

- Unlike solids and liquids, gases can compress and expand easily.
- Their volume changes are controlled by temperature (T), pressure (P), and moles (n).

Pressure

- Pressure equals force per unit area: $P = \frac{F}{A}$
- Force is exerted by gases due to limitations on volume (e.g., due to gravity).
- For P due to gravity, suppose an object has $m = 1.0 \times 10^{-3} \text{ kg}$ and $A = 5.00 \times 10^{-4} \text{ m}^2$
 $F = mg = (1.0 \times 10^{-3} \text{ kg})(9.81 \text{ m/s}^2) = 9.81 \times 10^{-3} \text{ kg}\cdot\text{m/s}^2 = 9.81 \times 10^{-3} \text{ Newtons (N)}$
 $P = \frac{F}{A} = \frac{0.00981 \text{ N}}{5.00 \times 10^{-4} \text{ m}^2} = 19.6 \frac{\text{N}}{\text{m}^2} = 19.6 \frac{\text{kg}}{\text{m}\cdot\text{s}^2} = 19.6 \text{ Pascals (Pa)}$

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} = 101.3 \text{ kPa} = 1.013 \text{ bar} = 760 \text{ mmHg} = 14.696 \text{ psi}$$

Ex 5.01 Using Conversion Factors for Pressure

- $(6.21 \text{ atm})\left(\frac{760 \text{ mmHg}}{1 \text{ atm}}\right) = 4.72 \times 10^3 \text{ mmHg}$
- $(4.72 \times 10^3 \text{ mmHg})\left(\frac{101.3 \text{ kPa}}{760 \text{ mmHg}}\right) = 629 \text{ kPa}$

Barometers/Manometers

- [Pressure of air](#) and other gases is measured by increase in height of a liquid in a column.
- The [barometer](#) equation $P = \rho gh$ can be derived from $P = \frac{F}{A}$, $F = mg$, $A = \frac{V}{h}$ and $V = \frac{m}{d}$.
- $P = \frac{F}{A} = \frac{mg}{V/h} = \frac{mgh}{V} = \frac{mgh}{(m/d)} = \frac{gh}{(1/d)} = \rho gh$
- For water, $d = 1000 \text{ kg/m}^3$
- With height (h) in meters, the result for pressure (P) is in units of Pa (or N/m^2).
- Use $760 \text{ mmHg} = 1.01 \times 10^5 \text{ Pa}$ to convert the pressure into mmHg.

Boyles' Law (Robert Boyle, 1661)

- Volume is inversely proportional to P at constant T. That is: $V \propto 1/P$.
- $PV = \text{constant}$ (at constant T and moles).
- $P_i V_i = P_f V_f$ Alternate equations: $P_f = P_i \left(\frac{V_i}{V_f}\right)$ and $V_f = V_i \left(\frac{P_i}{P_f}\right)$

Ex 5.02 Using Boyle's Law to Determine Volume when Pressure Changes

- $V_f = V_i \left(\frac{P_i}{P_f}\right) = (32.7 \text{ dm}^3) \left(\frac{85.0 \text{ kPa}}{101.3 \text{ kPa}}\right) = 27.4 \text{ dm}^3 = 27.4 \text{ L}$

Charles' Law (Jacques Charles, along with J. Dalton and J.L. Gay-Lussac, 1787)

- $V \propto T$ (at constant P and moles) if T is in Kelvins ($K = ^\circ C + 273$), so that $V/T = \text{constant}$.
- $\frac{V_f}{T_f} = \frac{V_i}{T_i}$ Alternate equations: $V_f = V_i \left(\frac{T_f}{T_i} \right)$ and $T_f = T_i \left(\frac{V_f}{V_i} \right)$

Ex 5.03 Using Charles' Law to Determine Volume when Temperature Changes

- $T_i = 10^\circ C + 273 = 283 \text{ K}$ $T_f = 36^\circ C + 273 = 309 \text{ K}$
- $V_f = V_i \left(\frac{T_f}{T_i} \right) = (27.4 \text{ L}) \left(\frac{309 \text{ K}}{283 \text{ K}} \right) = 29.9 \text{ L}$

Combined Gas Law

- $V \propto T/P$, so $PV/T = \text{constant}$ (if moles are constant)
- $\frac{V_f P_f}{T_f} = \frac{V_i P_i}{T_i}$ and $V_f = V_i \left(\frac{P_i}{P_f} \right) \left(\frac{T_f}{T_i} \right)$

Ex 5.04 Using the Combined Gas Law to Determine Volume when P and T both Change

- $V_f = V_i \left(\frac{P_i}{P_f} \right) \left(\frac{T_f}{T_i} \right) = (82.4 \text{ cm}^3) \left(\frac{752 \text{ mmHg}}{760 \text{ mmHg}} \right) \left(\frac{273 \text{ K}}{293 \text{ K}} \right) = 76.0 \text{ cm}^3 \times \left(\frac{1 \text{ mL}}{1 \text{ cm}^3} \right) = 76.0 \text{ mL}$

Avogadro's Law

- Equal volumes of any gases with the same T and P contain the [same number of molecules](#).
- The identity of the gases changes the volume only slightly due to intermolecular forces.
- Molar Volume (V_m) is the volume (in L) of one mole of gas. That is: $V_m = \text{liters} \div \text{moles}$
- For an ideal gas (no intermolecular forces): $V_m = 22.41 \text{ L/mol}$ at STP ($0^\circ C$ and 1 atm)
- To create water from $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)}$, 2 L of H_2 will react with exactly 1 L of O_2 . How many L of water vapor are formed?

Ideal Gas Law

- $V = (\text{constant})(T/P)$ if n is constant. V is proportional to moles, so $V/n = (\text{constant})(T/P)$.
- $V_m = V/n = (R)(T/P)$, where the molar gas constant (R) is $0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$.
- The equation rearranges to $PV = nRT$.
- Boyle's, Charles', and Avogadro's Laws can all be derived from the ideal gas law.

Ex 5.05 Rearrange the Ideal Gas Law to determine Volume as a function of n, P, and T

- $V = \frac{nRT}{P} = \frac{0.00324 \text{ mol} \times 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \times 294 \text{ K}}{0.952 \text{ atm}} = 0.0821 \text{ L} \times \left(\frac{1000 \text{ mL}}{1 \text{ L}} \right) = 82.1 \text{ mL}$

Ex 5.06 Use the Ideal Gas Law to Determine the Moles and Mass for 25.4 L of $\text{CO}_{2(g)}$ at STP

- $n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(25.4 \text{ L})}{\left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (273 \text{ K})} = 1.13 \text{ mol of } \text{CO}_{2(g)}$
- $\text{mass} = (n)(M_m) = (1.13 \text{ mol})(44.0 \text{ g/mol}) = 49.7 \text{ g}$

Gas Density

- **Density** (d) in g/L is mass/volume: $d = \frac{m}{V} = \frac{(M_m)(n)}{V} = \frac{(M_m)(P)}{RT}$
- The equation rearranges to $P(M_m) = dRT$ and $M_m = \frac{dRT}{P}$.

Ex 5.07 Determine the Density of $\text{CO}_{2(g)}$ at 35°C (308 K) and 1.08 atm

- $d = \frac{(P)(M_m)}{RT} = \frac{(1.08 \text{ atm})(44.00 \frac{\text{g}}{\text{mol}})}{(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(308 \text{ K})} = 1.88 \text{ g/L}$

Ex 5.08 Determine M_m for a 1.338 g sample of Xe gas in 250.0 ml at 19°C and 742 mmHg

- $V = 0.2500 \text{ L}$, $T = 19^\circ\text{C} + 273 = 292 \text{ K}$, and $P = 742 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.976 \text{ atm}$
- $d = m/V = (1.338 \text{ g})/(0.2500 \text{ L}) = 5.352 \text{ g/L}$
- $M_m = \frac{dRT}{P} = \frac{(5.352 \frac{\text{g}}{\text{L}})(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(292 \text{ K})}{0.976 \text{ atm}} = 131 \frac{\text{g}}{\text{mol}} = 131 \frac{\text{amu}}{\text{atom}}$

Stoichiometry with Gas Volumes

- Determine mole ratios from coefficients in the **balanced reaction**.
- Use the ideal gas law to determine moles.

Ex 5.09 Use Stoichiometry to Determine Amounts of Reactants

- $\text{Na}_2\text{CO}_{3(s)} + 2\text{HCl}_{(aq)} \rightarrow 2\text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(L)} + \text{CO}_{2(g)}$
- $V = 95.2 \text{ mL of CO}_2$, $P = 743 \text{ mmHg} \times \frac{1.00 \text{ atm}}{760 \text{ mmHg}} = 0.978 \text{ atm}$, $T = 20^\circ\text{C} + 273 = 293 \text{ K}$
- $n = \frac{PV}{RT} = \frac{(0.978 \text{ atm})(0.0952 \text{ L})}{(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(293 \text{ K})} = 0.00387 \text{ mol CO}_{2(g)}$
- $(0.00387 \text{ mol CO}_2) \left(\frac{2 \text{ mol HCl}}{1 \text{ mol CO}_2} \right) = 0.00774 \text{ mol HCl}_{(aq)}$
- $(0.00387 \text{ mol CO}_2) \left(\frac{1 \text{ mol Na}_2\text{CO}_3}{1 \text{ mol CO}_2} \right) = 0.00387 \text{ mol Na}_2\text{CO}_{3(s)}$
- $(0.00387 \text{ mol Na}_2\text{CO}_{3(s)})(106.0 \text{ g/mol}) = 0.410 \text{ g Na}_2\text{CO}_{3(s)}$

Gas Mixtures – Law of Partial Pressures (J. Dalton)

- Each gas in a mixture occupies the total volume and exhibits its own **partial pressure**.
- Each component follows the ideal gas law ($P_{\text{partial}} = nRT/V$).
- Sum of partial pressures for all components equals the total pressure.
- $P_{\text{total}} = P_a + P_b + P_c + \dots$

Mole Fraction is the moles of a component divided by the total moles in the mixture.

- Partial pressure is directly proportional to the number of moles because $P_a = (n_a)(RT/V)$.
- So, the mole fraction and the pressure fraction for gases are identical.
- Mole Fraction:
$$X_a = \frac{\text{moles of component a}}{\text{total of all moles in mixture}} = \frac{n_a}{n_{\text{total}}}$$
- Pressure ratio is identical:
$$X_a = \frac{\text{pressure of component a}}{\text{total pressure of mixture}} = \frac{n_a \left(\frac{RT}{V}\right)}{n_{\text{total}} \left(\frac{RT}{V}\right)} = \frac{P_a}{P_{\text{total}}}$$

Ex 5.10 Determine the Partial Pressure and Mole Fraction of Oxygen in Air

- A 1.000 L sample of dry air at 25.00 °C and 778 mmHg contains 0.281 g O₂.
- $P_{\text{total}} = 778 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 1.024 \text{ atm}$ $T = 25.00 \text{ °C} + 273.15 = 298.15 \text{ K}$
- $n_{\text{O}_2} = 0.281 \text{ g O}_2 \times \frac{1 \text{ mol}}{32.00 \text{ g}} = 0.00879 \text{ mol O}_2$
- $P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} = \frac{(0.00879 \text{ mol}) \left(0.08206 \frac{\text{L atm}}{\text{mol K}}\right) (298.15 \text{ K})}{1.000 \text{ L}} = 0.215 \text{ atm}$
- $X_{\text{O}_2} = \frac{P_{\text{O}_2}}{P_{\text{total}}} = \frac{0.215 \text{ atm O}_2}{1.024 \text{ atm total}} = 0.210 \frac{\text{atm O}_2}{\text{atm total}}$
- $X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{total}}} = 0.210 \frac{\text{mol O}_2}{\text{mol total}}$ $n_{\text{total}} = \frac{n_{\text{O}_2}}{X_{\text{O}_2}} = \frac{0.00879 \text{ mol O}_2}{0.210 \text{ mol O}_2 / \text{mol total}} = 0.0419 \text{ mol total}$

Gas collected over water

- All volatile liquids, including water, have a vapor pressure.
- Vapor pressure is caused by molecules leaving the liquid phase for the gas phase.
- The vapor pressure is measured when the substance's gas is in equilibrium with its liquid.
- Vapor Pressure increases with T, but not linearly.
- Vapor Pressure of Water ($P_{\text{water vapor}}$) versus T can be found in both [Table 9.2](#) and [Figure 9.22](#) of the text, as well as in Appendix C of the lab manual.
- Partial Pressure of a gas (P_{gas}) [collected over water](#) is $P_{\text{total}} - P_{\text{water vapor}}$ because Dalton's law tells us that $P_{\text{total}} = P_{\text{gas}} + P_{\text{water vapor}}$.

Ex 5.11 Determine the Mass for 98.6 mL of Carbon Dioxide Gas Collected over Water at 21 °C

- $P_{\text{total}} = 771.8 \text{ mmHg}$ and $P_{\text{water}} = 18.7 \text{ mmHg}$ at 21 °C (294 K)
- $P_{\text{CO}_2} = P_{\text{total}} - P_{\text{water}} = 771.8 - 18.7 = 753.1 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.991 \text{ atm}$
- $n_{\text{CO}_2} = \frac{P_{\text{CO}_2}V}{RT} = \frac{(0.991 \text{ atm})(0.0986 \text{ L})}{\left(0.08206 \frac{\text{L atm}}{\text{mol K}}\right) (294 \text{ K})} = 0.00405 \text{ mol}$
- $\text{mass} = (n)(M_m) = (0.00405 \text{ mol})(44.0 \text{ g/mol}) = 0.178 \text{ g CO}_2$

Kinetic – Molecular Theory of Gases

Developed by R. Hooke, D. Bernoulli, John Waterston, James Maxwell, and Ludwig Boltzmann

There is a set of postulates that leads to the ideal gas law.

1. The size of gas molecules is negligible compared with the distance between them.
Most of gas volume is empty space.
2. Molecules move in straight lines, in all directions, at various speeds.
Pressure is same in all directions.
3. Attractive and repulsive forces of molecules are weak or negligible, except during collisions.
Molecules move in straight lines at constant speeds until they collide.
4. When molecules collide, the collisions are elastic, which means Kinetic Energy is conserved.
5. Average Molecular Kinetic Energy (E_k) is directly proportional to T, where $E_k = (1/2)mv^2$.
 $E_k \propto T$, so we also have $(1/2)mv^2 \propto T$.

Real Gases

- The ideal gas law can be adjusted using two coefficients (a and b).
- The coefficients are each specific to a particular substance and are listed for several substances in [Table 9.3](#).
- The limitation on postulate 1 is that a small portion of the total volume is not empty because the molecules do take up some space.

Less than the total volume is actually available:

$$V_{\text{real}} = (V_{\text{total}} - nb).$$

- The limitation on postulate 3 is that intermolecular attractions [decrease](#) the effective (measured) pressure.

The real gas pressure is higher than the effective pressure:

$$P_{\text{real}} = P_{\text{effective}} + (a) \left(\frac{n}{V}\right)^2$$

- The Van der Waal's equation is based on those adjustments to the ideal gas law.

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

$$\text{This rearranges first to } P + (a) \left(\frac{n}{V}\right)^2 = \frac{nRT}{(V-nb)}$$

$$\text{Rearrange once more to get the equation for pressure: } \mathbf{P = \frac{nRT}{(V-nb)} - (a) \left(\frac{n}{V}\right)^2}$$

Ex 5.14 Determine Pressure using the Van der Waal's Equation

- Suppose there is 1.000 mole of $\text{H}_2\text{O}_{(g)}$ in 22.50 L at 100.00 °C.
- Coefficients for H_2O from [Table 9.3](#): $a = 5.46 \frac{\text{L}^2 \cdot \text{atm}}{\text{mol}^2}$ $b = 0.0305 \text{ L/mol}$
- $$\frac{nRT}{(V-nb)} = \frac{(1.000 \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (373.15 \text{ K})}{[22.50 \text{ L} - (1.000 \text{ mol}) \left(0.0305 \frac{\text{L}}{\text{mol}} \right)]} = \frac{30.62 \text{ L} \cdot \text{atm}}{22.47 \text{ L}} = 1.363 \text{ atm}$$
- $$(a) \left(\frac{n}{V} \right)^2 = (a) \left(\frac{n^2}{V^2} \right) = \left(\frac{5.46 \text{ L}^2 \cdot \text{atm}}{\text{mol}^2} \right) \left(\frac{1.000 \text{ mol}}{22.50 \text{ L}} \right)^2 = \left(\frac{5.46 \text{ L}^2 \cdot \text{atm}}{\text{mol}^2} \right) \left(\frac{1.000 \text{ mol}^2}{506.25 \text{ L}^2} \right) = 0.0108 \text{ atm}$$
- $$P = \frac{nRT}{V-nb} - (a) \left(\frac{n^2}{V^2} \right) = 1.363 \text{ atm} - 0.0108 \text{ atm} = 1.352 \text{ atm}$$
- Compare with the ideal gas law:
$$P = \frac{nRT}{V} = \frac{1.000 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 373.15 \text{ K}}{22.50 \text{ L}} = 1.361 \text{ atm}$$