

Chemical Principles

6. Gases

Outline

- Ideal Gases
- Kinetic Molecular Theory
- Gas Properties
- Non-ideal Gases

Pressure: what causes it

Molecules colliding exert a pressure on the sides of the container walls.

$$\text{Pressure} = \frac{\text{force}}{\text{area}} \quad \text{or} \quad P = \frac{F}{a}$$

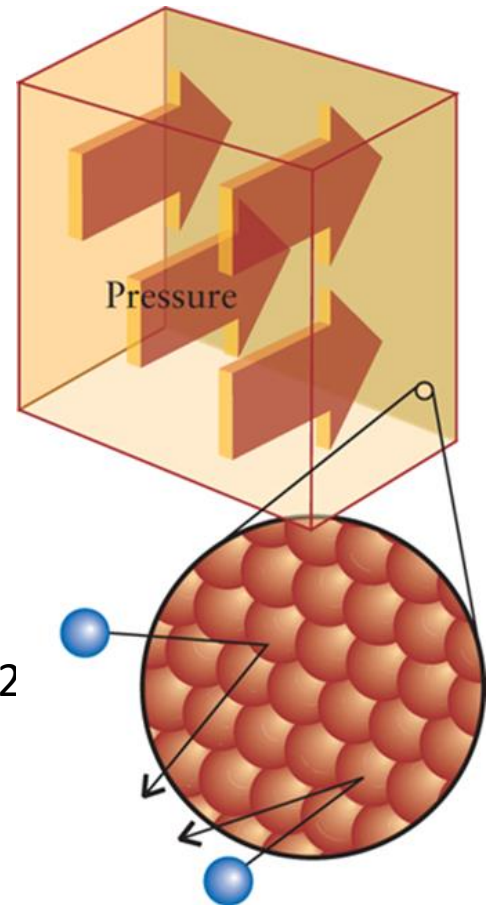
The SI unit of pressure is the pascal, Pa

$$1 \text{ Pa} = 1 \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$$

Other units:

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$760 \text{ Torr} = 760 \text{ mmHg} = 1 \text{ atm} = 14.7 \text{ lbs} \cdot \text{in}^2 \text{ (psi)} = 1.01325 \times 10^5 \text{ Pa}$$

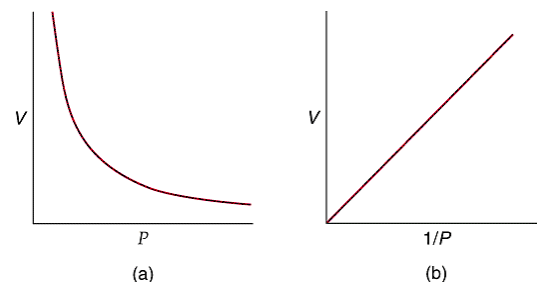


The Gas Laws

Gas Laws - about **pressure**, **volume**, **temperature**, and **moles**.

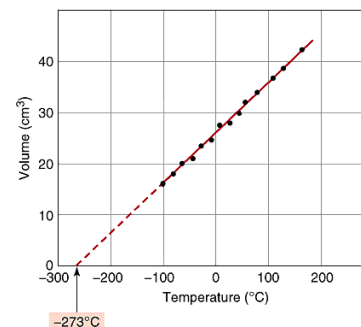
Boyle's Law

$$PV = \text{constant}$$



Charles's Law

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



Avogadro's Law

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

1 Mole of any gas occupies 22.4 L at 0°C and 1 atm

The Ideal Gas Equation

- Ideal gas equation:

$$PV = nRT.$$

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

Standard ambient temperature and pressure (SATP)

SATP means exactly 25°C (298.15 K) and exactly 1 bar, the molar volume of an ideal gas is **24.79 L·mol⁻¹**, which is about the volume of a cube, 1 ft on a side.

Standard temperature and pressure (STP)

STP means 0°C (273.15 K) and 1 atm (both exactly). At STP, the molar volume of an ideal gas is **22.41 L·mol⁻¹**.

Combined Gas Law

We note that, if the initial conditions of a gas are:

$$P_1V_1 = n_1RT_1$$

Then a change in conditions is: $P_2V_2 = n_2RT_2$

Because R is a constant, we can equate the two equations:

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

This expression is called the **combined gas law**. However, it is a direct consequence of the ideal gas law and is not a new law.

Mixtures of Gases - Dalton's Law

- A mixture of gases behaves like a single gas;
- Each component produces a partial pressure;
- The total pressure is the sum of the individual pressures of each component.

$$P = P_A + P_B + \dots$$

- The partial pressure is proportional to its molar fraction

$$P_A = \frac{n_A}{(n_A + n_B + \dots)} P = \chi_A P$$

$$\chi_A + \chi_B + \dots + \chi_N = 1$$

Dalton's Law of partial pressures: $P \propto n$

The total number of molecules is sum of each components,

$$P_T = n_T \frac{RT}{V} = (n_A + n_B + \dots) \frac{RT}{V} = P_A + P_B + \dots$$

Since $P_A = n_A \frac{RT}{V}$ and $P_T = n_T \frac{RT}{V}$,

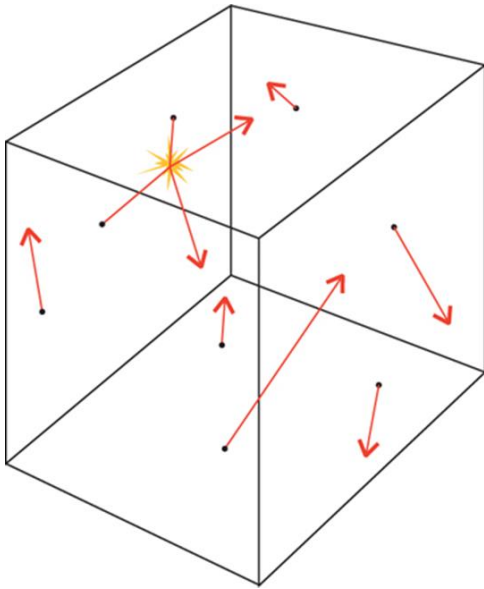
$$P_A = \frac{n_A}{(n_A + n_B + \dots)} P_T = \chi_A P_T$$

Molar fraction: $\chi_A = \frac{n_A}{n_A + n_B + \dots}$

Note that: $\chi_A + \chi_B + \dots + \chi_N = 1$

Kinetic Molecular Theory

- Theory developed to explain gas behavior.
- Theory of large number of moving molecules.



Kinetic molecular theory gives us an understanding of **pressure** and **temperature** on the molecular level - the speed of molecules.

Kinetic-Molecular Theory

- Gases consist of a large number of molecules in constant random motions.
- Volume of individual molecules is negligible compared to volume of the container.
- Potential energy (or force between gas molecules) is negligible.
- Kinetic energy of N particle with mass m and *average speed*:

$$E_K = \frac{1}{2} Nm \overline{v_{rms}^2}$$
$$\overline{v_{rms}^2} = \overline{v_x^2 + v_y^2 + v_z^2}$$

Kinetic Molecular Theory

Assume one mole (N) molecules confined in a cubic box with L as its edge lengths,

The pressure on one surface $P = \frac{F}{L^2}$

F is total pressure of N molecules

$$F = N \cdot f$$

Each molecule exerts a force

$$f = \frac{\Delta p}{\Delta t} = \frac{mv_x^2}{L}$$

$$\because \Delta p_x = p_{ix} - p_{fx} = 2mv_x, \Delta t = \frac{2L}{v_x}$$

Therefore

$$F = \frac{Nm\overline{v_x^2}}{L}$$

Kinetic Molecular Theory

Since

$$\overline{v_x^2} = \overline{v_{rms}^2} / 3$$

$$P = \frac{F}{L^2} = \frac{Nm\overline{v_{rms}^2}}{3V} = \frac{2E_K}{3V}$$

Compare with $PV = RT$

We have

$$T = \frac{2}{3} \frac{E_K}{R}$$

Temperature measures the kinetic energy is, rearrange

$$E_k = \frac{3}{2} RT$$

Kinetic energy is 3 times $RT/2$ – it is called energy equipartition as this is a three-dimension system, each dimension contribute $RT/2$ energy. More on this topic later.

Kinetic-Molecular Theory

$$P = \frac{Nm\overline{v_{rms}^2}}{3V} = \frac{2E_K}{3V}$$

- As the temperature increases, the average kinetic energy of the gas molecules increases, molecules move faster, hit the walls more often, so the pressure increases.
- As volume increases at constant temperature, the average kinetic of the gas remains constant. However, gas molecules have to travel further to hit the walls of the container. Therefore, pressure decreases.

Speed of motion

the mean square speed for a gas:

$$E_k = \frac{1}{2} M v_{rms}^2 = \frac{3}{2} RT$$

$$v_{rms}^2 = \frac{3RT}{M}$$

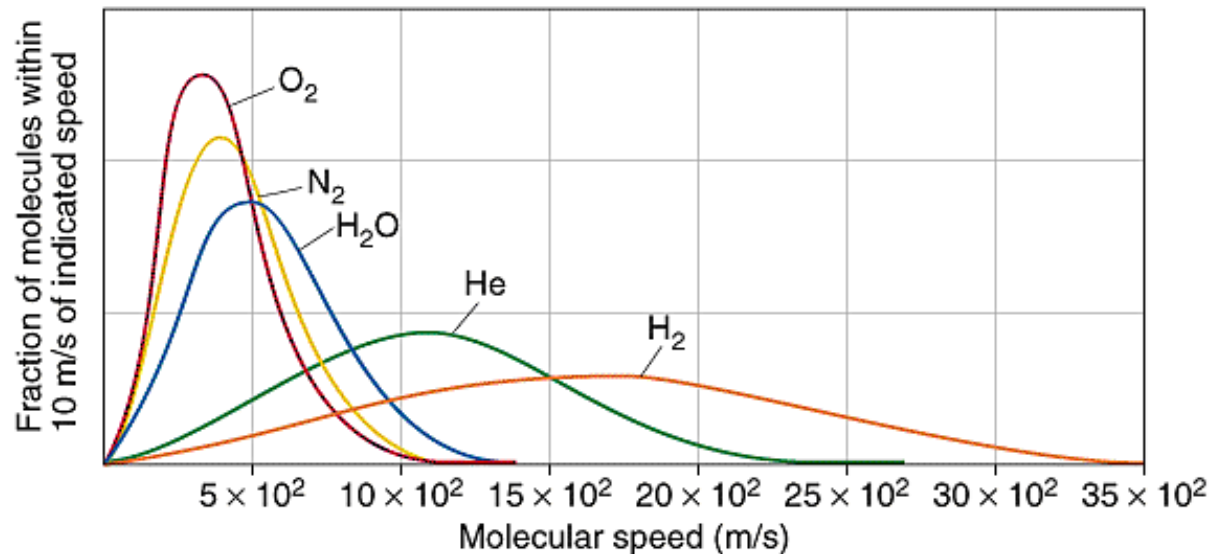
Calculate mean square speed of N₂ (511 m/s)

- For the same gas molecule, the temperature increases, the gas molecules move faster.
- At the same temperature: the lighter gas has a higher v_{rms} than the heavier gas

The Maxwell Distribution of Speeds

Not all molecules move at the same speed, there is a distribution of the speed, given by

$$\Delta N = N f(v) \Delta v \quad \text{with } f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

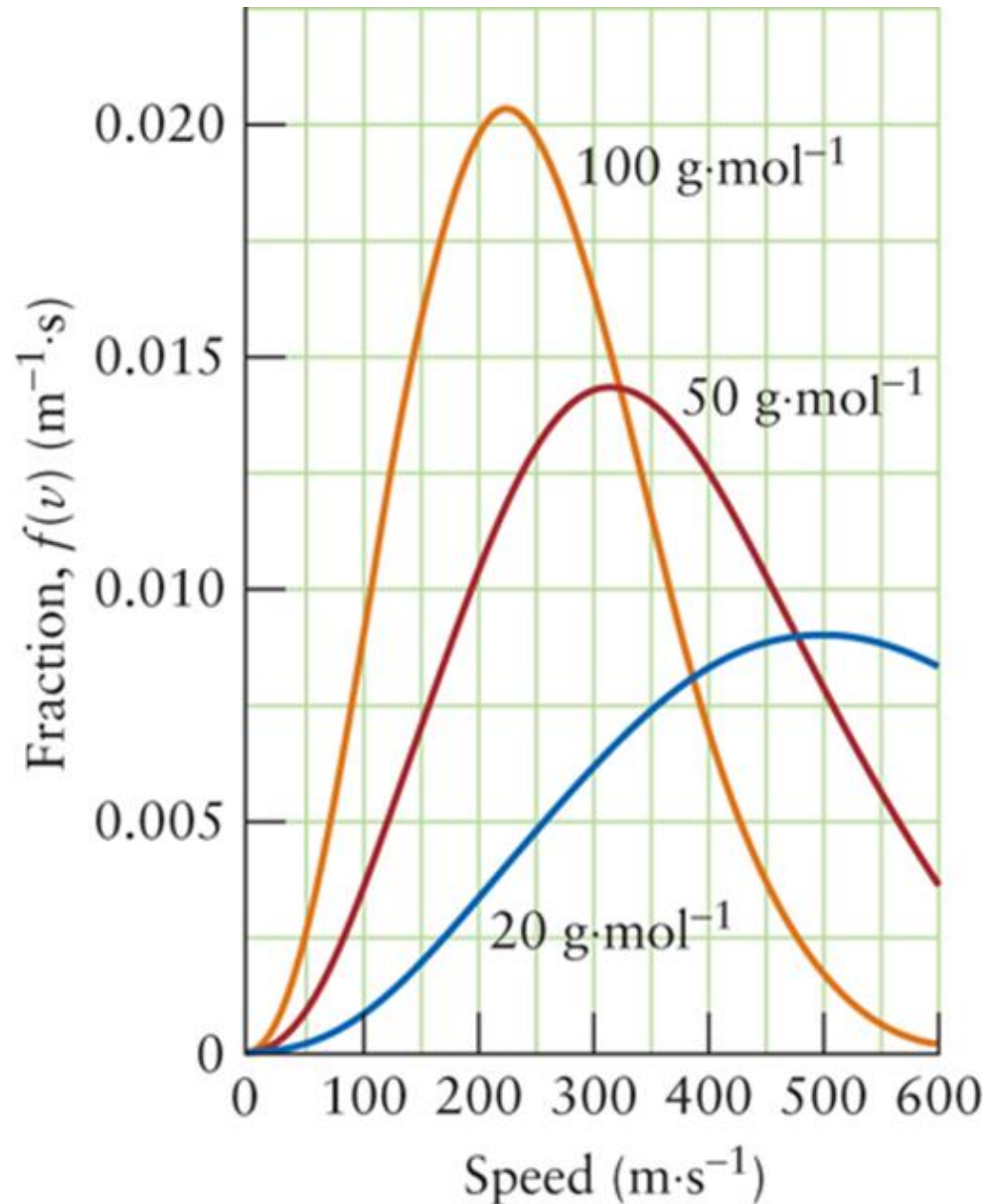


The Maxwell Distribution of Speeds

$$\Delta N = Nf(v)dv \quad \text{with} \quad f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 e^{-Mv^2/2RT}$$

- The exponential factor (which falls rapidly toward zero as v increases) means that very few molecules have very high speeds.
- The factor v^2 that multiplies the exponential factor goes to zero as v goes to zero, so it means that very few molecules have very low speeds.
- The factor $4\pi(M/2\pi RT)^{3/2}$ ensures that the total probability of a molecule having a speed between zero and infinity is 1.

Velocity of different masses, but at the same temperatures



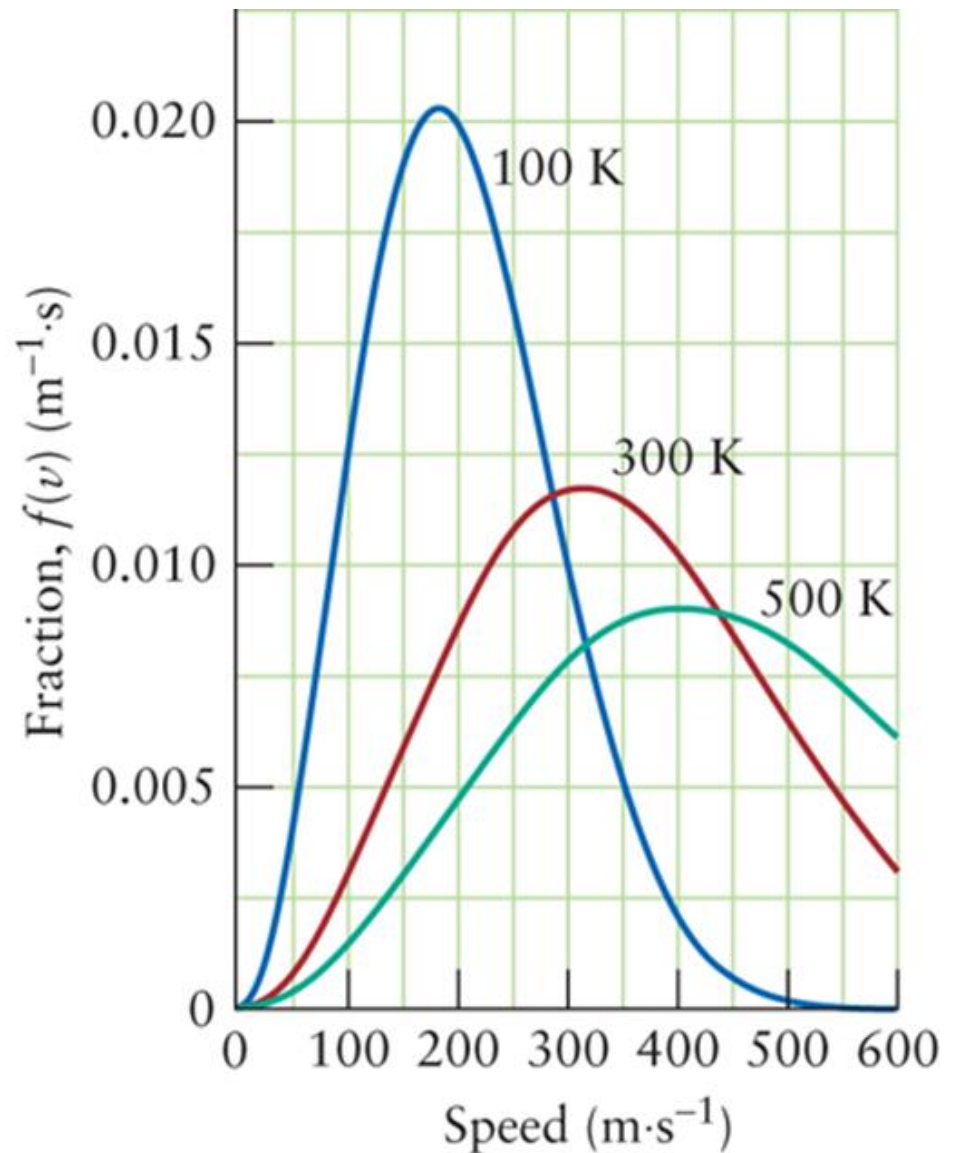
Maxwell distribution gives the range of molecular speeds for three gases.

All are for the same temperature 300K.

The greater the molar mass, the lower the speed.

The Maxwell distribution the curves correspond to the speeds of a single substance (of molar mass $50 \text{ g}\cdot\text{mol}^{-1}$) at different temperatures.

The higher the temperature, the higher the average speed and the broader the spread of speeds.



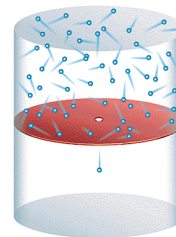
Same mass, different T

Molecular Effusion and Diffusion

Graham's Law of Effusion

- Effusion is the escape of a gas through a tiny hole (a balloon will deflate over time due to effusion).
- Two gases with molar masses m_1 and m_2 , the relative **rate** of effusion is given by

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$



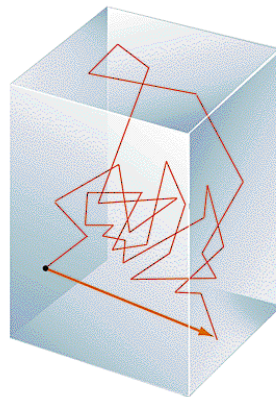
- Only those molecules that hit the small hole escapes through it. Therefore, the higher the average speed, the more likelihood of a gas molecule hitting the hole. At given temperature, kinetic energy is equality distributed, therefore:

$$\frac{1}{2}m_1\bar{v}_1^2 = \frac{1}{2}m_2\bar{v}_2^2$$

Molecular Effusion and Diffusion

Diffusion and Mean Free Path

- Diffusion of a gas is the spread of the gas through space.
- Diffusion is significantly slower than rms speed.
- Diffusion is slowed by gas molecules colliding with each other.
- Average distance of a gas molecule between collisions is called mean free path.
- The mean free path of gas is about 5×10^{-8} m.



Deviations from ideality

- In industry and in many research laboratories, gases must be used under high pressures, when the ideal gas law is not followed closely.
- The ideal gas law is a limiting law, valid only as $P \rightarrow 0$.
- All actual gases, which are called **real gases**, have properties that differ from those predicted by the **ideal gas** law.
- These differences are significant at high pressures and low temperatures.

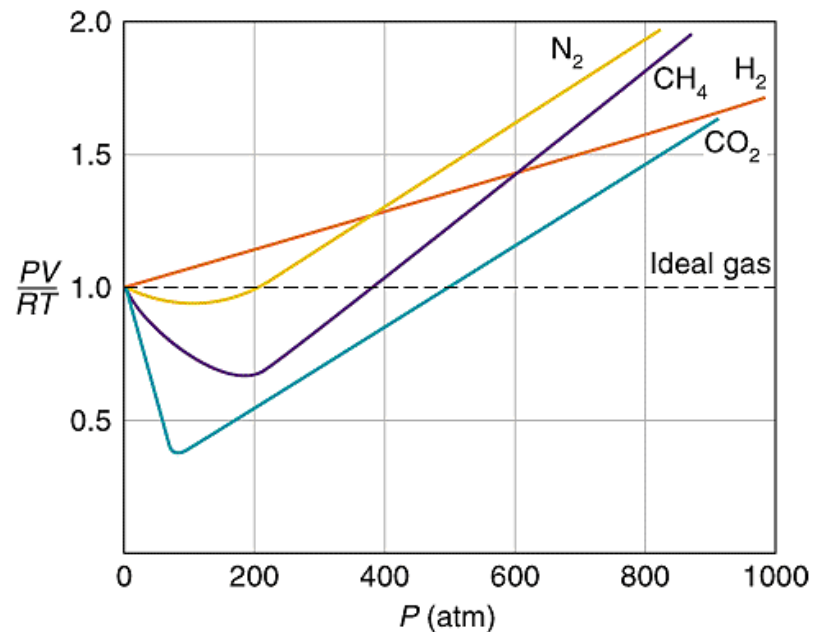
Compression Factor

- From the ideal gas equation, we have compression factor

$$Z = \frac{PV}{nRT}$$

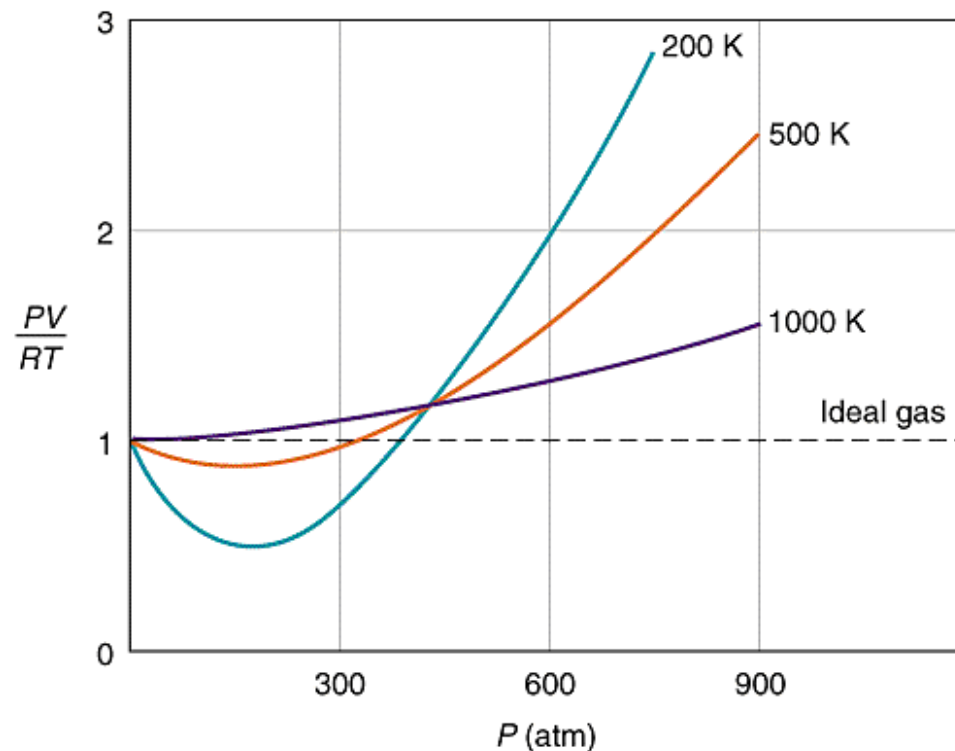
- For ideal gas, $Z = 1$ for all pressures.
- In a real gas, Z varies from 1 significantly.

The higher the pressure the more the deviation from ideal behavior.



Real Gases: Deviations from Ideal Behavior

As temperature increases, the gas molecules move faster, higher kinetic energy available to break intermolecular forces. Therefore, the higher the temperature, the more ideal is the gas.



Equations of State of Real Gases

A common procedure to describe the behavior of real gases is to write the following expression

$$PV = nRT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right)$$

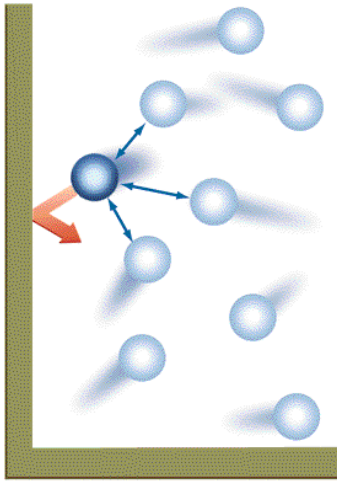
This expression is called the virial equation. The coefficients B , C , ... are called the second virial coefficient, third virial coefficient, and so on.

However, the virial coefficients are not always known for each gas at that temperature.

Real Gases

The assumptions in kinetic molecular theory breaks down:

- molecules have finite volume,
- molecules do interact



The van der Waals Equation

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

Here a and b are empirical positive parameters determined for each gas molecule. Parameter a represent **attraction**, b represent **repulsion** (volume)

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

The free volume is smaller than apparent, and total pressure is reduced.

Real Gases: Deviations from Ideal Behavior

Consider the compression factor

$$Z = \frac{V/n}{RT/P} = \frac{PV}{nRT}$$

$$Z = \frac{V}{nRT} \times \left(\frac{nRT}{V - nb} - a \frac{n^2}{V^2} \right) = \frac{V}{V - nb} - \frac{an}{RTV}$$

If $a=0$, $b=0$, $Z=1$

If repulsion b is stronger, $Z > 1$

If attraction a is stronger, $Z < 1$

