

GASES

Gases differ significantly from solids and liquids.

- A gas expands spontaneously to fill its container.
- Gases are highly compressible.
- Gases form homogeneous mixtures with each other regardless of the identities or relative proportions of the component gases.

Substances that are liquids or solids under ordinary conditions can usually also exist in the gaseous state, where they are often referred to as vapors.

PRESSURE

In general terms, pressure conveys the idea of a force. Pressure, P , is the force, F that acts on a given area, A :

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

ATMOSPHERIC PRESSURE

The force exerted by any object is the product of its mass, m , times its acceleration ($F=ma$). Earth's gravity exerts an acceleration of 9.8m/s^2 . A column of air 1 m^2 in cross section extending through the atmosphere has a mass of roughly $10,000\text{ kg}$.

$$F = (10,000\text{ kg})(9.8\text{ m/s}^2) = 1 \times 10^5\text{kg}\cdot\text{m/s}^2$$

The SI unit for forces is $\text{kg}\cdot\text{m/s}^2$ and is called the *newton* (N)

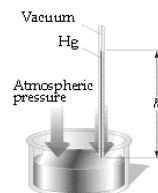
The pressure exerted by the column is the force divided by its cross-sectional area, A :

$$P = \frac{F}{A} = \frac{1 \times 10^5\text{ N}}{1\text{ m}^2} = 1 \times 10^5\text{ N/m}^2 = 1 \times 10^5\text{ Pa} = 1 \times 10^2\text{ kPa}$$

The SI unit of pressure is N/m^2 . It is given the name pascal (Pa) after Blaise Pascal (1623-1662), a French mathematician and scientist:

$$1\text{ Pa} = 1\text{ N/m}^2$$

$$1\text{ Joule} = 1\text{ m}^3 \cdot \text{Pa}$$



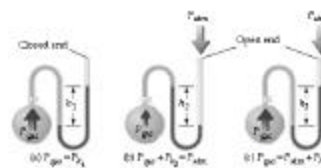
Atmospheric pressure can be measured by use of mercury barometer.

The mercury surface in the dish experiences the full force of Earth's atmosphere. Because there is no air in the tube, the mercury is pushed up the tube until the pressure due to the mass of the mercury column balances the atmospheric pressure.

Standard atmospheric pressure, which corresponds to the typical pressure at sea level, is the pressure sufficient to support a column of mercury 760 mm in height. In SI units, this pressure equals 1.01325×10^5 Pa.

It is used to define some non-SI units used to express gas pressures: the atmosphere (atm) and the millimeter of mercury (mm Hg). The latter unit is also called the torr, after the Italian scientist Evangelista Torricelli.

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 101.325 \text{ kPa}$$



•Shows a closed-tube manometer, used to measure pressures below atmospheric pressure.

(b) and (c) use an open-tube manometer to measure gas pressures that are near atmospheric pressure.

BOYLE'S LAW

The volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the the pressure.

In mathematical terms:

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

$$P_1V_1 = P_2V_2$$

CHARLES'S LAW

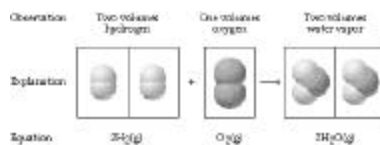
The volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature.

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

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

Avogadro's Law

Gay-Lussac carried out several experiments on the properties of gases. In 1808 he discovered the *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



Three years later Amdeo Avogadro interpreted Gay-Lussac's observation by proposing what is now known as Avogadro's hypothesis: Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

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

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

The Ideal-Gas Equation

We have examined three historically important gas laws. Each law was obtained by holding two variables constant in order to see how the other variables affect each other.

All three can be combined to make a more general gas law:

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

If we call the proportionality constant R , we obtain:

$$V = R \left(\frac{nT}{P} \right) \quad \text{or} \quad PV = nRT$$

TABLE 10.2 Numerical Values of the Gas Constant, R , in Various Units

Units	Numerical Value
L-atm/mol-K	0.08206
cal/mol-K	1.987
J/mol-K ^a	8.314
m ³ -Pa/mol-K ^a	8.314
L-torr/mol-K	62.36

^aSI unit.

Many times P , V , and T all change for a fixed number of moles of gas.

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

If the initial and final conditions of pressure, temperature, and volume by subscripts 1, and 2, respectively, we can write:

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

The ideal-gas equation can be arranged to yield:

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

Multiplying both sides of this equation by molar mass (M) yields:

$$\frac{n?}{V} = \frac{PM}{RT}$$

Thus, the density, d , of the gas is:

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

Which can be rearranged for empirically determining molar mass.

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

GAS MIXTURES AND PARTIAL PRESSURES

Thus far we have considered only the behavior of pure gases, those that consist of only one substance in the gaseous state.

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

The pressure exerted by a particular component of a mixture of a mixture of gases is called the **partial pressure** of the gas

If we let P_t equal the total pressure, and $P_1, P_2, P_3,$ and so forth. Dalton's law can be written as follows:

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

This equation implies that each gas in the mixture behaves independently of the other. Let $n_1, n_2, n_3,$ and so forth, be the number of moles of each of the gases in the mixture.

$$P_1 = n_1 \left(\frac{RT}{V} \right), \quad P_2 = n_2 \left(\frac{RT}{V} \right), \quad P_3 = n_3 \left(\frac{RT}{V} \right), \text{ and so forth.}$$

Because all the gases experience the same temperature and volume, RT/V can be factored out:

$$P_t = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V}$$

Here we see that sum of the moles present determine the total pressure.

$$P_t = n_t \left(\frac{RT}{V} \right)$$

PARTIAL PRESSURES AND MOLE FRACTIONS

Because each gas in mixture behaves independently, one can easily relate the amount of a given gas in a mixture to its partial pressure.

$$\frac{P_1}{P_t} = \frac{n_1 RT / V}{n_t RT / V} = \frac{n_1}{n_t}$$

$$\frac{P_1}{P_t} = \frac{n_1 RT / V}{n_t RT / V} = \frac{n_1}{n_t}$$

The ratio n_1/n_t is called the **mole fraction** of gas 1, which we denote X_1 . The mole fraction, X , is a dimensionless number that expresses the ratio of the number of moles of one component to the total number of moles in the mixture.

Thus, the partial pressure of a gas in a mixture is its mole fraction times the total pressure.

$$P_1 = \left(\frac{n_1}{n_t} \right) P_t = X_1 P_t$$

The sum of the mole fraction of a mixture must equal 1, i.e.

$$\sum X_i = 1$$

KINETIC MOLECULAR THEORY

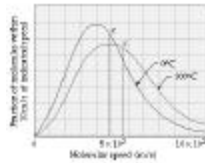
1. Gases consist of large numbers of molecules that are in continuous random motion (molecules, as used here, means smallest particles of any gas).
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained.
 - Attractive and repulsive forces between gas molecules are negligible.
 - Energy can be transferred between molecules during collision, but the average kinetic energy of the molecules does not change with time, as long as the temperature of the gas remains constant (i.e. the collisions are perfectly elastic).
 - The average kinetic energy of the molecules is proportional to the absolute temperature. At any given temperature the molecules of all gases have the same average kinetic energy.

The kinetic-molecular theory gives us an understanding of both pressure and temperature at a molecular level.

The pressure of a gas is caused by collisions of the molecules with the walls of the container.

The magnitude of the pressure is determined by both how "often" and how "hard" the molecules strike the walls.

Although the molecules in a sample of gas have an average kinetic energy and hence an average speed, the individual molecules move at varying speeds.



Distribution of molecular speeds. Root-mean-square (rms) speed μ , of the molecules at each temperature.

The rms speed is important because the average kinetic energy of the gas molecules, e , is related directly to μ^2

$$e = \frac{1}{2}m\mu^2$$

MOLECULAR EFFUSION AND DIFFUSION

For all gases at the same temperature, the average kinetic energies are identical.

Thus, at a fixed temperature, the average speed of a light gas is greater than that of a heavier gas.

An equation that expresses this fact quantitatively can be derived from the theory:

$$\mu = \sqrt{\frac{3RT}{M}}$$

Notice that molar mass, M , appears in the denominator. Thus, the less massive the gas molecules, the higher the rms speed, μ .

The dependence of molecular speeds on mass has several interesting consequences.

Thomas Graham discovered that the effusion rate of a gas is inversely proportional to the square of its molar mass.

