Gases

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Chapter 10

Characteristics of Gases

- There are three phases for all substances: solid, liquid and gases.
- Gases are highly compressible and occupy the full volume of their containers.
- When a gas is subjected to pressure, its volume decreases.
- Gases always form homogeneous mixtures with other gases.
- Gases only occupy about 0.1 % of the volume of their containers.

Pressure

Atmospheric Pressure and the Barometer

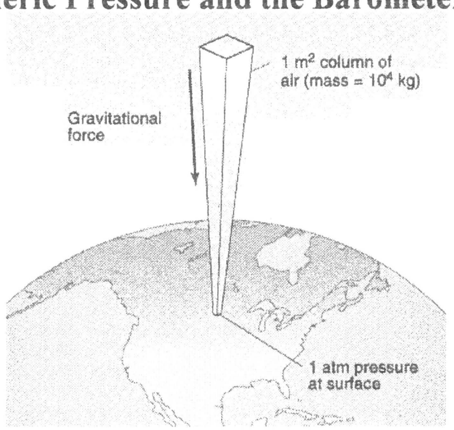
- Pressure is the force acting on an object per unit area:

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

- Gravity exerts a force on the earth's atmosphere
- A column of air 1 m^2 in cross section exerts a force of 10^5 N.
- The pressure of a 1 m^2 column of air is 100 kPa.

Pressure

Atmospheric Pressure and the Barometer



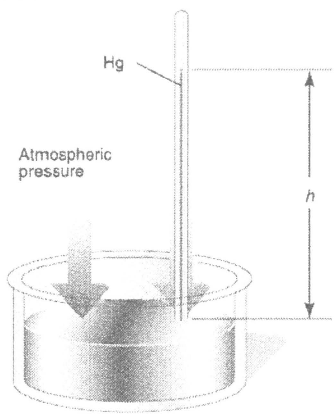
Pressure

Atmospheric Pressure and the Barometer

- SI Units: 1 N = 1 kg.m/s^2; 1 Pa = 1 N/m^2.
- Atmospheric pressure is measured with a barometer.
- If a tube is inserted into a container of mercury open to the atmosphere, the mercury will rise 760 mm up the tube.
- Standard atmospheric pressure is the pressure required to support 760 mm of Hg in a column.
- Units: 1 atm = 760 mmHg = 760 torr = 1.01325×10^5 Pa = 101.325 kPa.

Pressure

Atmospheric Pressure and the Barometer



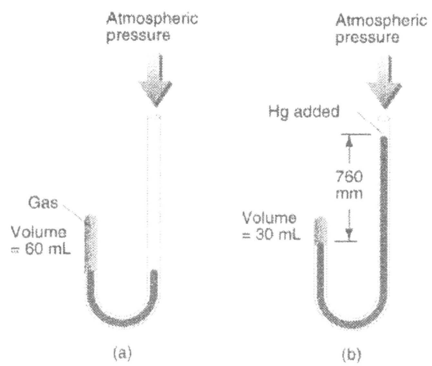
Pressure

Pressures of Enclosed Gases and Manometers

- The pressures of gases not open to the atmosphere are measured in manometers.
- A manometer consists of a bulb of gas attached to a U-tube containing Hg.
- If the U-tube is closed, then the pressure of the gas is the difference in height of the liquid (usually Hg).
- If the U-tube is open to the atmosphere, a correction term needs to be added:
  - If $P_{gas} < P_{atm}$ then $P_{gas} + P_{h2} = P_{atm}$.
  - If $P_{gas} > P_{atm}$ then $P_{gas} = P_{atm} + P_{h2}$.

Pressure

Pressures of Enclosed Gases and Manometers



The Gas Laws

The Pressures-Volume Relationship: Boyle's Law

- Weather balloons are used as a practical consequence to the relationship between pressure and volume of a gas.
- As the weather balloon ascends, the volume decreases.
- As the weather balloon gets further from the earth's surface, the atmospheric pressure decreases.
- Boyle's Law: the volume of a fixed quantity of gas is inversely proportional to its pressure.

The Gas Laws

The Pressures-Volume Relationship: Boyle's Law

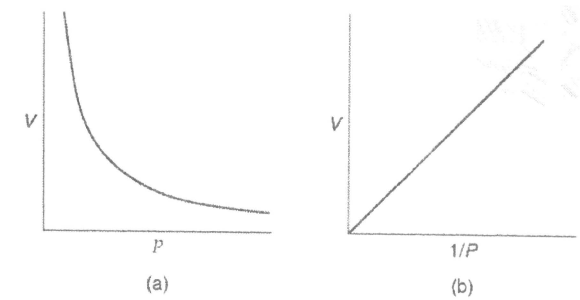
- Mathematically:

$$V = \text{constant} \times \frac{1}{P} \qquad PV = \text{constant}$$

- A plot of V versus P is a hyperbola.
- Similarly, a plot of V versus 1/P must be a straight line passing through the origin.

The Gas Laws

The Pressures-Volume Relationship: Boyle's Law



The Gas Laws

The Temperature-Volume Relationship: Charles's Law

- We know that hot air balloons expand when they are heated.
- Charles's Law: the volume of a fixed quantity of gas at constant pressure increases as the temperature increases.
- Mathematically:

$$V = \text{constant} \times T \qquad \frac{V}{T} = \text{constant}$$

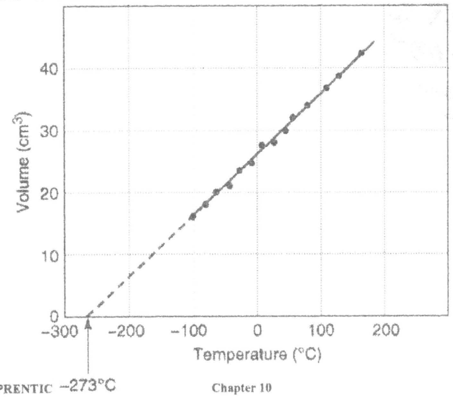
The Gas Laws

The Temperature-Volume Relationship: Charles's Law

- A plot of V versus T is a straight line.
- When T is measured in °C, the intercept on the temperature axis is -273.15°C.
- We define absolute zero, 0 K = -273.15°C.
- Note the value of the constant reflects the assumptions: amount of gas and pressure.

The Gas Laws

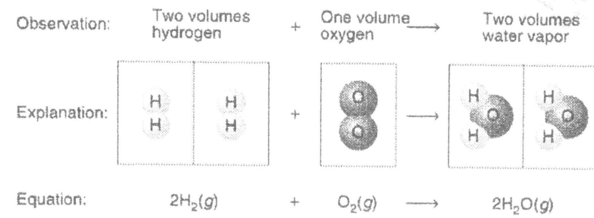
The Temperature-Volume Relationship: Charles's Law



The Gas Laws

The Quantity-Volume Relationship: Avogadro's Law

- Gay-Lussac's Law of combining volumes: at a given temperature and pressure, the volumes of gases which react are ratios of small whole numbers.



The Gas Laws

The Quantity-Volume Relationship: Avogadro's Law

- Avogadro's Hypothesis: equal volumes of gas at the same temperature and pressure will contain the same number of molecules.
- Avogadro's Law: the volume of gas at a given temperature and pressure is directly proportional to the number of moles of gas.

The Gas Laws

The Quantity-Volume Relationship: Avogadro's Law

- Mathematically:

$$V = \text{constant} \times n.$$

- We can show that 22.4 L of any gas at 0°C contain 6.02×10^{23} gas molecules.

The Ideal Gas Equation

- Summarizing the Gas Laws

Boyle: (constant n, T)

Charles: $V \propto T$ (constant n, P)

Avogadro: $V \propto n$ (constant P, T).

- Combined:

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

- Ideal gas equation:

$$V = R\left(\frac{nT}{P}\right)$$

The Ideal Gas Equation

- Ideal gas equation:

$$PV = nRT.$$

- R = gas constant = 0.08206 L•atm/mol-K.
- We define STP (standard temperature and pressure) = 0°C, 273.15 K, 1 atm.
- Volume of 1 mol of gas at STP is 22.4 L.

The Ideal Gas Equation

Relationship Between the Ideal-Gas Equation and the Gas Laws

- If $PV = nRT$ and n and T are constant, then $PV =$ constant and we have Boyle's law.
- Other laws can be generated similarly.
- In general, if we have a gas under two sets of conditions, then

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

Further Applications of The Ideal-Gas Equation

Gas Densities and Molar Mass

- Density has units of mass over volume.
- Rearranging the ideal-gas equation with $\mathcal{M}$ as molar mass we get

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{n\mathcal{M}}{V} = d = \frac{P\mathcal{M}}{RT}$$

Further Applications of The Ideal-Gas Equation

Gas Densities and Molar Mass

- The molar mass of a gas can be determined as follows:

$$\mathcal{M} = \frac{dRT}{P}$$

Volumes of Gases in Chemical Reactions

- The ideal-gas equation relates *P*, *V*, and *T* to number of moles of gas.
- The *n* can then be used in stoichiometric calculations.

Gas Mixtures and Partial Pressures

- Since gas molecules are so far apart, we can assume they behave independently.
- Dalton's Law: in a gas mixture the total pressure is given by the sum of partial pressures of each component:

$$P_t = P_1 + P_2 + P_3 + \ldots$$

- Each gas obeys the ideal gas equation:

$$P_i = n_i\left(\frac{RT}{V}\right)$$

- Combining equations:

$$P_t = (n_1 + n_2 + n_3 + \cdots)\left(\frac{RT}{V}\right)$$

Gas Mixtures and Partial Pressures

Partial Pressures and Mole Fractions

- Let n_i be the number of moles of gas *i* exerting a partial pressure P_i, then

$$P_i = X_i P_t,$$

where X_i is the mole fraction (n_i/n_t).

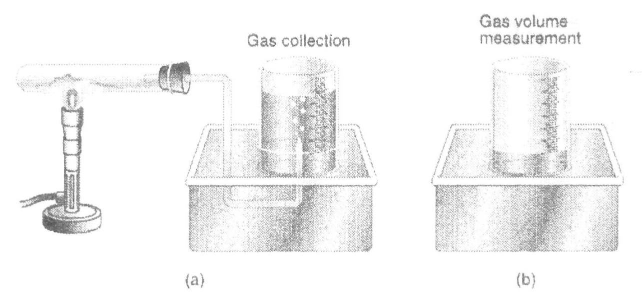
Collecting Gases over Water

- It is common to synthesize gases and collect them by displacing a volume of water.
- To calculate the amount of gas produced, we need to correct for the partial pressure of the water:

$$P_{total} = P_{gas} + P_{water}$$

Gas Mixtures and Partial Pressures

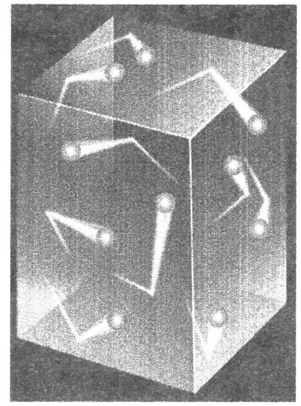
Collecting Gases over Water



Kinetic-Molecular Theory

- Theory developed to explain gas behavior.
- Theory of moving molecules.
- Assumptions:
  - Gases consist of a large number of molecules in constant random motion.
  - Volume of individual molecules negligible compared to volume of container.
  - Intermolecular forces (forces between gas molecules) negligible.
  - Energy can be transferred between molecules, but total kinetic energy is constant at constant temperature.
  - Average kinetic energy of molecules is proportional to temperature.

Kinetic-Molecular Theory

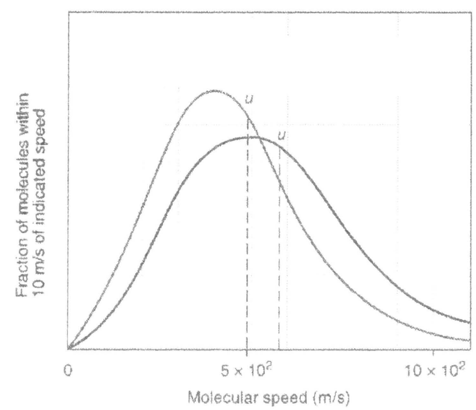


- Kinetic molecular theory gives us an understanding of pressure and temperature on the molecular level.
- Pressure of a gas results from the number of collisions per unit time on the walls of container.

Kinetic-Molecular Theory

- Magnitude of pressure given by how often and how hard the molecules strike.
- Gas molecules have an average kinetic energy.
- Each molecule has a different energy.
- There is a spread of individual energies of gas molecules in any sample of gas.
- As the temperature increases, the average kinetic energy of the gas molecules increases.

Kinetic-Molecular Theory



Kinetic-Molecular Theory

- As kinetic energy increases, the velocity of the gas molecules increases.
- Root mean square speed, u, is the speed of a gas molecule having average kinetic energy.
- Average kinetic energy, ε, is related to root mean square speed:

$$\varepsilon = \tfrac{1}{2}mu^2$$

Kinetic-Molecular Theory

Application to the Gas Laws

- As volume increases at constant temperature, the average kinetic of the gas remains constant. Therefore, u is constant. However, volume increases so the gas molecules have to travel further to hit the walls of the container. Therefore, pressure decreases.
- If temperature increases at constant volume, the average kinetic energy of the gas molecules increases. Therefore, there are more collisions with the container walls and the pressure increases.

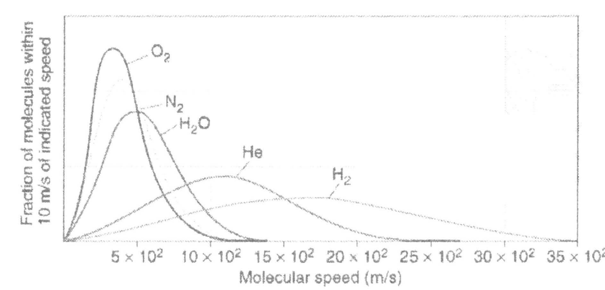
Molecular Effusion and Diffusion

- As kinetic energy increases, the velocity of the gas molecules increases.
- Average kinetic energy of a gas is related to its mass:
  - $\varepsilon = \tfrac{1}{2}mu^2$.
- Consider two gases at the same temperature: the lighter gas has a higher rms than the heavier gas.
- Mathematically:

$$u = \sqrt{\frac{3RT}{\mathcal{M}}}$$

- The lower the molar mass, $\mathcal{M}$, the higher the rms for that gas at a constant temperature.

Molecular Effusion and Diffusion



Molecular Effusion and Diffusion

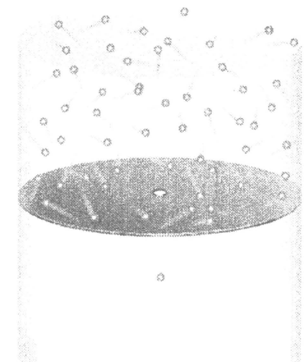
Graham's Law of Effusion

- As kinetic energy increases, the velocity of the gas molecules increases.
- Effusion is the escape of a gas through a tiny hole (a balloon will deflate over time due to effusion).
- The rate of effusion can be quantified.
- Consider two gases with molar masses $\mathcal{M}_1$ and $\mathcal{M}_2$, the relative rate of effusion is given by

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Molecular Effusion and Diffusion

Graham's Law of Effusion



Molecular Effusion and Diffusion

Graham's Law of Effusion

- Only those molecules that hit the small hole will escape through it.
- Therefore, the higher the rms the more likelihood of a gas molecule hitting the hole.
- We can show

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \sqrt{\frac{3RT/\mathcal{M}_1}{3RT/\mathcal{M}_2}} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

Molecular Effusion and Diffusion

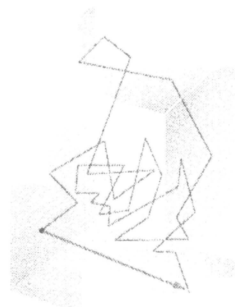
Diffusion and Mean Free Path

- Diffusion of a gas is the spread of the gas through space.
- Diffusion is faster for light gas molecules.
- Diffusion is significantly slower than rms speed (consider someone opening a perfume bottle: it takes while to detect the odor but rms speed at 25°C is about 1150 mi/hr).
- Diffusion is slowed by gas molecules colliding with each other.
- Average distance of a gas molecule between collisions is called mean free path.

Molecular Effusion and Diffusion

Diffusion and Mean Free Path

- At sea level, mean free path is about 6×10^{-6} cm.



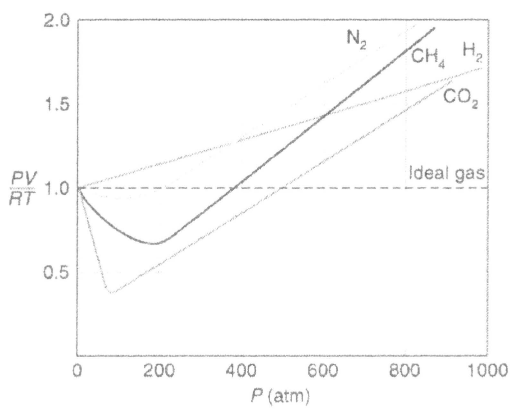
Real Gases: Deviations from Ideal Behavior

- From the ideal gas equation, we have

$$\frac{PV}{RT} = n$$

- For 1 mol of gas, $PV/RT = 1$ for all pressures.
- In a real gas, PV/RT varies from 1 significantly.
- The higher the pressure the more the deviation from ideal behavior.

Real Gases: Deviations from Ideal Behavior



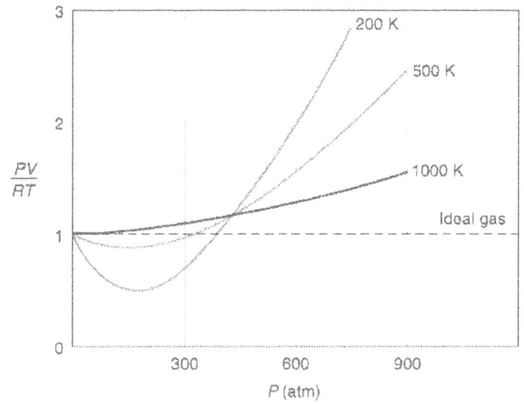
Real Gases: Deviations from Ideal Behavior

- From the ideal gas equation, we have

$$\frac{PV}{RT} = n$$

- For 1 mol of gas, $PV/RT = 1$ for all temperatures.
- As temperature increases, the gases behave more ideally.
- The assumptions in kinetic molecular theory show where ideal gas behavior breaks down:
  - the molecules of a gas have finite volume;
  - molecules of a gas do attract each other.

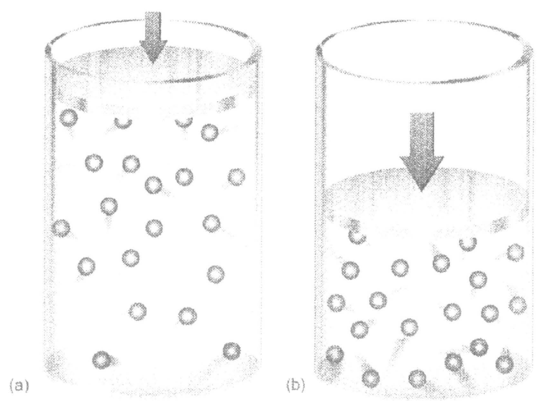
Real Gases: Deviations from Ideal Be'



Real Gases: Deviations from Ideal Behavior

- As the pressure on a gas increases, the molecules are forced closer together.
- As the molecules get closer together, the volume of the container gets smaller.
- The smaller the container, the more space the gas molecules begin to occupy.
- Therefore, the higher the pressure, the less the gas resembles an ideal gas.
- As the gas molecules get closer together, the smaller the intermolecular distance.

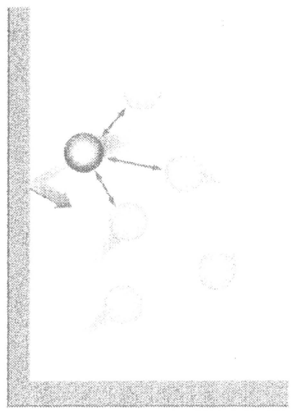
Real Gases: Deviations from Ideal Behavior



Real Gases: Deviations from Ideal Behavior

- The smaller the distance between gas molecules, the more likely attractive forces will develop between the molecules.
- Therefore, the less the gas resembles and ideal gas.
- As temperature increases, the gas molecules move faster and further apart.
- Also, higher temperatures mean more energy available to break intermolecular forces.
- Therefore, the higher the temperature, the more ideal the gas.

Real Gases: Deviations from Ideal Behavior



Real Gases: Deviations from Ideal Behavior

The van der Waals Equation

- We add two terms to the ideal gas equation one to correct for volume of molecules and the other to correct for intermolecular attractions
- The correction terms generate the van der Waals equation:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

where a and b are empirical constants.

Real Gases: Deviations from Ideal Behavior

The van der Waals Equation

- To understand the effect of intermolecular forces on pressure consider a molecule that is about to strike the wall of the container: the striking molecule is attracted by neighboring molecules. Therefore, the impact on the wall is lessened.

Gases

End of Chapter 10

