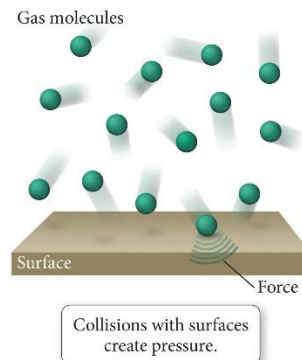


PRESSURE AND ITS MEASUREMENT

- **Pressure** is the result of *collision* of gas particles with the sides of the container. Pressure is defined as the *force per unit area*.
- **Pressure** is measured in several different units. The common units of pressure are listed below:

TABLE 5.1 Common Units of Pressure		
Unit	Abbreviation	Average Air Pressure at Sea Level
Pascal (1 N/m^2)	Pa	101,325 Pa
Pounds per square inch	psi	14.7 psi
Torr (1 mmHg)	torr	760 torr (exact)
Inches of mercury	in Hg	29.92 in Hg
Atmosphere	atm	1 atm

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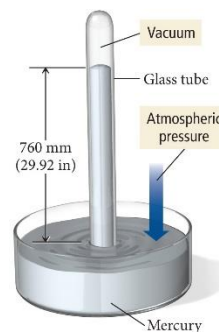
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Pressure and Density



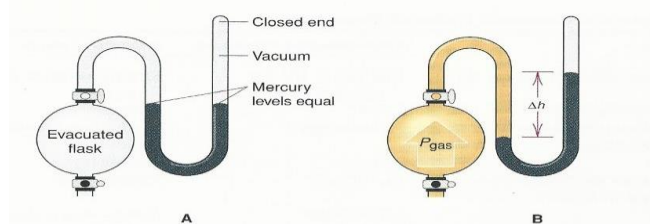
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The Mercury Barometer



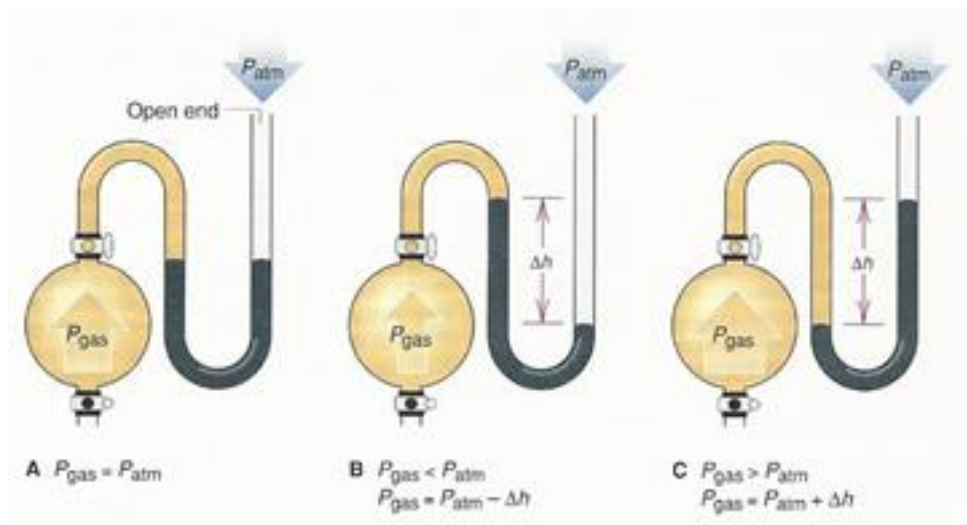
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- The **pressure** of a gas is *directly proportional* to the **number of particles** of gas present. As a result, low pressure indicates low density of gas particles and high pressure indicates high density of gas particles.
- Atmospheric **pressure** can be *measured* with the use of a **barometer**. Mercury is used in a barometer due to its high density. At sea level, the mercury stands at 760 mm above its base.
- In the laboratory, pressure of a gas is measured using a manometer. Two types of manometers are used for these measurements: closed-end and open end.
- With the closed-end manometer (shown below), when attached to an evacuated flask, the mercury levels are equal (A). When attached to a flask (B) the pressure of the gas is indicated by the difference in the height (Δh) of mercury between the two sides.



PRESSURE AND ITS MEASUREMENT

- With the open-end manometer, when pressure of gas is equal to the atmospheric pressure, the heights of mercury in the tubes are equal (A). When the pressure of gas is less than the atmospheric pressure, the mercury level on the gas side is higher by Δh (B), and when the pressure of gas is greater than the atmospheric pressure, the mercury level on the gas side is lower by Δh .

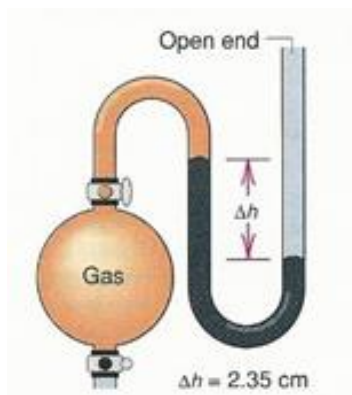
**Examples:**

- A high pressure road bicycle tire is inflated to a total pressure of 132 psi. What is this pressure in mmHg?
- A geochemist heats a limestone sample and collects the CO_2 released in an evacuated flask attached to a closed-end manometer. After the system comes to room temperature, $\Delta h = 291.4 \text{ mmHg}$. What is this pressure in torr, atmospheres and kilopascals?

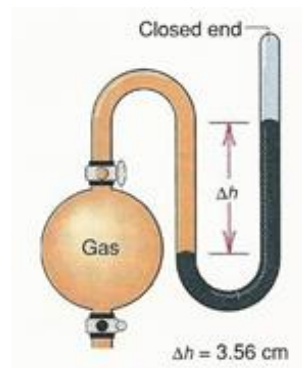
PRESSURE AND ITS MEASUREMENT**Examples (cont's):**

3. If the barometer reads 768.2 mmHg, what is the pressure of gas in each flask shown below in mmHg?

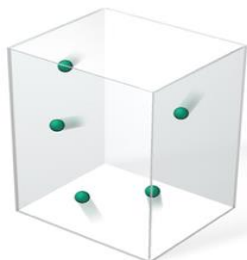
a)



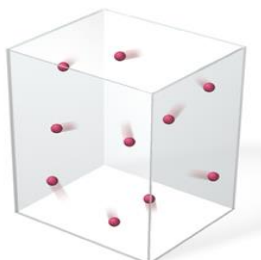
b)

 $P_{\text{gas}} = \underline{\hspace{2cm}}$ $P_{\text{gas}} = \underline{\hspace{2cm}}$

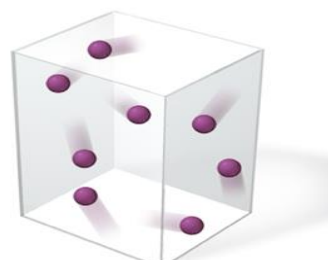
4. Which gas sample representation shown below has the greatest pressure? Assume all are at the same temperature and the same volume.



(a)



(b)



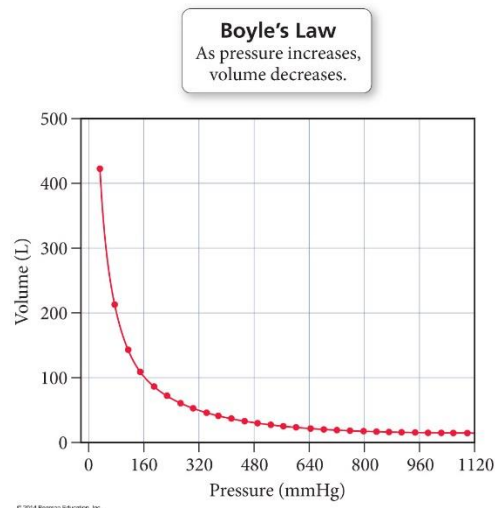
(c)

THE SIMPLE GAS LAWS

Boyle's Law:

- At *constant temperature*, the *volume of a fixed amount* of gas is *inversely proportional* to its *pressure*.

$$P_1V_1 = P_2V_2$$

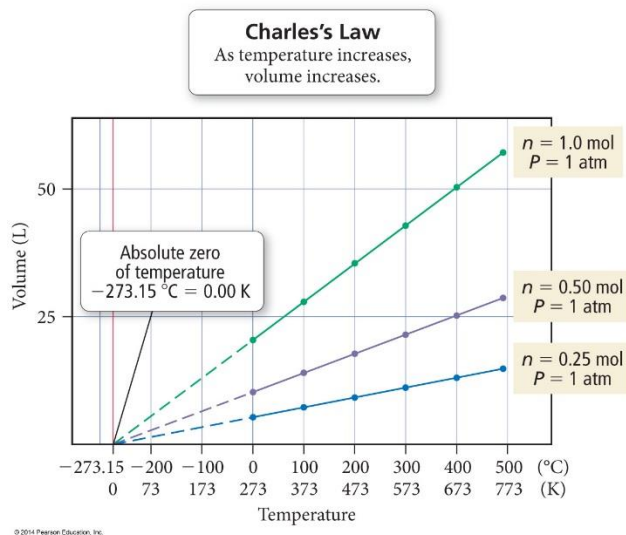


Charles's Law:

- At *constant pressure*, the *volume of a fixed amount* of gas is *directly proportional* to its *absolute temperature*.

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

Note: T must be in unit of K

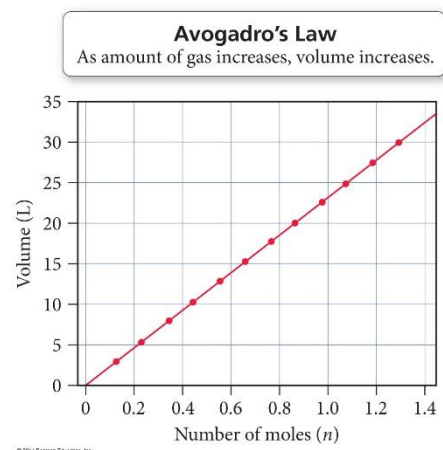


THE SIMPLE GAS LAWS

Avogadro's Law:

- At *constant temperature and pressure*, the *volume* of a gas is *directly proportional* to the *number of moles*.

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



Examples:

- A sample of gas has an initial volume of 13.9 L at a pressure of 1.22 atm. If the sample is compressed to a volume of 10.3 L, what is its pressure?
- A cylinder with a movable piston contains 0.553 mole of a gas and has a volume of 253 mL. What is its volume if an additional 0.365 mol of gas is added to the cylinder? (Assume constant temperature and pressure.)
- A 93-L sample of dry air is cooled from 155°C to −32°C while the pressure is maintained at 1.85 atm. What is the final volume of the gas?

IDEAL GAS LAW

- Combining the three laws discussed earlier, one can obtain a useful relationship that relates the volume of a gas to the temperature, pressure and number of moles.

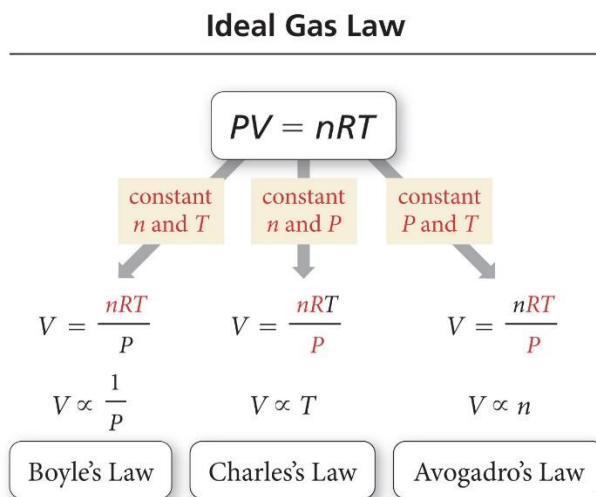
$$V = \frac{nRT}{P}$$

$$R = \text{Universal Gas Constant} = 0.0821 \frac{\text{L atm}}{\text{mol K}}$$

- This relationship is called the ***Ideal Gas Law***, and commonly written as:

$$\begin{array}{ccccc} \mathbf{P} & \mathbf{V} & = & \mathbf{n} & \mathbf{R} & \mathbf{T} \\ \uparrow & \uparrow & & \uparrow & & \uparrow \\ \text{atm} & \text{L} & & \text{mol} & & \text{K} \end{array}$$

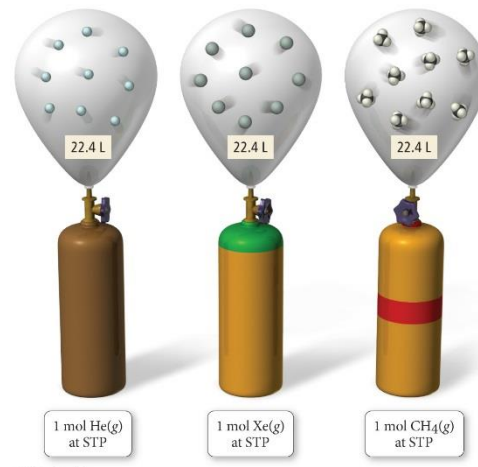
- The ideal gas law contains all the simple gas laws within it, as shown below:



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MOLAR VOLUME, DENSITY & MOLAR MASS OF A GAS

- The volume occupied by one mole of a substance is its **molar volume**. For gases, molar volume is often specified under conditions known as **standard temperature and pressure** (abbreviated at **STP**).
- STP conditions are defined as: $T = 0^\circ\text{C}$ or 273 K and $P = 1.00\text{ atm}$.
- One mole of any gas at STP occupies 22.4 L of volume.
- Since density is mass/volume and mass of one mole of gas is its molar mass and molar volume of a gas at STP is 22.4 L , the density of a gas at STP can be calculated as follows:



$$\text{Density} = \frac{\text{molar mass}}{\text{molar volume}} = \frac{\text{molar mass}}{22.4\text{ L}}$$

- For example, density of helium and nitrogen gases at STP are:

$$d_{\text{He}} = \frac{4.00\text{ g/mol}}{22.4\text{ L/mol}} = 0.179\text{ g/L} \qquad d_{\text{N}_2} = \frac{28.02\text{ g/mol}}{22.4\text{ L/mol}} = 1.25\text{ g/L}$$

- Density of a gas under any condition can be calculated by using the ideal gas law:

$$PV = nRT \qquad \text{rearranging,} \qquad \frac{n}{V} = \frac{P}{RT}$$

- Since n/V represents the molar density with units of mol/L , density in g/L can be obtained by multiplying it with molar mass:

$$\frac{\text{moles}}{\text{liter}} \times \frac{\text{grams}}{\text{mole}} = \frac{\text{grams}}{\text{liter}}$$

Molar density
Molar mass
Density in grams/liter

- Therefore,

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

where,

d = density (in g/L)

P = pressure (in atm)

M = molar mass (in g/mol)

R = gas constant

T = temperature (in K)

MOLAR VOLUME, DENSITY & MOLAR MASS OF A GAS
--

Examples:

1. Calculate the density of nitrogen gas at 125°C and a pressure of 755 mmHg.
2. Arrange the following gases in order of increasing density at STP: Ne, Cl₂, F₂, and O₂.
3. A gas has a density of 1.43 g/L at a temperature of 23°C and a pressure of 0.789 atm. Calculate its molar mass.
4. A sample of gas has a mass of 0.311 g. Its volume is 0.225 L at a temperature of 55°C and a pressure of 886 mmHg. Determine its molar mass.

MIXTURE OF GASES & PARTIAL PRESSURES

- Many gas samples are mixture of gases. For example, dry air is a mixture containing nitrogen (78%), oxygen (21%), argon (0.9%) and a few other gases in trace amounts.
- Since the gas particles in an ideal gas do not interact, each component in an ideal gas mixture acts independently of the others. For example, the nitrogen molecules in air exert a certain pressure—78% of total pressure—that is independent of the other gases in the mixture.
- The pressure due to any individual component in a gas mixture is its **partial pressure** (P_n). This partial pressure can be calculated from the ideal gas law as shown below:

$$P_n = n_n \frac{RT}{V}$$

- The sum of the partial pressures in a gas mixture is equal to the total pressure of the gas mixture. This relationship is known as **Dalton's law of partial pressures**.

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

- Combining the two relationships above, we get:

$$\begin{aligned} P_{\text{total}} &= P_1 + P_2 + P_3 + \dots \\ P_{\text{total}} &= n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V} + \dots \\ P_{\text{total}} &= n_{\text{total}} \frac{RT}{V} \end{aligned}$$

- The partial pressure of each gas in a mixture is proportional to the amount (mol) of gas present in the mixture. To see this more clearly, the ratio of the partial pressure of a gas to the total pressure of the gas can be calculated as:

$$\frac{P_n}{P_{\text{total}}} = \frac{n_n (RT/V)}{n_{\text{total}} (RT/V)} = \frac{n_n}{n_{\text{total}}}$$

- The ratio of the number of moles of a component in a mixture to the total number of moles of gas in the mixture is called the mole fraction (X_n):

$$X_n = \frac{n_n}{n_{\text{total}}}$$

- Rearranging the two equations above:

$$\frac{P_n}{P_{\text{total}}} = \frac{n_n}{n_{\text{total}}} = X_n \quad \text{and} \quad P_n = X_n P_{\text{total}}$$

PARTIAL PRESSURES

Examples:

1. A 1.00-L mixture of helium, neon and argon has a total pressure of 662 mmHg at 298 K. If the partial pressure of helium is 341 mmHg and the partial pressure of neon is 112 mmHg, what mass of argon is present in the mixture?

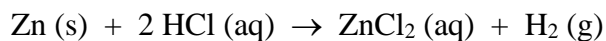
2. A sample of hydrogen gas is mixed with water vapor. The mixture has a total pressure of 755 torr and the water vapor has a partial pressure of 24 torr. How many moles of hydrogen gas is contained in 1.55 L of this mixture at 298 K?

3. A diver breathes a heliox mixture with an oxygen mole fraction of 0.050. When he dives, what must be the total pressure be for the partial pressure of oxygen to be 0.21 atm?

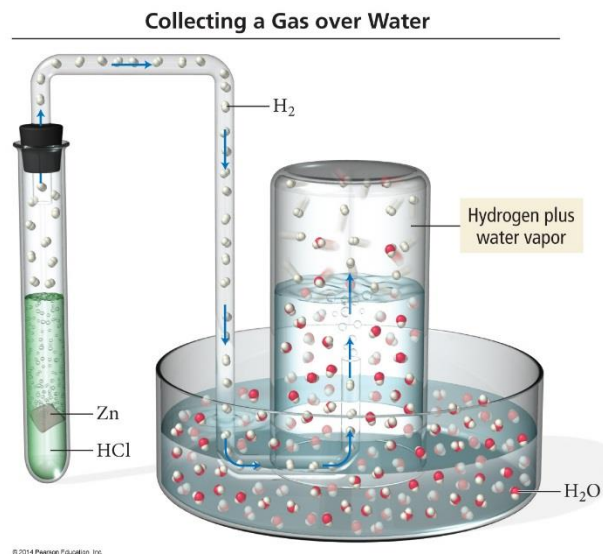
4. A 1.20-g sample of dry ice is added to a 755 mL flask containing nitrogen gas at a temperature of 25.0°C and a pressure of 725 mmHg. The dry ice sublimates (converts from solid to gas) and the system returns to 25.0°C. What is the total pressure in the flask?

COLLECTING GASES OVER WATER

- When the desired product in a chemical reaction is a gas, it is often collected by the displacement of water. For example, suppose we use the reaction of zinc metal and hydrochloric acid as a source of hydrogen gas:



- The gas can be collected by using an apparatus similar to one shown below. As hydrogen is produced, it bubbles through the water and gathers in the collection flask. The hydrogen gas collected in this way is not pure and is mixed with water vapor present in the reaction mixture.
- The partial pressure of the water in the mixture is called its vapor pressure and depends on the temperature. Vapor pressure increases with increasing temperature because higher temperature causes more water molecules to evaporate.
- To determine the partial pressure of the hydrogen gas produced, the total pressure measured in the flask must be corrected for the water vapor present, as shown below:



$$P_{\text{total}} = P_{\text{H}_2} + P_{\text{H}_2\text{O}}$$

$$P_{\text{H}_2} = P_{\text{total}} - P_{\text{H}_2\text{O}}$$

Examples:

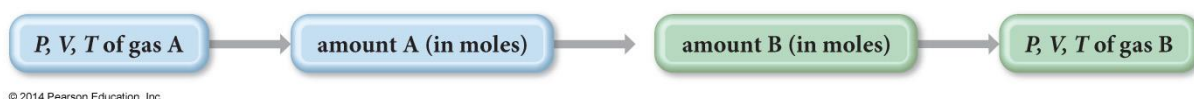
- In an experiment in the laboratory, 1.02 L of oxygen gas is collected over water at a temperature of 293 K and a total pressure of 755.2 mmHg. If the vapor pressure of water at this temperature is 17.55 mmHg, what mass of oxygen gas (in g) is formed during this experiment?

GAS STOICHIOMETRY

- In reactions involving gaseous reactants and products, the quantities of the gas are usually specified in terms of its volume at a given temperature and pressure. Since stoichiometric coefficients involve relationships between moles, ideal gas law can be used to determine the number of moles from the volumes, or vice versa:

$$n = \frac{PV}{RT} \qquad V = \frac{nRT}{P}$$

- The general conceptual plan for these kinds of calculations are shown below:

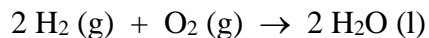


Examples:

- What mass of Ag_2O is required to form 388 mL of oxygen gas at 734 mmHg and 25.0°C , as shown below:



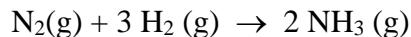
- How many liters of oxygen (at STP) are required to form 10.5 g of water, as shown below:



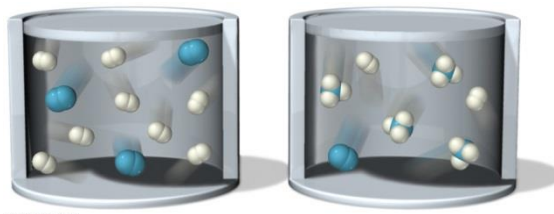
GAS STOICHIOMETRY

Examples (cont'd):

3. Nitrogen and hydrogen react to form ammonia, as shown below:

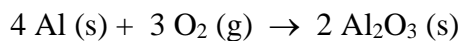


The diagrams below are representations of an initial reaction mixture and the resulting mixture after the reaction has been allowed to react for some time.



If the volume is kept constant, and nothing has been added to the mixture, what happens to the total pressure during the course of the reaction?

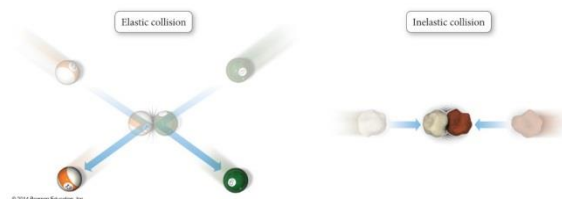
- a) the pressure increases
 - b) the pressure decreases
 - c) the pressure does not change
4. Oxygen gas reacts with powdered aluminum according to the reaction:



What volume of oxygen gas (in L), measured at 782 mmHg and 25°C, completely reacts with 53.2 g of Al?

KINETIC MOLECULAR THEORY

- A simple model developed to understand the behavior of gases is the **kinetic molecular theory (KMT)**. In this theory, the gas is modeled as a collection of particles in constant motion. A single particle moves in straight line until it collides with another particle or the walls of the container.
- The basic postulates of this theory are:
 - The size of the particle is negligibly small.** KMT assumes the particles of gas themselves occupy no volume, although they have mass. This assumption is justified, because under normal pressures, the space between gas molecules is much larger compared to the size of the particles themselves.
 - The average kinetic energy of a particle is proportional to the temperature in kelvin.** The motion of the particles in gas is due to its thermal energy, distributed among all the particles. At any given moment, some particles are moving faster than others—there is a distribution of velocities—but the higher the temperature, the greater the overall motion and the greater the kinetic energy.
 - The collision of the particles with another (or the wall of the container) are completely elastic.** This means that when two particles collide, they may exchange energy, but there is no loss of kinetic energy.
- Using the postulates of the kinetic molecular theory, one can mathematically derive the ideal gas law, indicating that the assumptions of the theory are valid under conditions where ideal gas law applies.
- Use of kinetic molecular theory also allows a conceptual understanding of the concepts of pressure and the simple gas laws studied earlier in this chapter.



Examples:

- A flask at room temperature contains exactly equal amounts (in moles) of nitrogen and xenon gases.
 - Which of the two gases exerts the greater partial pressure?
 - The particles of which gas has the greater KE?
 - The particles of which gas has the greater average velocity?

ROOT MEAN SQUARE VELOCITY

- According to the kinetic molecular theory, particles of different masses have the same average kinetic energy at the same temperature. The kinetic energy of a particle depends on its mass and velocity according to the equation:

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

- The only way for the particles of different masses to have the same kinetic energy is for them to have different velocities. ***In a gas mixture at a given temperature, the lighter particles move faster (on average) than the heavier ones.***
- In kinetic molecular theory, the root mean square velocity (u_{rms}) of a particle is defined as:

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

where $\overline{u^2}$ is the average of the squares of the particles velocities.

- Even though the root mean square velocities of a sample of gas particles is not identical to the average velocity, the two are close in value and conceptually similar.
- The average kinetic energy of one mole of particles of gas, and the proportionality of the average kinetic energy to the temperature are given by the equations below:

$$KE_{\text{avg}} = \frac{1}{2} N_A \overline{mu^2} \quad \text{and} \quad KE_{\text{avg}} = \frac{3}{2} RT$$

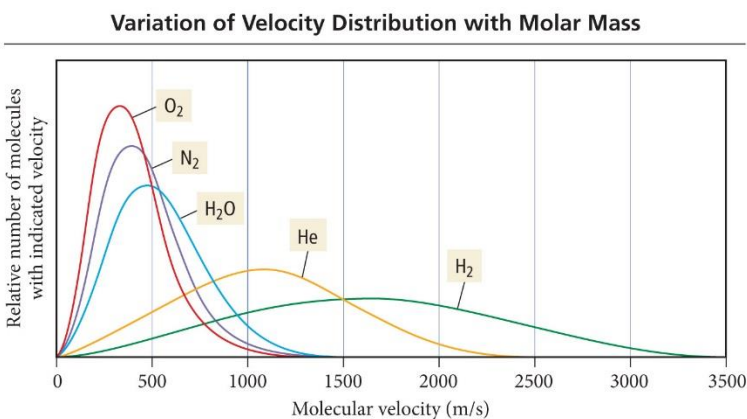
- Combining these equations, an expression for the root mean square velocity as a function of temperature can be obtained as follows:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}} \quad \text{where,} \quad \begin{array}{l} u_{\text{rms}} = \text{root mean square velocity} \\ R = \text{gas constant (8.314 J/molK)} \\ T = \text{temperature (in K)} \\ M = \text{molar mass (in kg/mol)} \end{array}$$

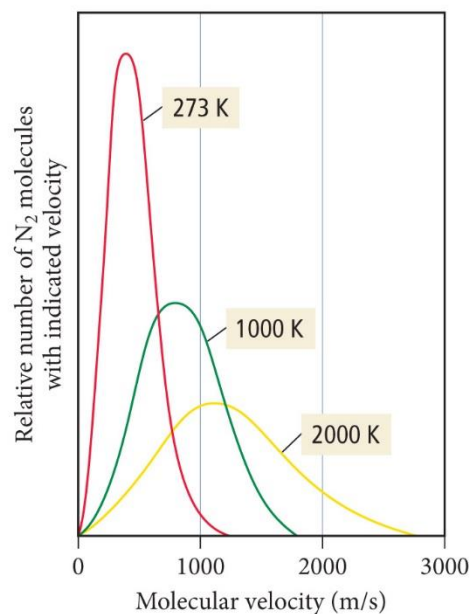
- The root mean square velocity of a collection of gas particles is directly proportional to the square root of the temperature in K, and inversely proportional to the square root of the molar mass of the gas particles.

ROOT MEAN SQUARE VELOCITY

- The diagrams below show the variation of the velocity distribution with molar mass and temperature for gas samples.

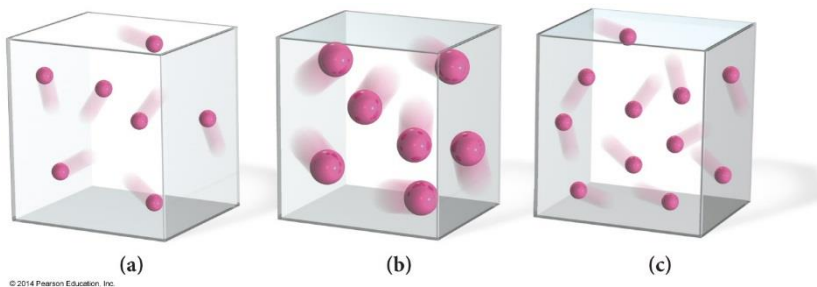


Variation of Velocity Distribution with Temperature



Examples:

- Calculate the root mean square velocity of oxygen molecules at 25°C .
- Which sample of ideal gas shown below has (a) greatest pressure, (b) greatest average kinetic energy, and (c) lowest average velocity? Assume all samples are at the same temperature.



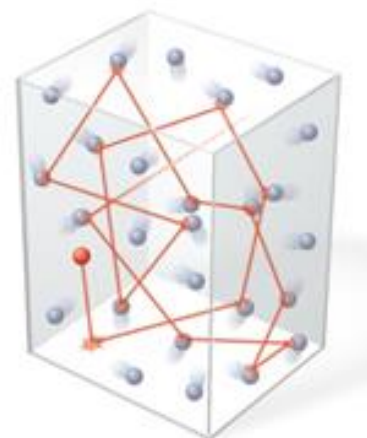
DIFFUSION & EFFUSION OF GASES

- Even though gas molecules travel at very fast speeds, they also travel in a very haphazard way across a path. The molecules travel only a short distance before colliding with another and changing direction. The average distance a molecule travels between collisions is its *mean free path*.
- The process by which gas molecules spread out in a given space is called *diffusion*. Even though during this process the molecules undergo many collisions, the root mean square velocity influences the rate of diffusion. As a result, heavier molecules (with lower u_{rms}) diffuse more slowly than lighter ones.
- The process by which a gas escapes from a container into a vacuum through a small hole is called *effusion*. The rate of effusion is also related to the root mean square velocity. Heavier molecules effuse more slowly than lighter ones.
- The rate of effusion—the amount of gas that effuses in a given time—is inversely proportional to the square root of the molar mass.

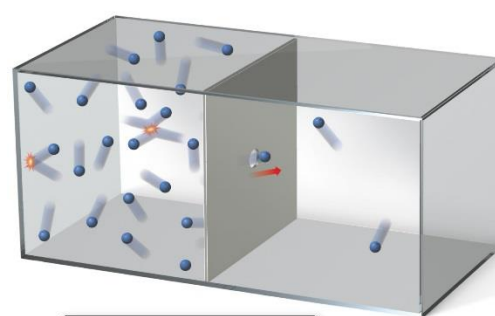
$$\text{rate} \propto \frac{1}{\sqrt{M}}$$

- The ratio of the rates of effusion of two different gases is given by *Graham's law of effusion*:

$$\frac{\text{rate A}}{\text{rate B}} = \sqrt{\frac{M_B}{M_A}}$$



Effusion



Gas escapes from container into a vacuum through a small hole

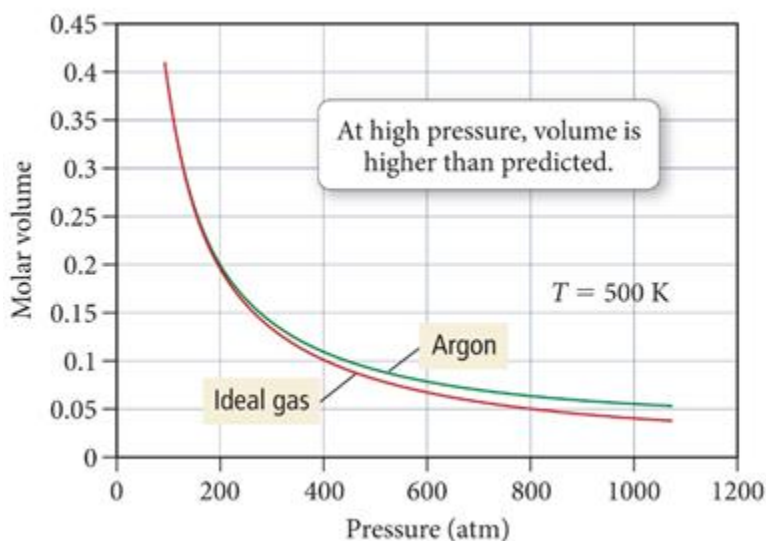
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Examples:

1. An unknown gas effuses at the rate that is 0.462 times that of nitrogen (at the same temperature). Calculate the molar mass of the unknown gas.
2. An unknown gas effuses through a capillary in 60 s. The same volume of hydrogen escapes in 10 s. Calculate the molar mass of the unknown gas. (Report answer to 2 sig figs; Note that rate of effusion is inversely related to time of effusion)
3. If it takes 3.52 s for 10.0 mL of helium to effuse through a hole in a container at a particular temperature and pressure, how long would it take for 10.0 mL of oxygen gas to effuse from the same container at the same conditions?

NON-IDEAL BEHAVIOR OF GASES

- Gases behave ideally when both of the following are true:
 1. The volume of the gas particles are small compared to the space between them.
 2. The forces between the gas particles are not significant.
- At STP, these assumptions are valid for most gases. However, these assumptions break down at higher pressures and lower temperatures.
- The finite volume of the gas particles—their actual size—becomes more important at high pressure because the volume of the particles themselves occupies a significant portion of the gas volume.
- The effect of particle volume at different pressures is shown for argon in the diagram below.

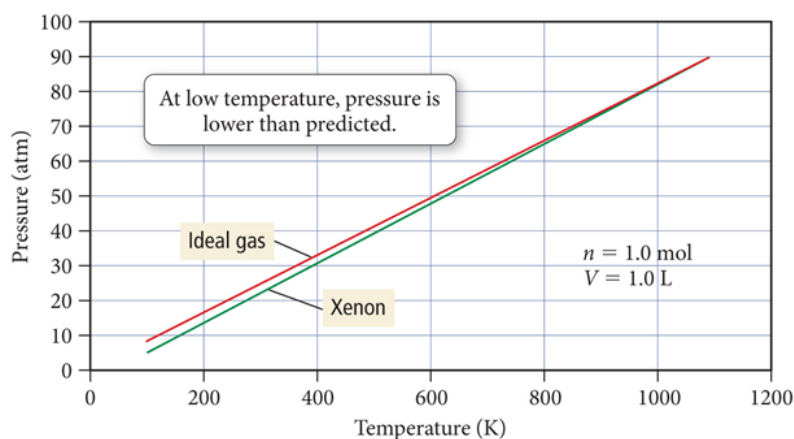


- The deviation from ideal gas law for the molar volume of gas can be corrected by using the Van der Waals equation and adding a correction factor (nb) for the volume of gas particles themselves:

$$V = \frac{nRT}{P} + nb$$

NON-IDEAL BEHAVIOR OF GASES

- The forces of attraction between molecules—intermolecular forces—are typically small for gases and therefore can be ignored at low pressure because the molecules are too far apart to “feel” the attractions.
- These attractions also do not matter much at high temperatures, because they are too small compared to the large kinetic energies of the two particles colliding.
- At low temperature, however, these weak intermolecular forces between the molecules could affect the collision and cause a decrease in the number of collisions between the particles, and a corresponding decrease in the pressure compared to that of an ideal gas.
- The effect of the intermolecular forces at different temperatures is shown for xenon in the diagram below:



- The deviation from ideal gas law for the intermolecular forces between gas particles can be corrected by using the *van der Waals* equation and subtracting a correction factor $[a(\frac{n}{V})^2]$ for the volume of gas particles themselves:

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

- The effects of the particle volume and intermolecular forces corrections can be combined together into one equation, called the van der Waals equation. This equation can be used to calculate properties of gases under non-ideal conditions.

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

Correction for
intermolecular forces

Correction for
particle volume

REAL GASES

- The van der Waals equation provides a much better fit with the behavior of a real gas than ideal gas equation. But it does so at the cost of loss in generality. The ideal gas equation is equally valid for any gas, whereas the van der Waals equation contains a pair of constants (*a* and *b*) that are different for different gases (see table 5.5).
- The combined effect of particle volume and intermolecular forces can be examined by plotting PV versus P for 1 mole of several real gases, as shown below:

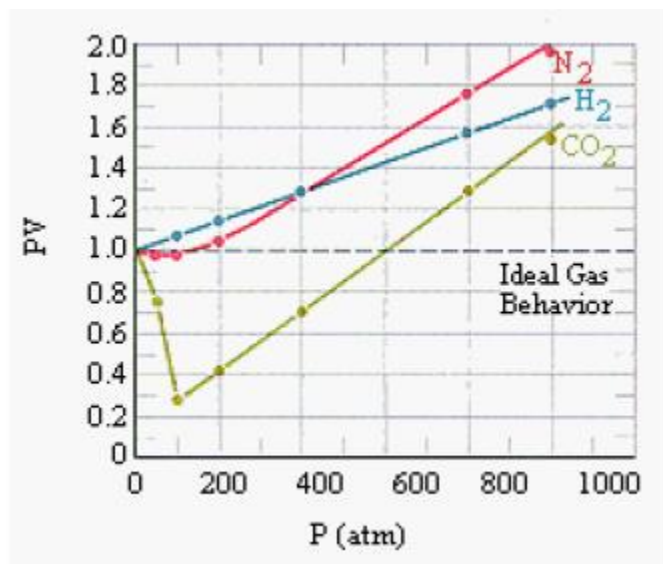


TABLE 5.5 Van der Waals Constants for Common Gases

Gas	<i>a</i> (L ² · atm/mol ²)	<i>b</i> (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

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- The ideal gas equation predicts that a plot of PV vs. P for a gas would be a horizontal line because PV should be constant. The deviations from ideal gas behavior can be illustrated by comparing the results of calculations using the ideal gas equation and the van der Waals equation for 1.00 mole of CO₂ at 0°C in containers of different volumes.

Volume of CO ₂	P (ideal gas)	P (van der Waals)
22.4 L	1.00 atm	0.995 atm
0.200 L	112 atm	52.6 atm
0.0500 L	448 atm	1620 atm

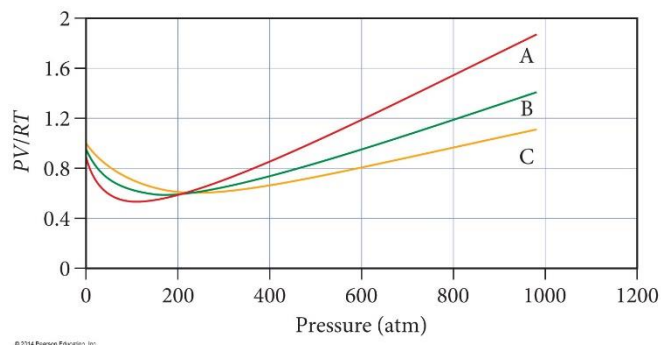
- Note that
 - at normal temperature and pressures, the ideal gas and van der Waals equations give essentially the same results.
 - As the pressure of CO₂ increases, the van der Waals equation initially gives values that are smaller than ideal gas equation, due to the strong force of attraction between the CO₂ molecules.
 - As pressure of CO₂ continues to increase, the van der Waals equation give results that are larger than ideal gas equation due to the volume occupied by the CO₂ molecules.

Summary:

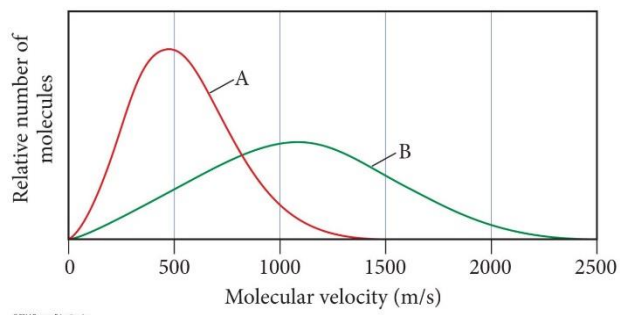
- Real gases behave near ideally at: ***low pressures*** and ***high temperatures***. Therefore, they are called ***ideal gases*** and Ideal Gas law is used to determine their properties.
- Real gases do not behave ideally at: ***high pressures*** and ***low temperatures***. Therefore, they are called ***real gases*** and Van der Waal's equation is used to determine their properties.

Examples:

1. The graph below shown PV/RT for CO_2 at three different temperatures. Rank the curves in order of increasing temperatures.



2. The plot below represents the velocity distribution of 1 L of He and Cl_2 gases at STP. Which plot represents which gas?



Answers to In-Chapter Problems:

<i>Page</i>	<i>Example No.</i>	<i>Answer</i>
2	1	6820 mmHg
	2	291.4 torr; 0.3834 atm; 38.85 kPa
3	3	a) 744.7 mmHg b) 803.8 mmHg
	4	b
5	1	
	2	
	3	
7	1	16.0 L
	2	8.02 L
	3	56.7%
9	1	0.852 g/L
	2	Ne < O ₂ < F ₂ < Cl ₂
	3	44.0 g/mol
	4	31.9 g/mol
11	1	
	2	
	3	
	4	