Properties of Gases

CHEM 361A: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry
California State University, Fullerton

Lecture 2

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Learning Objective: Understand some of the theories that predict the properties of gases and describe when they fail.

References:

- Atkins and de Silva Focus 1
- Chang §2.1 - §3.5

Kinetic Model of Gases

The kinetic model of gases of based on three assumptions:

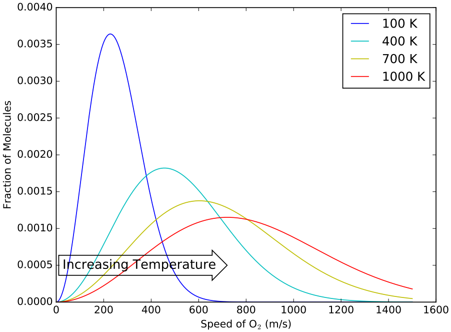
1. A gas consists of molecules in ceaseless random motion.
2. The size of molecules is negligible in the sense that their diameters are much smaller than the average distance travelled between collisions.
3. The molecules do not interact, except during collisions.

In terms of energy:

- Assuming that molecules do not interact unless in direct contact implies that E_p is independent of their separation and can be set to zero.
- The total energy is therefore based on gas' E_k. Thus the faster the molecules move, the greater the total energy of the gas.

Maxwell Distribution of Speeds

Not all the molecules travel at the same speed. James Clerk Maxwell determined $\rho(v)\ dv$, the probability of finding a particle with a speed between v and $v + dv$:



$$\rho(v)\ dv = 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 \exp\left(\frac{-Mv^2}{2RT}\right)\ dv$$

Pressure According to the Kinetic Model of Gases

The kinetic model accounts for the pressure that a gas exerts in terms of the collisions that the molecules make with the walls of the container:

$$p = \frac{nMv_{rms}^2}{3V}$$

where M is the molar mass of the gas and v_{rms} is the gas' root-mean-square speed:

$$v_{rms} = \langle v^2 \rangle^{\frac{1}{2}} = \left(\frac{v_1^2 + v_2^2 + v_3^2 + ... + v_N^2}{N} \right)^{\frac{1}{2}}$$

The relationship between rms speed and the average speed is:

$$\langle v \rangle = \left(\frac{8}{3\pi} \right)^{\frac{1}{2}} v_{rms} \approx 0.921 v_{rms}$$

This relationship between the two should only be used for large sample sizes.

v_{rms} from the Maxwell Distribution of Speeds

The v_{rms} can alternatively be determined from the Maxwell Distribution of Speeds

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\int_0^\infty v^2 \, \rho(v) \, dv}$$

$$= \sqrt{\int_0^\infty v^2 \, 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 \exp\left(\frac{-Mv^2}{2RT}\right) \, dv}$$

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

$$\checkmark \quad \frac{\cancel{\mathrm{kg}}\,\frac{\mathrm{m}^2}{\mathrm{s}^2}}{\mathrm{K\ mol}}$$

$$\frac{\cancel{\mathrm{kg}}}{\mathrm{mol}}$$

The relationship that $v_{rms} \propto T^{\frac{1}{2}}$ has implications for (example) the speed of sound in air.

The Ideal Gas Law

Putting together our expressions of pressure and v_{rms}:

$$p = \frac{nMv_{rms}^2}{3V} \quad \text{and} \quad v_{rms}^2 = \frac{3RT}{M}$$

gives the **Ideal Gas Law**:

$$pV = nRT$$

where

- p is the pressure (kPa) of the gas
- V is the volume (dm^3 or L) of the gas
- n is the amount (mol) of the gas
- T is the temperature of the gas (typically in K)
- R is the gas constant ($8.31447\ \text{dm}^3\ \text{kPa}\ \text{K}^{-1}\ \text{mol}^{-1}$)

The gas constant, R, is an empirically determined value that is the same for all gases.

Mixtures of Gases: Partial Pressures

Dalton's Law: The pressure exerted by a mixture of perfect gases is the sum of the pressures that each gas would exert if it were alone in the container at the same temperature:

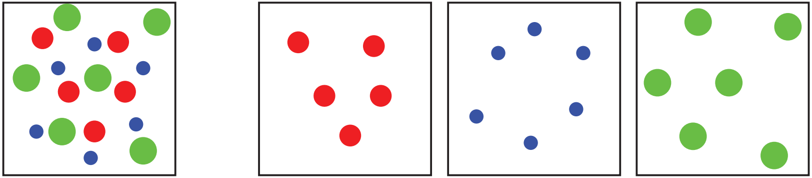
$$p = p_A + p_B + \dots$$

The partial pressure of a given gas is defined as

$$p_A = x_A p$$

where x_A is the mole fraction of gas A.

Dalton's Law Visualised



$$P_{\text{total}} = P_{\text{red}} + P_{\text{blue}} + P_{\text{green}}$$

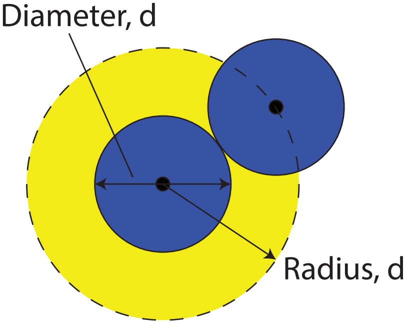
Dalton's Law Practice Problem

1. Calculate the mole fractions of N_2, O_2 and Ar in dry air at sea level, given that 100.0 g of air consists of 75.5 g of N_2, 23.2 g of O_2, and 1.3 g of Ar.

   Hint: N_2 28.02 g/mol; O_2 32.00 g/mol; Ar 39.95 g/mol
2. Given the answer from above, when the atmospheric pressure is 100 kPa, what is the partial pressure of N_2, O_2, and Ar.

Collision Cross-Section

Collision Cross-Section, σ (m^2): The target area presented by one molecule to another.



If the center one molecule comes within the yellow shaded area ($\sigma = \pi d^2$), then the molecules have collided.

Molecular Collisions

Building the kinetic model with collisional cross-section in mind, it is possible to show:

Mean Free Path, λ (m): The average distance that a molecule travels between collisions.

$$\boxed{\lambda} = \frac{\cancel{RT}}{\cancel{\sqrt{2}}\cancel{N_A}\cancel{\sigma}\cancel{p}}$$

Collision Frequency, z (s^{-1}): The average rate of collisions made by one molecule.

$$\boxed{z} = \frac{\cancel{\sqrt{2}N_A\sigma}\,\langle v\rangle\,\cancel{p}}{\cancel{RT}}$$

These two quantities can be related to the average velocity by:

$$\underline{\langle v\rangle} = \lambda z$$

Perfect versus Real Gases

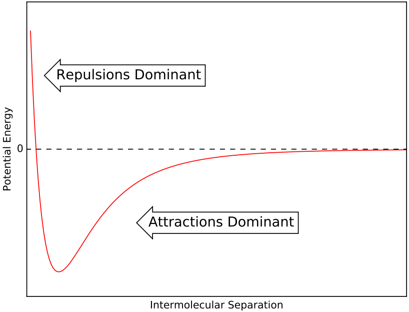
We can treat gases as perfect when:

$$\lambda \gg d$$

When this relationship is not satisfied, then molecule-molecule interactions should be taken into account.

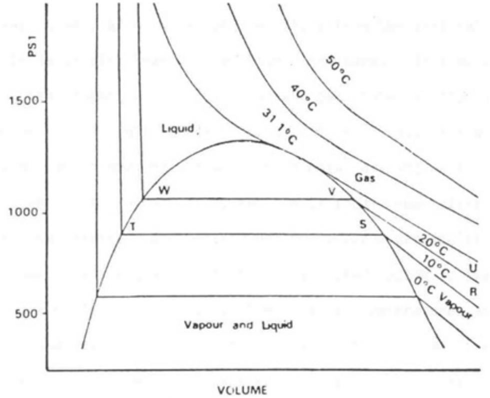
For example, according to the van der Waals potential:

- At relatively long separations, molecules attract one another.
- At very short distances, molecules repel each other.



CO_2 Isotherms

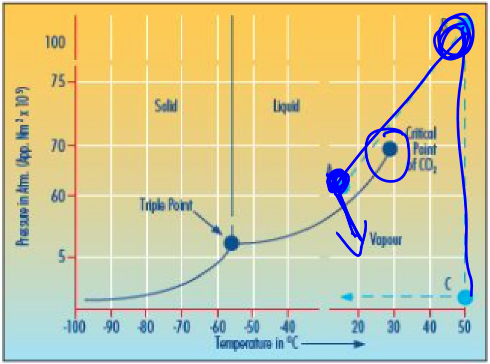
For all gases, below a certain temperature, the Ideal Gas Law no longer holds (this plot is for CO_2):



The horizontal lines in the isotherms represent the phase change between gas and liquid.

CO_2 Phase Diagram

At temperatures above the critical temperature, a gas can not be compressed to a liquid.



By going around the critical point, a supercritical fluid can be used to dry fragile structures or act as a non-toxic solvent to extract organic compounds.

van der Waals Equation of State

Dutch Physicist Johannes van der Waals proposed changes to the Ideal Gas law to account for real gas interactions:

Molecules are not free to travel through the entire volume of the container (due to repulsive interactions).

$$Pressure\ with\ Repulsion = \frac{nRT}{V - nb}$$

Attractive interactions reduces the pressure that the gas exerts. It is proportional to the concentration of the gas:

$$Pressure\ with\ Attraction = a\left(\frac{n}{V}\right)^2$$

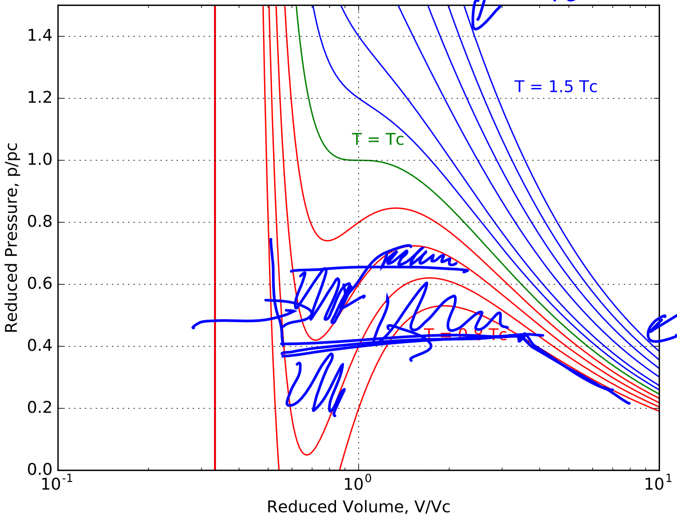
The equation of state with both repulsive and attractive forces is:

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

Plot of van der Waals Equation of State for CO_2

High p

low V



low p

High V

Finding the Critical Values

Writing $V_m = V/n$, the van der Waals equation of state can be re-written as:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

For $T = T_c$, the curve has a flat inflection at V_c. This means that the derivative and the second derivative can be used to find all the critical values. Setting $T = T_c$, $V = V_c$ as well as the derivative and the second derivative to zero gives:

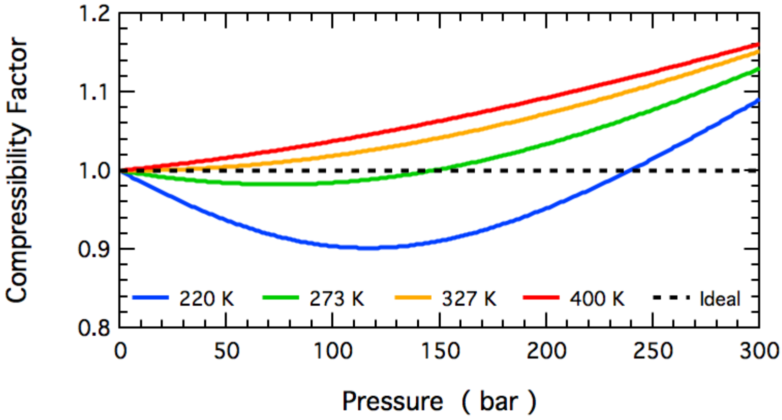
$$\begin{aligned} -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} &= 0 \\ \frac{2RT_c}{V_c - b)^3} - \frac{6a}{V_c^4} &= 0 \end{aligned}$$

Rearranging and solving for V_c, T_c, and p_c gives:

$$V_c = 3b \quad T_c = \frac{8a}{27Rb} \quad p_c = \frac{a}{27b^2}$$

Compressibility

Compressibility, (Z), is the property of a gas that defines the change in pressure as the volume changes. For N_2:



Virial Equation of State

The Ideal Gas Law can be rewritten to include compressibility:

$$Z = \frac{pV_m}{RT}$$

where the compressibility curves in the previous plot can be fit to a series expansion according to

$$Z = 1 + \frac{B}{V_m} + \cancel{\frac{C}{V_m^2}} + \cancel{\frac{D}{V_m^3}} + \cdots = 1 + B'P + C'P^2 + D'P^3 + \ldots$$

where the terms B, C, D,... (or B', C', D', ...) are temperature dependent. This fit is accurate for real gases, however, these coefficients have no physical meaning.

Gas Law Example

Calculate the molar volume of methane at 300 K and 100 atm, given that the second Virial coefficient (B') of methane is -0.0017 atm^{-1}. Assume that all other coefficients are zero. Compare your result with that obtained using the ideal gas equation and the van der Waals Equation of State if $p_c = 45.4$ atm, $V_{m,c} = 0.0990$ L mol^{-1} and $T_c = 190.2$ K.

Summary

- Kinetic Model of Gases provides a starting framework to quantitatively describe gases.
- The Ideal Gas Law is derived from the Kinetic Model of Gases and is valid at low pressures and high temperatures.
- Intermolecular interactions are important at higher pressures. The van der Waals Equation of State takes into account repulsive and attractive forces. It is valid for a larger domain of temperatures and pressures compared to the Ideal Gas Law but still performs poorly at high pressures and low temperatures.
- The Virial Equation of State is accurate for real gases. However, it is a fit of experimental data where the coefficients of the series expansion hold no direct physical meaning.