideal gas, Cl_2, CO_2, NH_3, N_2, He, H_2

Molar volume (L)

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VIII. High *P* and Low *T*

- At high pressures and low temperatures, deviations from ideal behavior are seen.

- At high pressures, gas particle size becomes important.

- At low temperatures, intermolecular forces (attractions between molecules) become important.
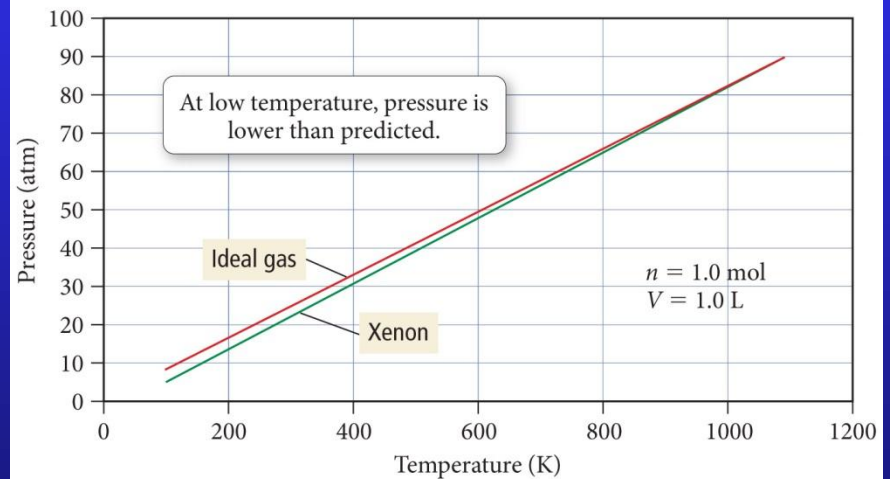
VIII. Extreme Conditions

Nonideal Behavior: The Effect of Particle Volume

At high pressure, volume is higher than predicted.

$T = 500$ K

Argon

Ideal gas

Nonideal Behavior: The Effect of Intermolecular Forces

At low temperature, pressure is lower than predicted.

Ideal gas

$n = 1.0$ mol
$V = 1.0$ L

Xenon

VIII. van der Waals Equation

- Under extreme conditions, ideal gas law cannot be used.

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

correction terms for IMF and particle volume

VIII. van der Waals Constants

TABLE 11.4 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

VIII. Real Gases