

Chapter 10: Gases

10.1 Characteristics of Gases

- Gases expand spontaneously to fill containers in which they are held, equaling their volume. Consequently, they are highly compressible.
- Gases form homogeneous mixtures with each other *regardless* of the identities or relative proportions of the component gases
- The characteristic properties of gases arise because the individual molecules are relatively far apart, hence, acting largely as though they were alone.

10.2 Pressure

- Pressure, P , is the Force, F , that acts on a given Area, A : $P = F / A$

Atmospheric Pressure and the Barometer

- The force, F , exerted by any object is the product of its mass, m , times its acceleration, a : $F = ma$
- SI unit for force is $\text{kg}\cdot\text{m}/\text{s}^2$ and is called the *Newton* (N)
- SI unit of pressure is N/m^2 , called a Pascal
- Standard atmospheric pressure**: defined as 760 torr (760 mm Hg), or, in SI units, 101.325 kPa
- Atmosphere**: unit of pressure equal to 760 torr; 1 atm = 101.325 kPa

10.3 The Gas Laws

The Pressure-Volume Relationship: Boyle's Law

- Boyle's law**: states that the volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure. When two measurements are inversely proportional, one gets smaller as the other one gets larger.

$$PV = \text{constant} \quad P = \text{pressure, } V = \text{volume}$$

The Temperature-Volume Relationship: Charles's Law

- Charles's law**: states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature. Thus, as the pressure gets higher, so does the temperature.

$$V / T = \text{constant} \quad V = \text{volume, } T = \text{Temperature}$$

The Quantity-Volume Relationship: Avogadro's Law

- Law of combining volumes**: at a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. (ie: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$)
- Avogadro's hypothesis**: equal volumes of gases at the same temperature and pressure contain equal number of molecules

-Avogadro's law: The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas

$$V = \text{constant} \times n \quad V = \text{volume, } n = \text{number of moles}$$

10.4 The Ideal-Gas Equation

-Ideal-gas equation: $PV = nRT$, P = pressure, V = volume, n = number of moles, R = gas constant, T = Temperature (always expressed on absolute-temperature scale, usually Kelvin)

-Gas constant: R , constant of proportionality in the ideal-gas equation. Some values of R are given below

Units	Numerical value
L-atm/mol-K	0.08206
Cal/mol-K	1.987
J/mol-K	8.314
M ³ -Pa/mol-K	8.314
L-torr/mol-K	62.36

-Standard temperature and pressure (STP): 0°C and 1atm. 1 mol of gas at STP has a volume of 22.41 L (*molar volume*)

10.5 Molar Mass and Gas Densities

-Density of a gas (d = density, M = molar mass):

$$d = PM / RT$$

-Molar mass of a gas:

$$M = dRT / P$$

10.6 Gas Mixtures and Partial Pressures

-Partial pressure: the pressure exerted by a particular gas in a mixture

-Dalton's law of partial pressures: law stating that the total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone

-The total pressure at constant temperature and volume is determined by the total number of moles of gas present, whether that total represents just one substance or a mixture

Partial Pressures and Mole Fractions

-Mole fraction: the ratio of the number of one component of a mixture to the total moles of all components; abbreviated X , with a subscript to identify the components.

-The partial pressure of a gas in a mixture is its mole fraction times the total pressure

10.8 Kinetic-Molecular Theory

-Kinetic-molecular theory: set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation

1. Gases consist of large numbers of molecules that are in continuous, random motion

2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained
3. Attractive and repulsive forces between gas molecules are negligible
4. Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does *not* change with time, as long as the temperature of the gas remains constant
5. The average kinetic energy of the molecules is proportional to absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy

-The pressure of a gas is caused by collisions of molecules with the walls of the container. The magnitude of the pressure is determined by how often and how “hard” the molecules strike the walls.

-If two different gases are at the same temperature, they have the same average kinetic energy. If the temperature of a gas is doubled, its kinetic energy also doubles. Hence, molecular motion increases with increasing temperature.

-Root-mean-square (rms) speed: the square root of the squared speeds of the gas molecules in a gas sample. This quantity is the speed of a molecule possessing average kinetic energy.

-The rms speed is important because the average kinetic energy of the gas molecules, ϵ , is related directly to u^2 :

$$\epsilon = \frac{1}{2} mu^2, \text{ where } m \text{ is the mass of the molecule}$$

-Because mass doesn't change with temperature, the rms speed (and also the average speed) of molecules must increase as temperature increases

Applications to the Gas Laws

1. *Effect of a volume increase at constant temperature:* If the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases.
2. *Effect of a temperature increase at constant volume:* An increase in temperature means an increase in the average kinetic energy of the molecules. If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore, the molecules strike harder, hence explaining how the observed pressure increases.

10.9 Molecular Effusion and Diffusion

-A gas composed of light gas particles will have the same average kinetic energy as one composed of much heavier particles, provided that the two gases are at the same temperature. The mass, m , of the particles in the lighter gas is smaller than that in the heavier gas. Consequently, the particles of the lighter gas must have a higher rms speed, u , than the heavier one:

$$u = \sqrt{3RT / M}$$

-Since M is in the denominator, the less massive the gas molecules, the higher the rms speed

-Effusion: the escape of a gas through an orifice or hole. The rate of effusion depends on the molecular mass of the gas.

-Diffusion: the spreading of one substance through a space or through another substance

Graham's Law of Effusion

-**Graham's law:** law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight

$$r_1 / r_2 = \sqrt{M_2 / M_1} \quad \text{where } r \text{ is the rate of effusion}$$

-The rate of effusion is also directly proportional to the rms speed of the molecules. This is because the only way for the molecule to escape is to "collide" with the opening. Hence, the faster the molecules are moving, the greater the likelihood that a molecule will hit the opening and effuse.

Diffusion and Mean Free Path

-Diffusion, like effusion, is faster for light molecules than for heavy ones. The diffusion of gases is much slower than molecular speeds because of molecular collisions. Because of these collisions, the direction of motion of a gas molecule is constantly changing, making this a slow process.

-**Mean free path:** average distance traveled by a molecule between collisions. The higher the density of a gas, the smaller the mean free path

10.10 Deviations from Ideal Behavior

-The ideal gas equation may be rearranged as follows to understand deviations from ideal-gas behavior:

$$PV / RT = n$$

-For a mole of ideal gas ($n = 1$), the quantity $PV / RT = 1$ at all pressures. However, real gases do not behave in such a way. At high pressures, the deviation is very high, however it is less with lower pressures. In general, the deviations from ideal behavior increase as temperature decreases, becoming significant near the temperature at which the gas is converted into a liquid.

-Basic assumptions in the kinetic molecular theory suggest that molecules of an ideal gas occupy no space and have no attraction for each other. *Real molecules, however, do have finite volumes, and they do attract one another.*

-Also, if the volume of the container in which the gas is contained is large, the molecules have plenty of free space, and do not take much of the container's volume itself. However, as pressure increases, the gas molecules occupy a much larger fraction of the container's volume.

-In addition, the attractive forces between molecules come into play at short distances, as when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened.

-Temperature determines how effective attractive forces between gas molecules are. As the gas is cooled, the average kinetic energy decreases, while intermolecular attractions remain constant.

The Van der Waals Equation

-According to the ideal gas equation:

$$P = nRT / V \quad \text{(ideal gas)}$$

-According to Van der Waals:

$$(P = nRT / V - nb) - (n^2a / V^2)$$

Correction for volume of molecules – Correction for molecular attractions

-The Van der Waals constant b is a measure of the actual volume occupied by a mole of gas molecules; b has units of L/mol.

-The Van der Waals constant a has units of L²-atm/mol². The magnitude of a reflects how strongly the gas molecules attract each other

-Van der Waals equation:

$$[P + (n^2a / V^2)] (V - nb) = nRT$$

-The Van der Waals constants a and b are different for each gas. The values of these constants generally increase with an increase in mass of the molecule and with an increase in the complexity of its structures.