

화학 General Chemistry

034.020-005

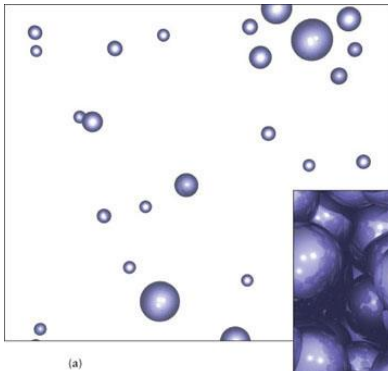
2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

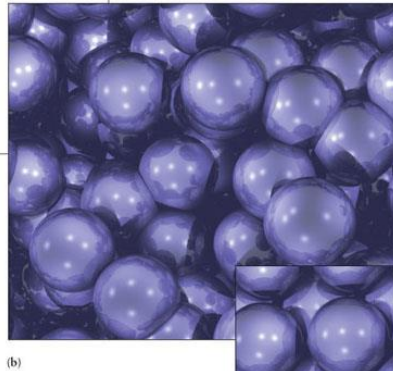
송윤주 woonjusong@snu.ac.kr

Why study the gas phase?

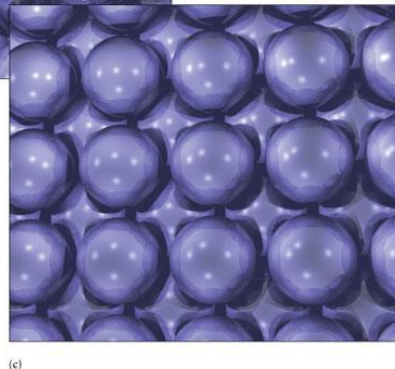
- Movement of molecules in gas phase is very easy to understand.



gas: Inter-atomic distance \gg molecular size



liquid: Inter-atomic distance
= molecular size



solid: Inter-atomic
distance = molecular size

Chapter 4: Gas Phase

- ❑ The Nature of Gases
- ❑ The Gas Laws
- ❑ Molecular Motion
- ❑ Real Gases vs Ideal Gases

The Nature of Gases

4.1. Observing Gases

- Regardless of the identity of the gas, many of physical properties are very similar.
- Bulk matter consists of large numbers of molecules

TABLE 9.1

Composition of Dry Air at Sea Level

Constituent	% Volume	% Mass
N ₂	78.08	75.52
O ₂	20.95	23.14
Ar	0.93	1.29
CO ₂	0.037	0.05
Ne	1.82×10^{-3}	1.27×10^{-3}
He	5.24×10^{-4}	7.24×10^{-5}
CH ₄	1.7×10^{-4}	9.4×10^{-5}
Kr	1.14×10^{-4}	3.3×10^{-4}

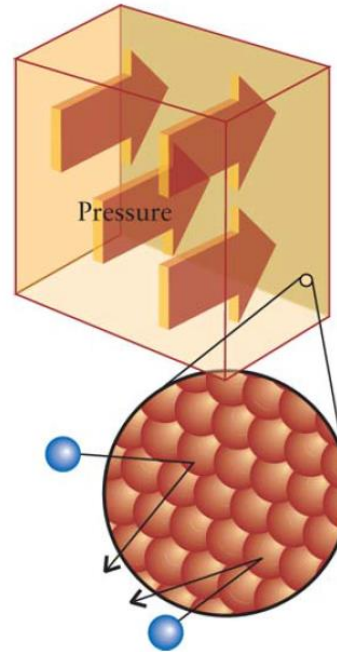
4.2.-4.3 Pressure/Units

- Definition of pressure:

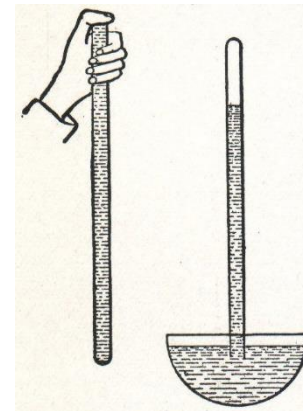
- SI unit: **Pa** (pascal)
 $1\text{Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$

$$F \text{ (N)} = ma: \text{kg} \times (\text{m/s}^2)$$
$$\text{Area: m}^2$$

$$P = \text{kg} \times (\text{m/s}^2)/\text{m}^2 = \text{kg m}^{-1} \text{ s}^{-2}$$



Blaise Pascal
(1623 – 1662)

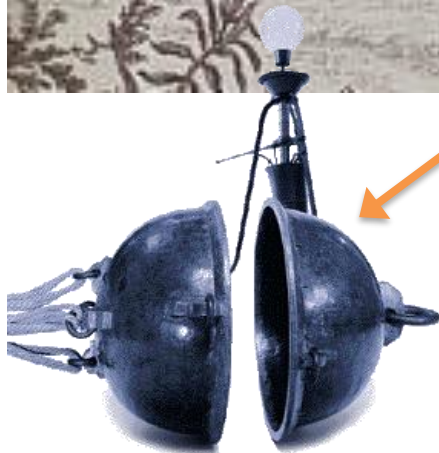


E. Torricelli
(1608 – 1647)

E. Torricelli (student of Galileo):

- Gas can exert pressure.
- At the surface of the Earth, **EVERYTHING** is pressurized by “air molecules”.
- The first experimental proof for the existence of the **vacuum**

Guericke (1602 – 1686)'s experiment in 1657, Germany



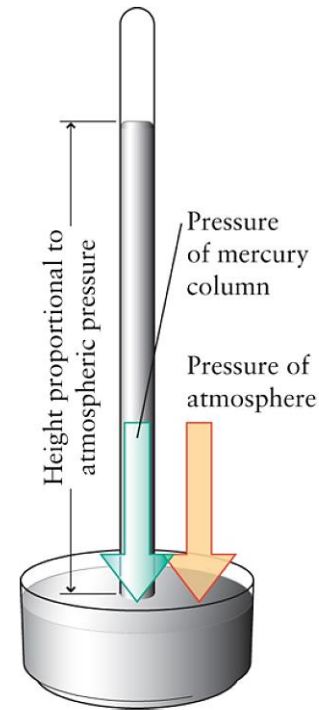
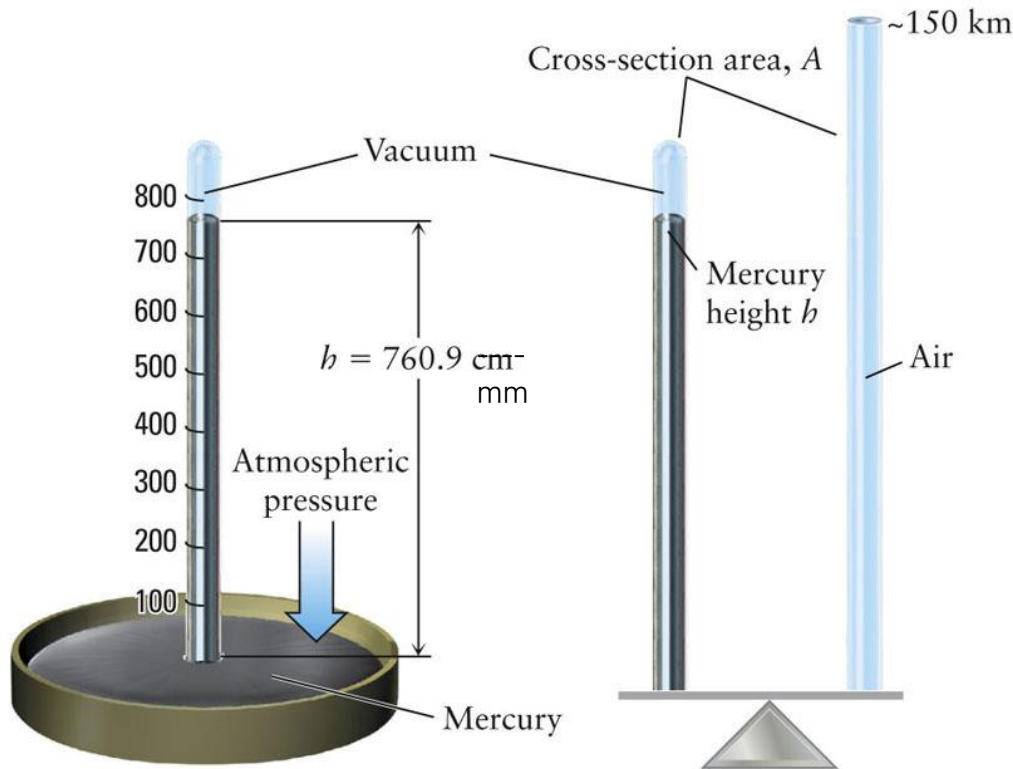
16 horses were unable to separate two evacuated copper hemispheres!!!

The original Magdeburg hemispheres and Guericke's vacuum pump in the Deutsches Museum, Munich, Germany

Pressure from atmosphere and gases

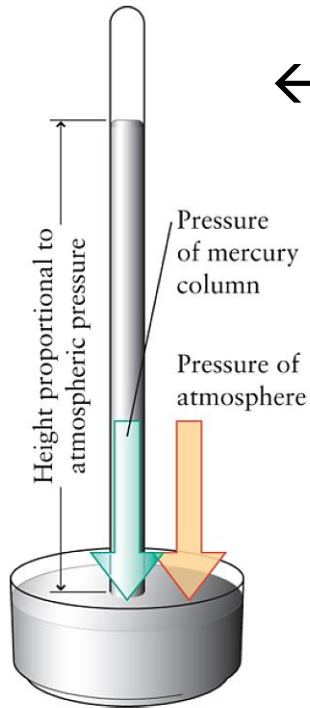
Atmospheric pressure results from the weight of air

$$: P = F/\text{area} = (m \times a) / \text{area}$$



The height of Hg column
= 760 mm at sea level

Measurements of Pressure



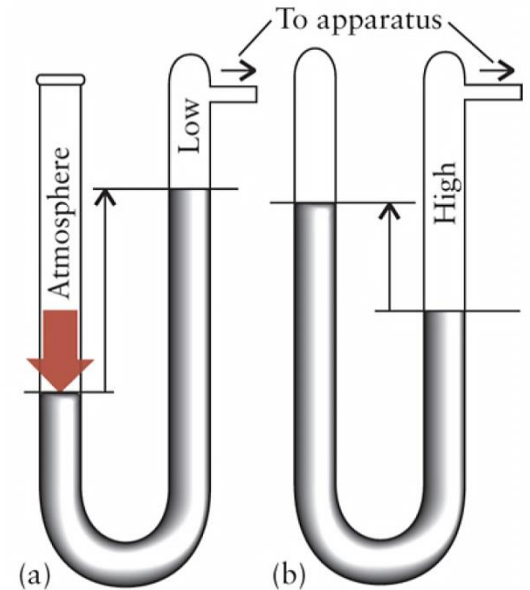
m: mass of mercury
 ρ : density = mass/volume

- SI unit: Pa (pascal)
 $1\text{Pa} = 1\text{ kg m}^{-1}\text{ s}^{-2}$
 $1\text{bar} = 10^5\text{ Pa}$, $1\text{mbar} = 10^2\text{ Pa}$

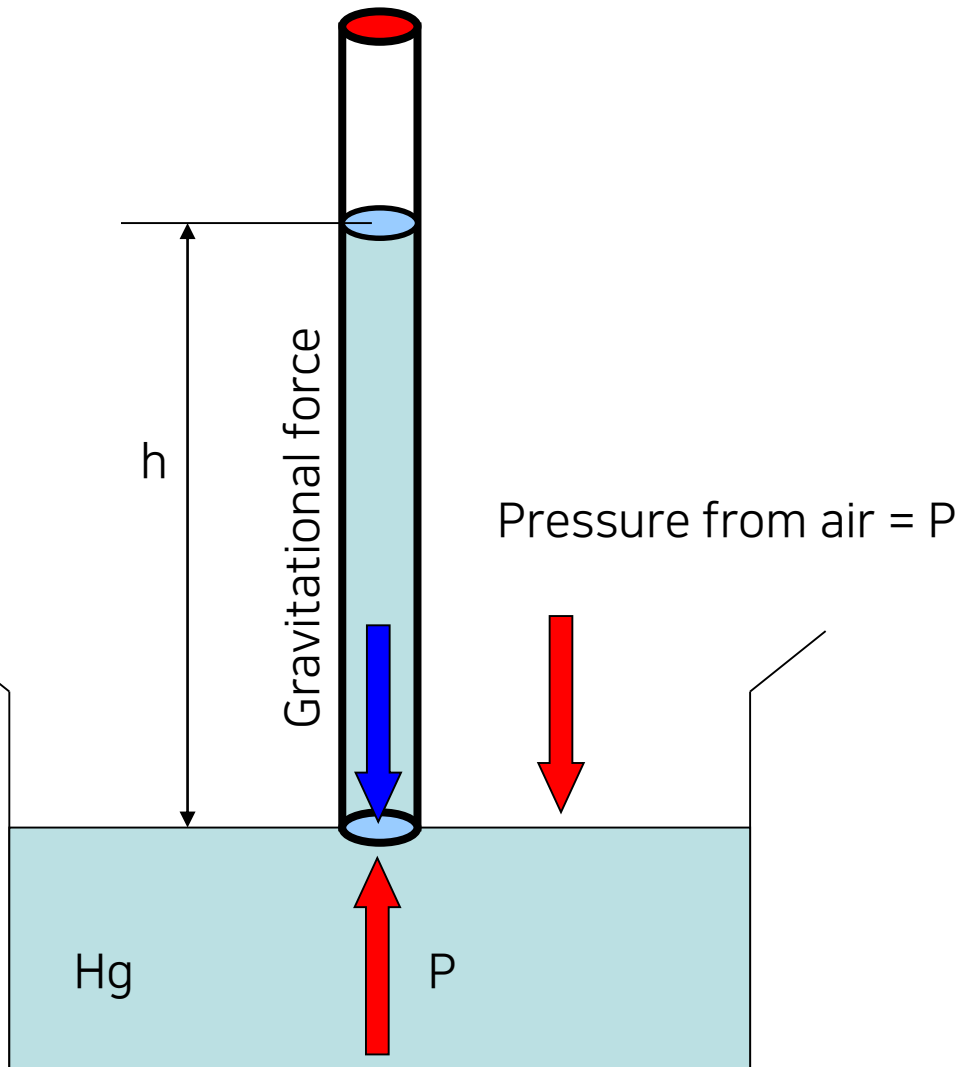
Atmosphere (atm) = $1.01325 \times 10^5\text{ Pa} = 1.01\text{ bar}$

- $1\text{ atm} = 760\text{ Torr} = 760\text{ mmHg}$: height of the mercury column

Manometer →



Area of column = A



Experimentally, $h = 760 \text{ mm}$
at sea level.

Downward gravitational force
by mercury column

$$= Mg = \rho Ahg$$

$$P_{\text{atm}} = (\rho g)h$$



Upward Force by atmospheric
pressure

$$= AP_{\text{atm}}$$

For mercury,
 $\rho = 13.5 \text{ g/cm}^3$
 $g = 9.8 \text{ m/s}^2$

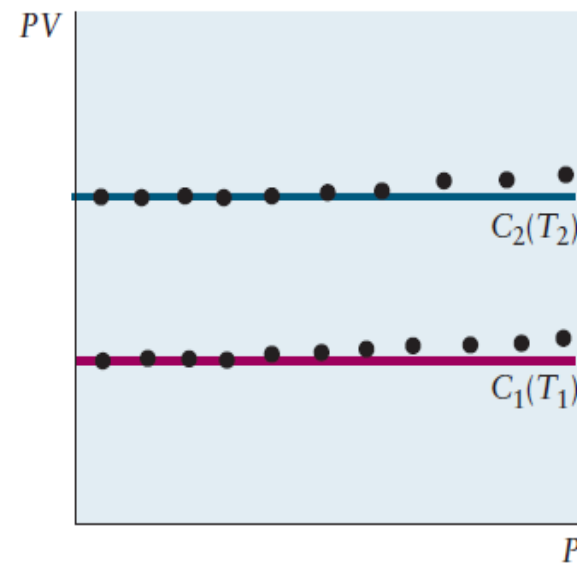
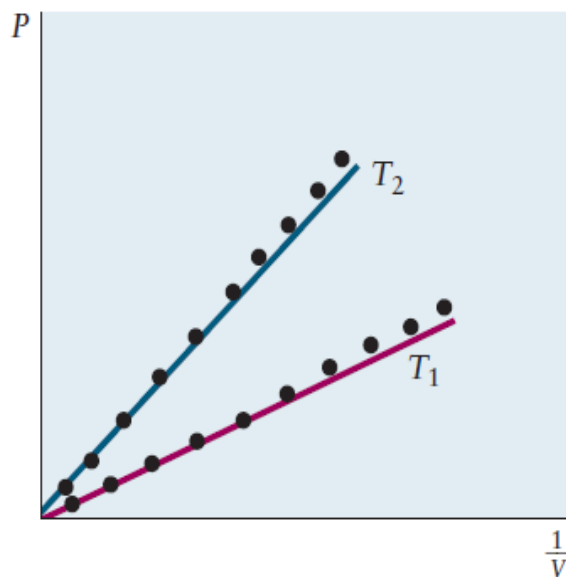
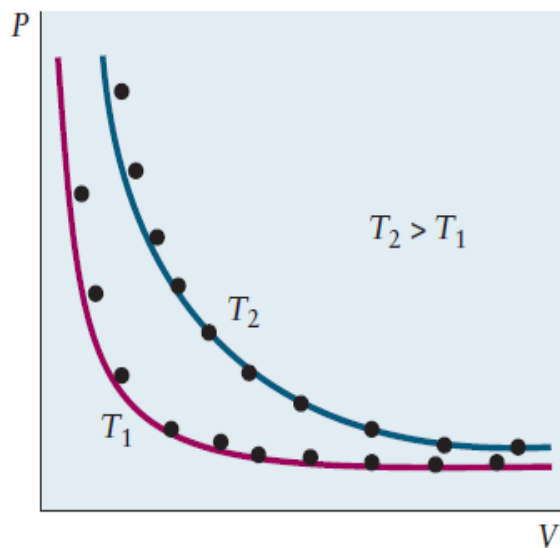
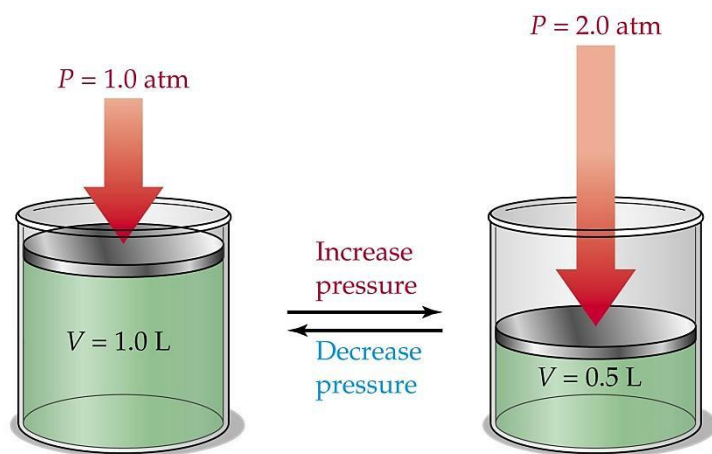
At sea level, we find $h = 760 \text{ mm}$.

$$\begin{aligned} P_{\text{atm}} &= 1.01325 \times 10^5 \text{ N/m}^2 \\ &= 1.01325 \times 10^5 \text{ Pa} \\ &= 1.01325 \text{ bar} \\ &= 1 \text{ atm} \\ &= 760 \text{ torr} \end{aligned}$$

The Gas Laws

4.4. The Experimental Observations

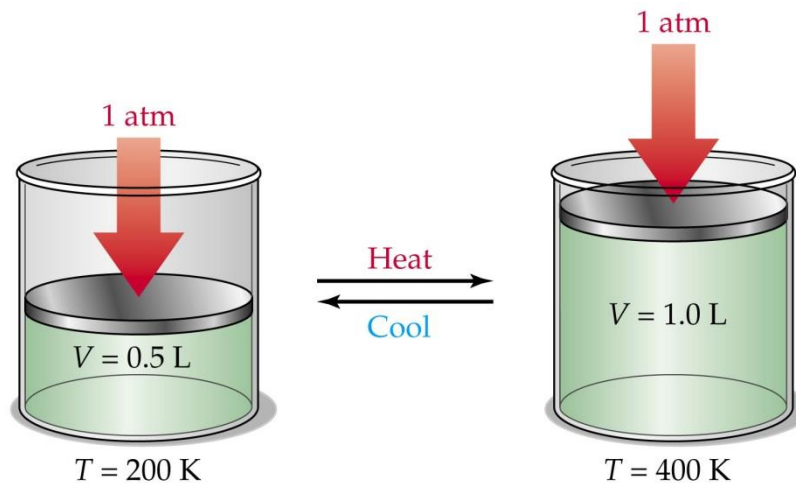
Boyle's Law: for a fixed amount of gas at a constant T,



Charles's Law: for a fixed amount of gas under a constant P,

At constant pressure,

The volume of a gas is linearly proportional to temperature. The volume of *any gas* is zero at $-273.15\text{ }^{\circ}\text{C}$

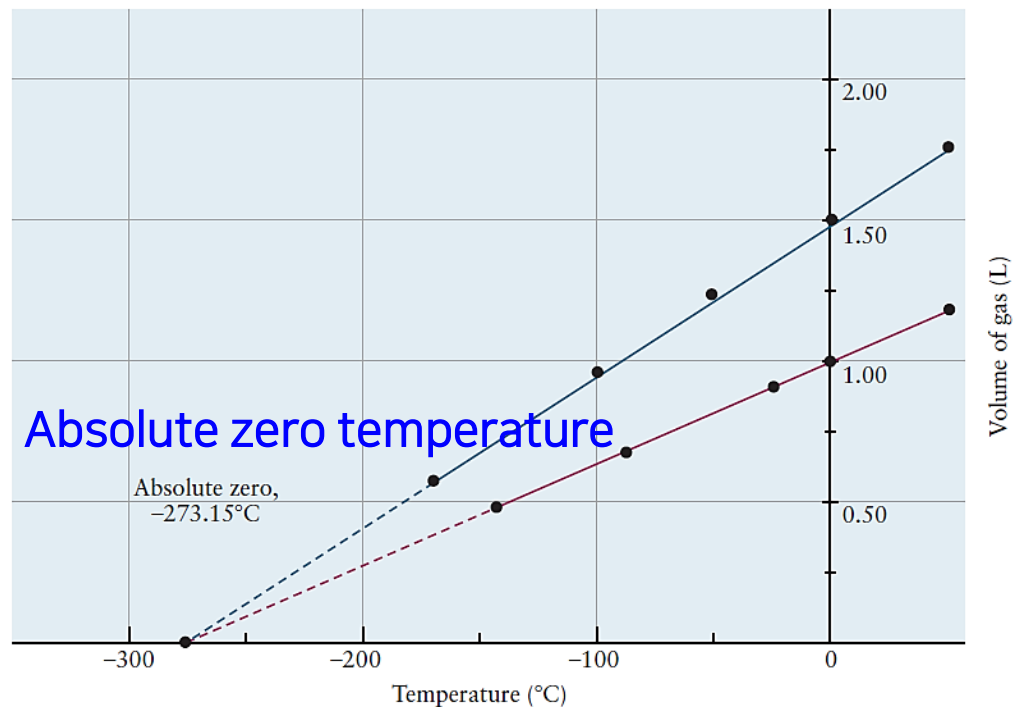


Absolute temperature (K)

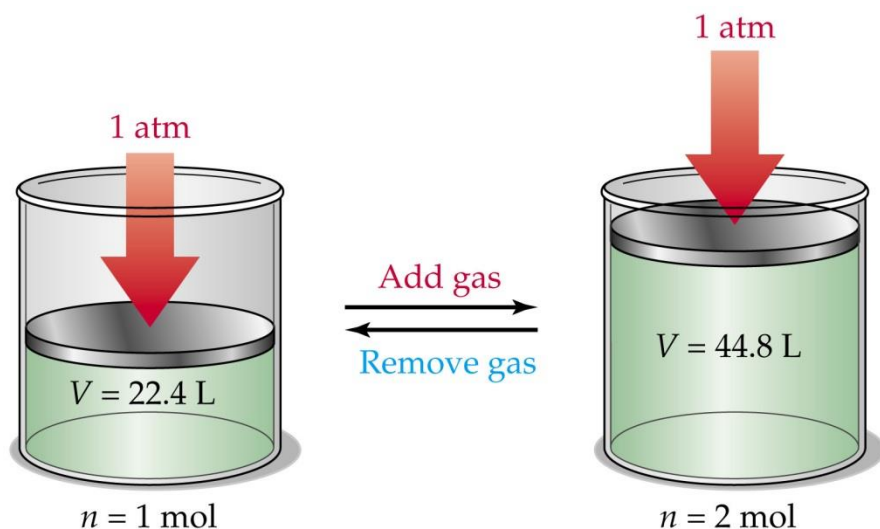
$$T\text{ (K)} = t\text{ (}^{\circ}\text{C)} + 273.15$$

Volume of gas cannot be negative!

Therefore, temperature **cannot be lower than $-273.15\text{ }^{\circ}\text{C}$**



Avogadro's Law: at constant T and P, a given number of gas molecules occupy the same V regardless of their chemical identity.



Ideal Gas Law

$$R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1} = 0.082 \text{ atm liter K}^{-1} \text{ mole}^{-1}$$

(J= kg m²/s²)

Combines all of the:

Boyle's law

Charles's law

Avogadro's principle

Table 4.2. The Gas Constant, R

$8.205\,74 \times 10^{-2} \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.314\,47 \times 10^{-2} \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.314\,47 \text{ L}\cdot\text{kPa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.314\,47 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$62.364 \text{ L}\cdot\text{Torr}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

What is the “mole”?

→ One mole (mol) is the amount of a substance that contains as many elementary entities as Avogadro's number (N_A).

$$N_A \equiv 6.022 \times 10^{23}$$

Molar atomic mass

→ Mass (g) of 1 mole of atoms

→ For example,

$$\text{mass of } {}^{12}_6\text{C } 1 \text{ mol} = 12.00 \text{ g}$$

$$\text{mass of } {}^{12}_6\text{C} = 6.02 \times 10^{23} \text{ atoms}$$

4.5. Applications of the Ideal Gas Law

$$PV = nRT$$

$$P_1 V_1 = n_1 R T_1$$

$$P_2 V_2 = n_2 R T_2$$

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

Standard ambient
temperature and
pressure (SATP):

25 °C, 1 bar:

24.79 L/mol

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

Molar volume

At STP (Standard Temperature and Pressure)

→ 273 K and 1 bar (~1 atm)

$$V_m (STP) = \frac{(8.206 \times 10^{-2} \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273 \text{ K})}{1 \text{ atm}}$$

$$= 22.4 \text{ L}$$

Units

SI (international Standard) unit:

- Kilogram, meter, second, Pascal
- $R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$

Non SI units:

- atm, torr, liter

$$1 \text{ liter} = (10 \text{ cm})^3$$

$$1 \text{ atm} = 1.013 \times 10^5 \text{ Pascal}$$

$$R = 0.082 \text{ atm L K}^{-1} \text{ mole}^{-1}$$

Units should be consistent!!!!

At STP (Standard Temperature and Pressure)

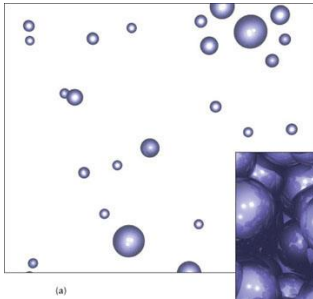
: 298 K and 1 bar (~1 atm), 1 Molar volume

Gas: 22.4 L

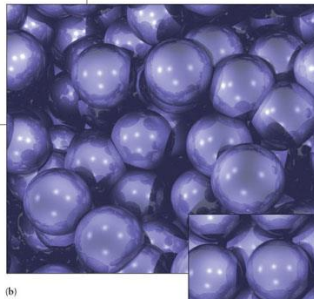
~1000 배!

Liquid (H₂O): 18 ml

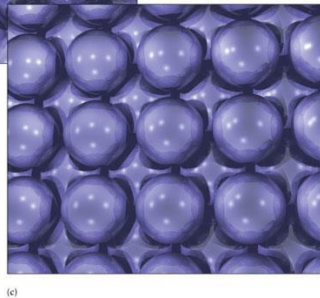
Solid: comparable to the liquid.



gas: Inter-atomic distance \gg molecular size



liquid: Inter-atomic distance
= molecular size

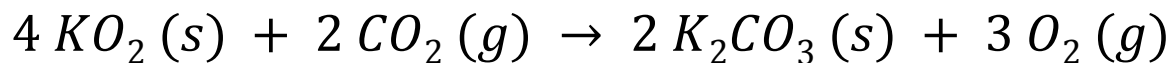


solid: Inter-atomic
distance = molecular size

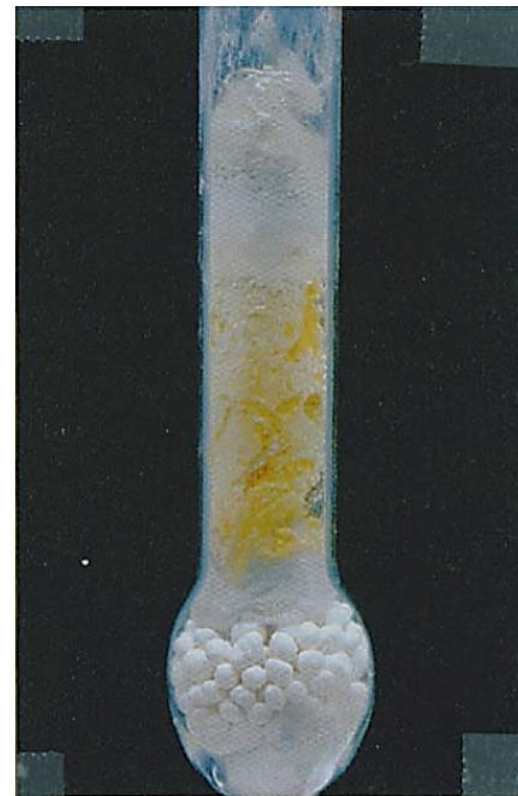
4.7. The Stoichiometry of Reacting Gases

Example I

The **carbon dioxide** generated by the personnel in the artificial atmosphere of submarines and spacecraft must be removed from the air and the oxygen recovered. Submarine design teams have investigated the use of **potassium superoxide**, KO_2 , as an air purifier because this compound reacts with carbon dioxide and releases **oxygen**,



Calculate the mass of KO_2 needed to react with 50 L of CO_2 at 25°C and 1.0 atm.



4.8. Partial Pressure

For a A&B gas mix

moles = n_A and n_B with $n = n_A + n_B$

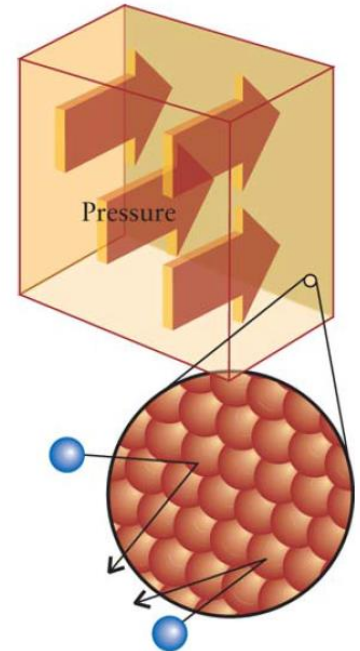
total pressure P

Mole fraction, $X_A = n_A/n = n_A/(n_A + n_B)$

Partial Pressure of A:
portion of pressure caused by A

$$P_A = X_A P$$

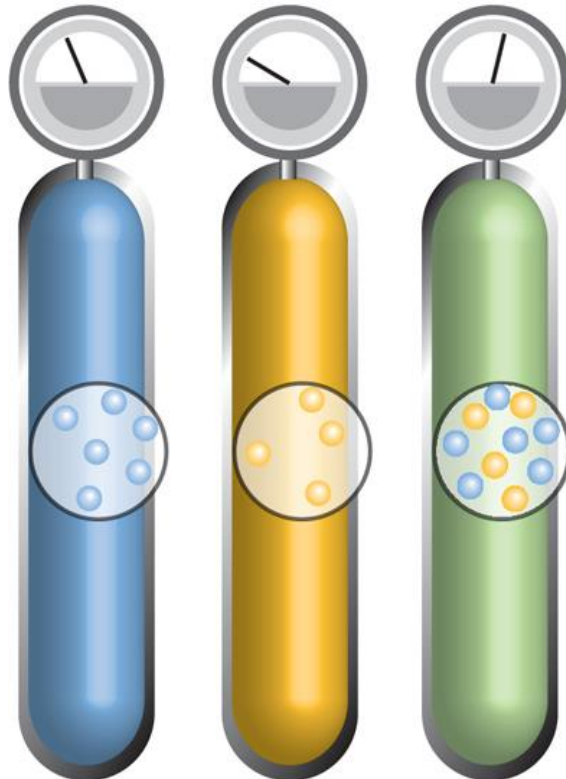
Question: Can we directly measure the partial pressure?



Dalton's law: The partial pressures of mixture of ideal gas are additive

$$P = P_A + P_B$$

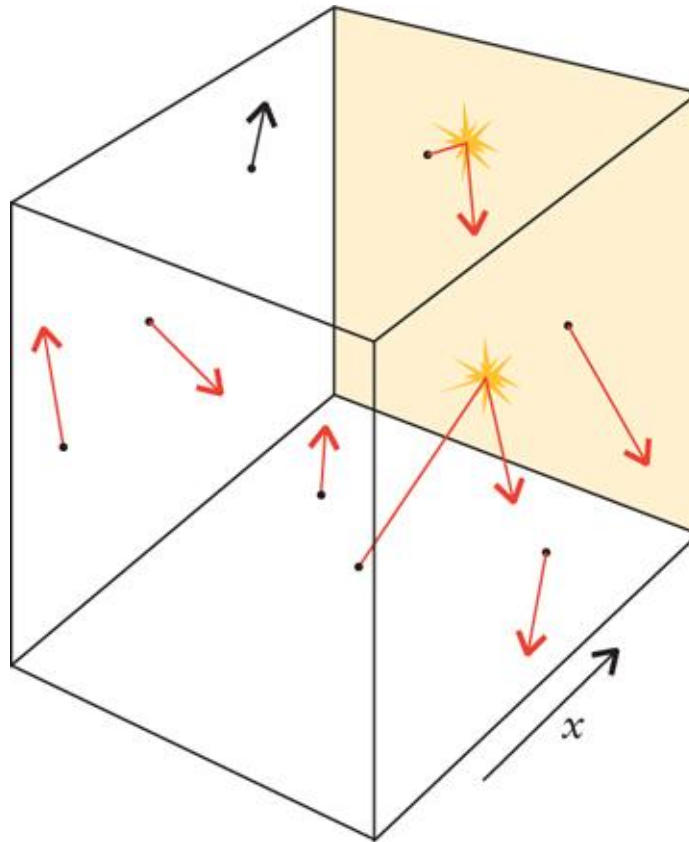
$$P_A = 0.6 \text{ atm} \quad P_B = 0.4 \text{ atm} \quad P = P_A + P_B = 1.0 \text{ atm}$$



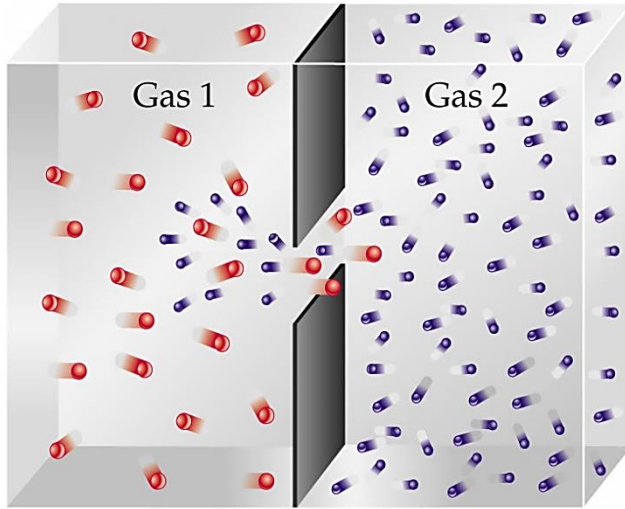
Assumption: No chemical reaction between A and B gases.

Molecular Motion

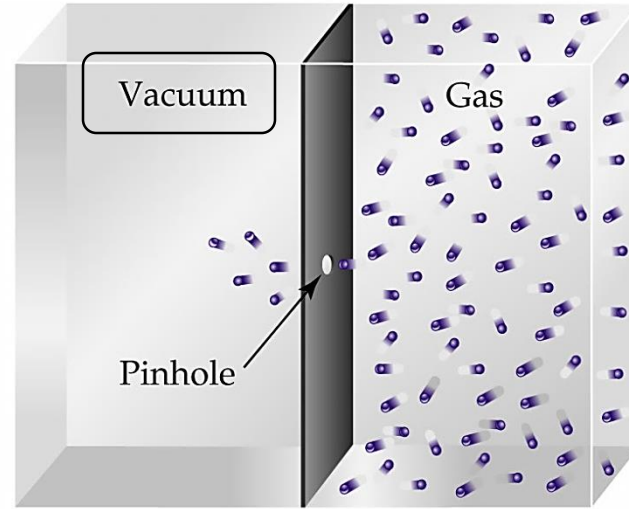
Molecules inside of cubic container
→ ping-pong ball?



4.7. Diffusion and Effusion



diffusion



effusion

Diffusion: spontaneous mixing of gas molecules by random motion under conditions where molecular **collision** occur

Effusion: the escape of a gas through a pinhole **without** molecular collisions; easier to explain

4.8. The Kinetic Model of Gases

Kinetic Molecular theory :Assumptions

Size of molecule is negligible compared with the distance between molecules. (Molecules do not collide with each other).

Gas molecules are constantly moving in random directions with a distribution of speed.

Molecules move in straight line until they hit the walls.

The molecules do not influence one another except during collisions.

The collisions of molecules with the walls of the container are elastic (no energy is lost).

Review of elementary Physics

Linear momentum: $p = mv$

$$\mathbf{p} = (p_x, p_y, p_z)$$

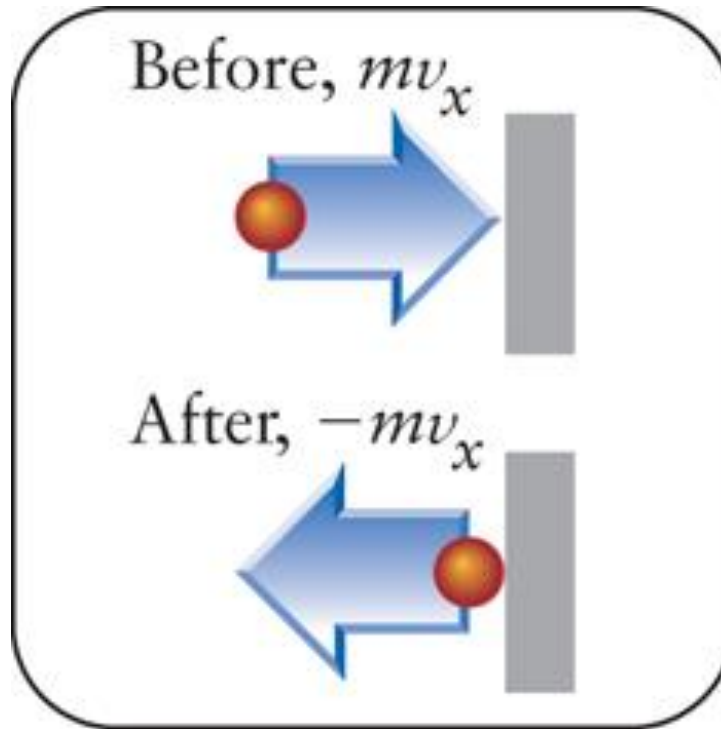
$$\mathbf{v} = (v_x, v_y, v_z) \quad \text{Velocity (vector)}$$

$$|\mathbf{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2} = v \quad \text{Speed (scalar)}$$

Force: change in momentum in unit time

$$F = ma = m \, dv/dt = dp/dt$$

Elastic Collision in 1-D



Momentum Change of particle

$$= \Delta P_{\text{particle}} = P_{\text{final}} - P_{\text{initial}} = -2mv$$

Momentum Change of Wall

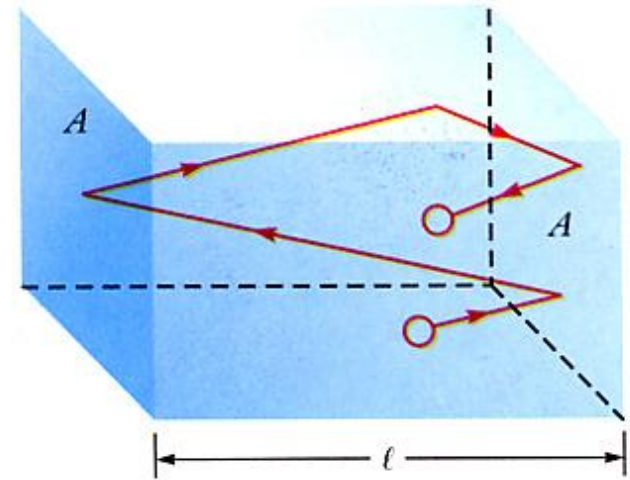
$$= \Delta P_{\text{wall}} = -\Delta p_{\text{particle}} = 2mv$$

Total momentum is
conserved

Bounced particle will hit the same wall again in time Δt

- Round trip time for the particle
= $\Delta t = 2l / v_x$
- Momentum transferred to the wall
in one second = **Force**

$$F_x = \frac{\Delta p_{x,wall}}{\Delta t} = \frac{2mv_x}{(2l / v_x)} = \frac{mv_x^2}{l}$$



Force on the wall by N-number of molecules

$$\begin{aligned} F_{x,tot} &= \frac{mv_{x1}^2}{l} + \frac{mv_{x2}^2}{l} + \dots + \frac{mv_{xN}^2}{l} \\ &= \frac{m}{l} (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2) \\ &= \frac{mN}{l} \cdot \frac{(v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2)}{N} = \frac{mN}{l} \cdot \overline{v_x^2} \end{aligned}$$

Average of the square of v_x

Pressure on X-direction

$$P = \frac{F_x}{A} = \frac{mN / l}{A} \cdot \overline{v_x^2} = \frac{mN}{lA} \cdot \overline{v_x^2} = \frac{mN}{V} \cdot \overline{v_x^2}$$

The gas molecules have no preferred direction of motion. Therefore,

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$$

and

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

$$P = \frac{Nm}{V} \cdot \overline{v^2} / 3 = \frac{nN_{avogadro}m}{V} \cdot \overline{v^2} / 3$$

N: total number
of gas molecules

n: mole number
= $N/N_{avogadro}$

Empirically, we know:

$$P = \frac{nRT}{V}$$

Average kinetic energy of
One molecule

Therefore,

$$RT = \frac{1}{3} N_{avogadro} \overline{mv^2} = \frac{2}{3} \cdot \left(N_{avogadro} \left(\frac{1}{2} \overline{mv^2} \right) \right)$$

= 2/3 x (Total kinetic energy of one mole of molecule)

= 2/3 (KE)

- Physical meaning of temperature:

“Temperature is a measure of random kinetic energy”

High-temperature → Molecules move faster

Low-temperature → Molecules move slower

With absolute zero temperature

→ Molecules do not move at all.

Root-mean-square(RMS) speed of molecules

$$RT = \frac{1}{3} N_{\text{avogadro}} m \overline{v^2} = \frac{2}{3} \cdot \left(N_{\text{avogadro}} \frac{1}{2} m \overline{v^2} \right) = \frac{1}{3} M \overline{v^2}$$

Molecules move fast with higher temperature.

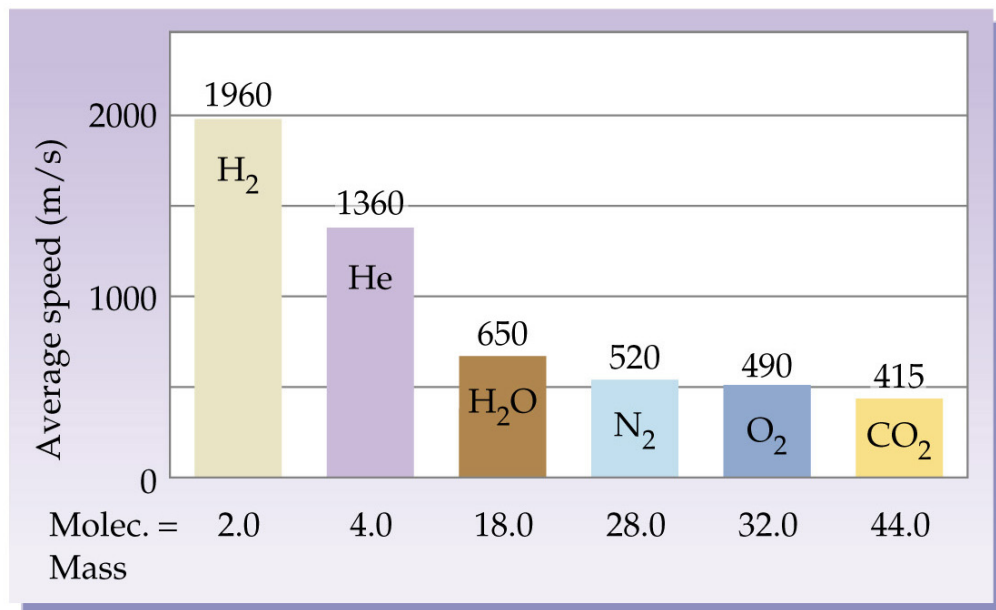
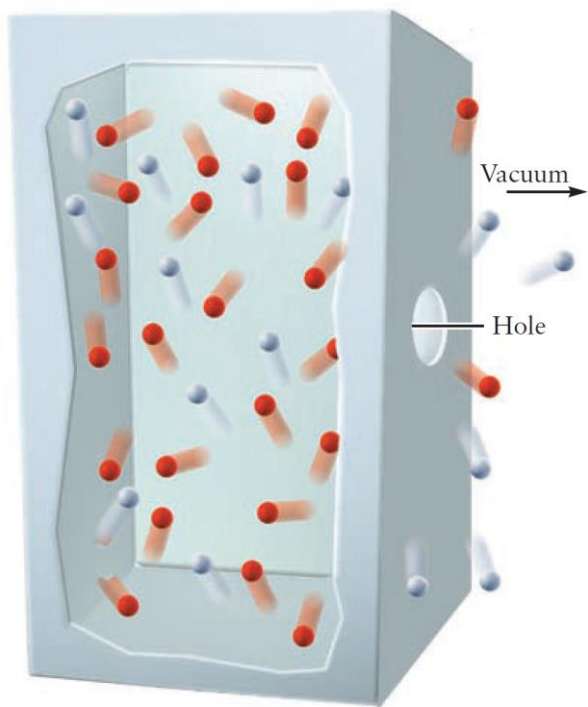
Heavy molecules move slower

rms: root mean square speed

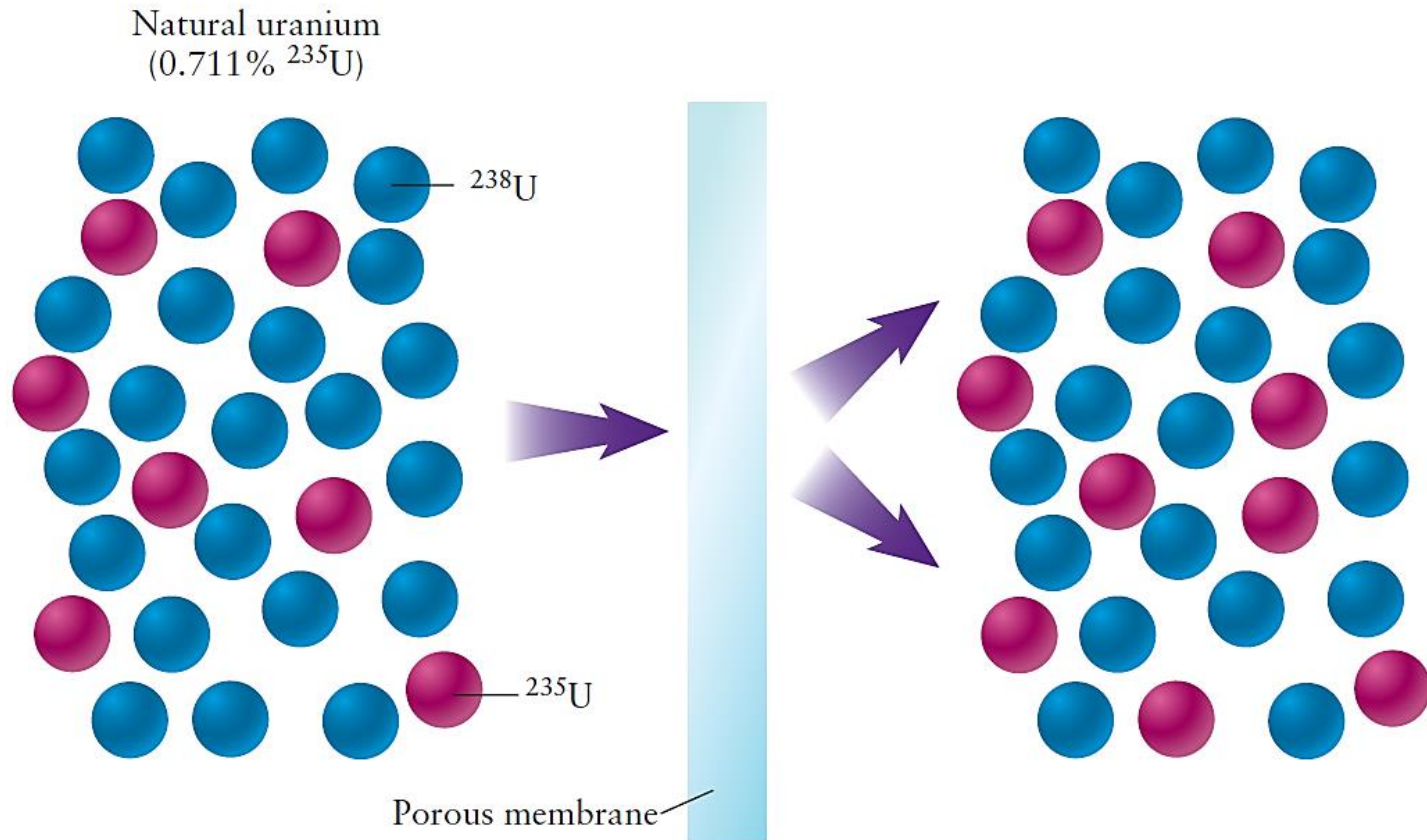
Graham's law of effusion (at const T)

$$\text{rate of effusion} \propto \frac{1}{\sqrt{M}} \rightarrow \text{average speed } (\bar{v}) \propto \frac{1}{\sqrt{M}}$$

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\bar{v}_A}{\bar{v}_B} = \sqrt{\frac{M_B}{M_A}}$$



Gaseous Diffusion Uranium Enrichment Process



$$\frac{\text{rate of Diffusion of A}}{\text{rate of Diffusion of B}} = \sqrt{\frac{M_B}{M_A}}$$

4.8. The Kinetic Model of Gases

for 1 mol of ideal gas, $\overline{E_k} = \frac{1}{2} M \overline{v^2} = \frac{3}{2} RT$

atomic mass

for each molecule, $\overline{E_k} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$

mass of an atom

- What is the root mean square speed of nitrogen in air at 20°C?
- Calculate the average kinetic energy of one N₂ molecule.

But.....

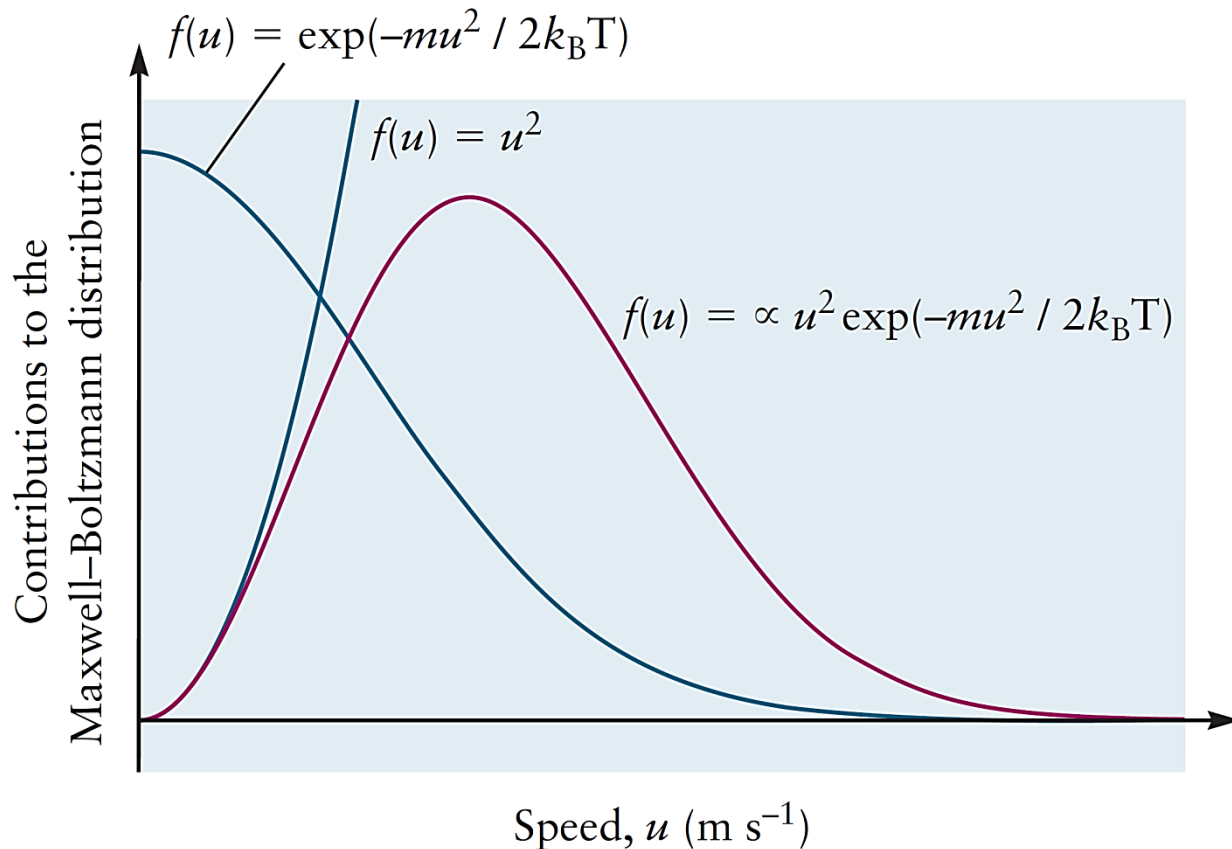
- Individual molecules have speeds that vary over a wide range.
- A molecule might be brought almost to a standstill when it collides with another.

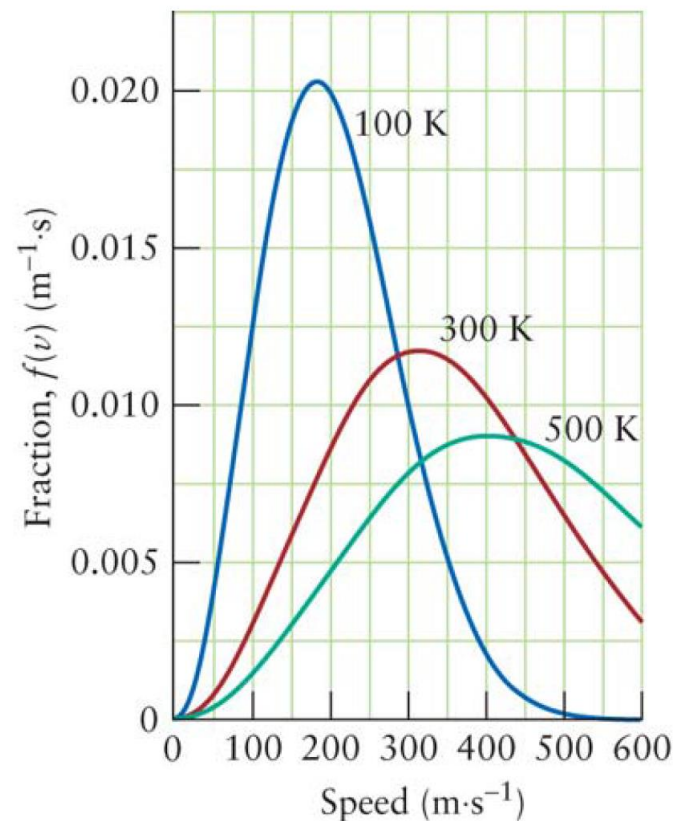
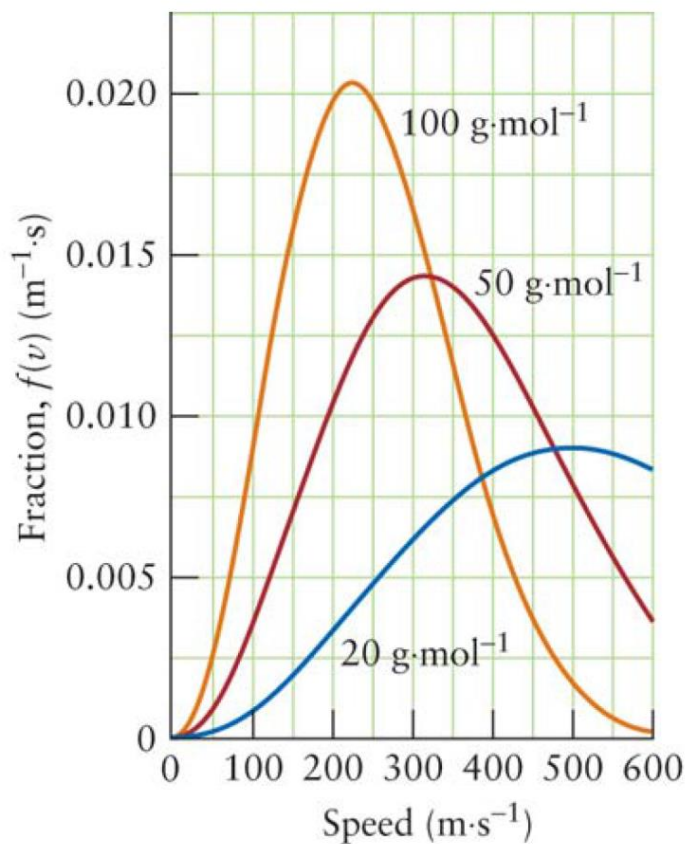
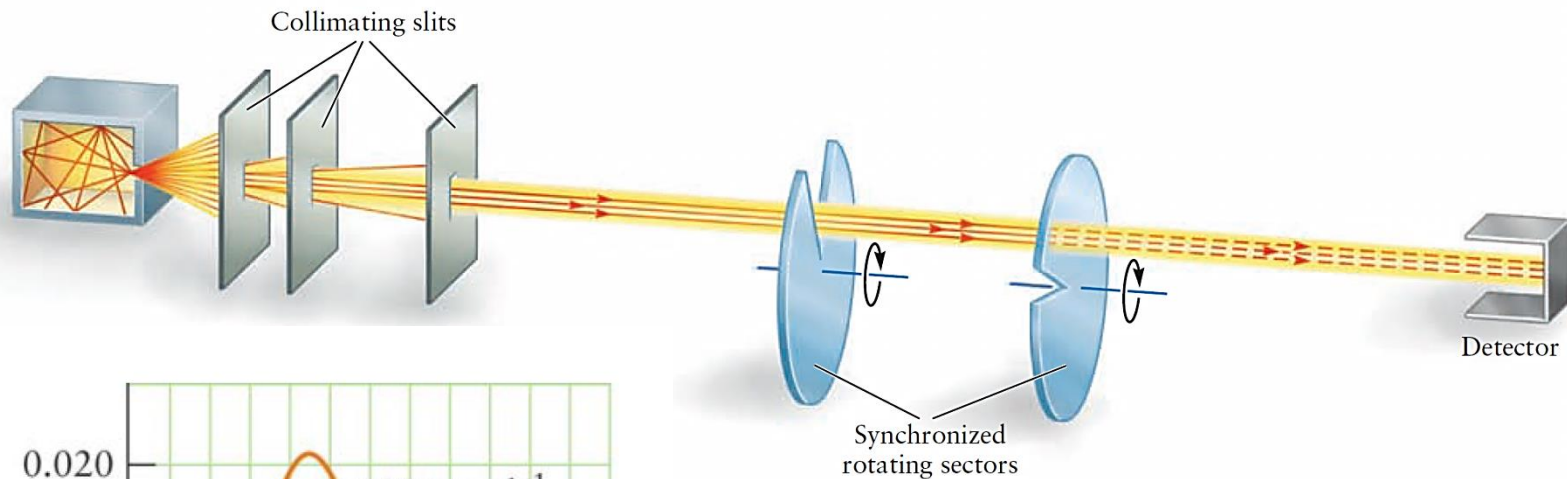
$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}}$$

4.9. The Maxwell Distribution of Speeds

Maxwell – Boltzmann speed distribution

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp(-mv^2/2k_B T)$$





Lower mass: higher average speed and wider distribution in the speed

Real , non-ideal gases

PV=nRT relation holds only if:

a. **Size of the molecule is negligible** compared with molecule-molecule distance.

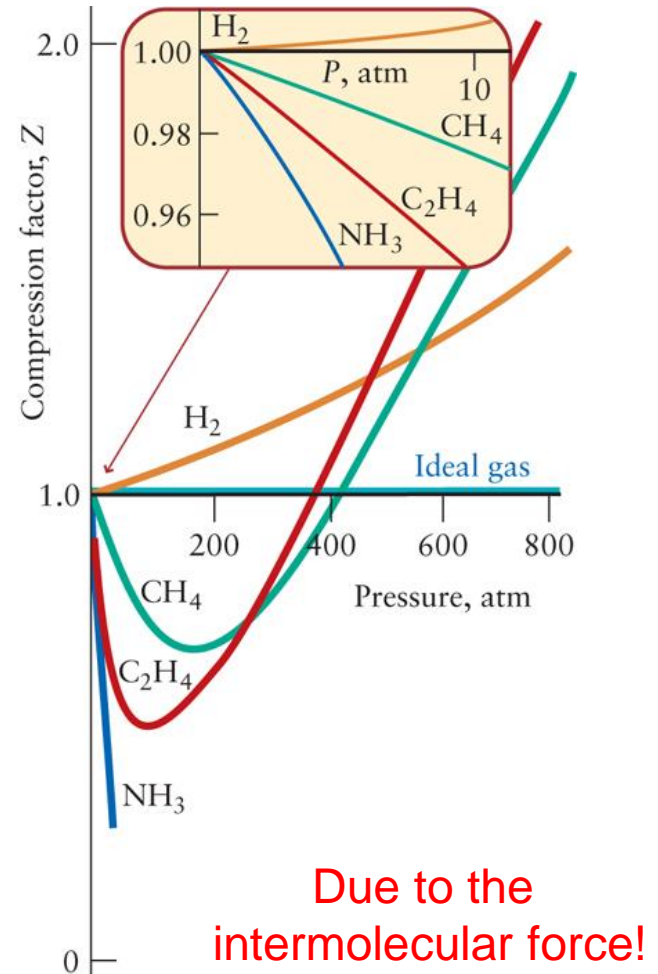
b. Molecules **do not interact each other**.

- Compression factor**

$$Z = \frac{V_m}{V_m^{ideal}} = \frac{PV}{nRT}$$

* Low P → long distance btw. molecules → attraction dominant → $Z < 1$

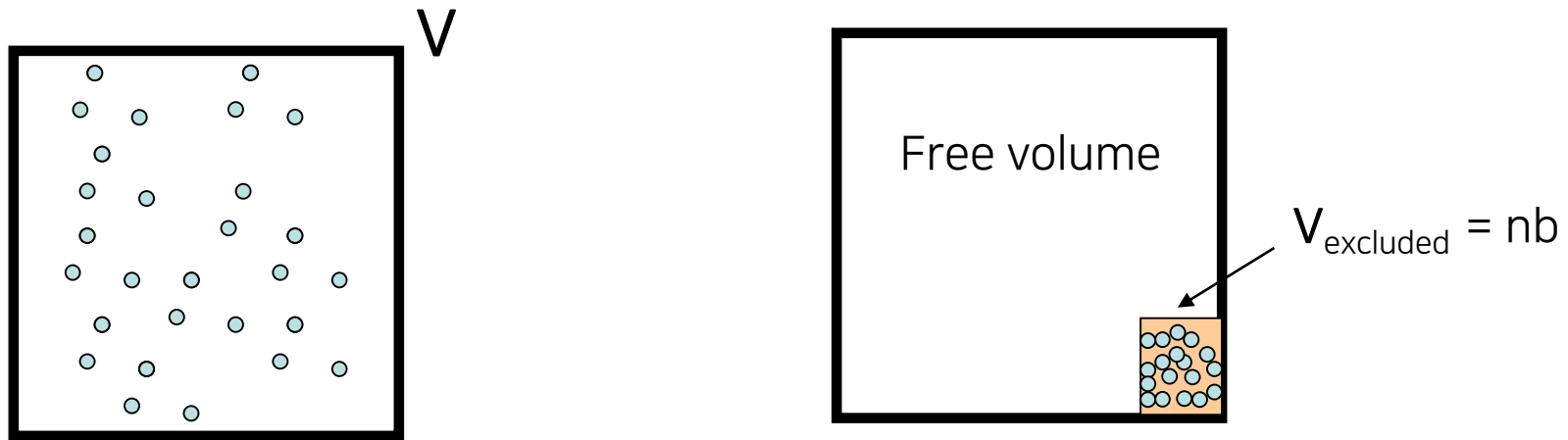
* High P (vice versa)



Corrections to this problem

Free Volume:

Real molecules occupy finite volume in container and reduce the effective free volume.



$$V_{\text{free}} = V - nb$$

n : number of moles, b : constant

$b \rightarrow$ a measure of molecular size

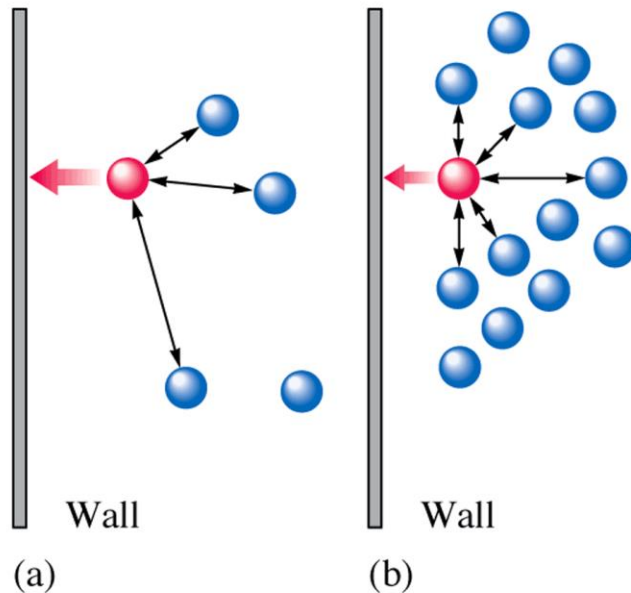
Pressure correction:

With high density of molecules,

→ molecule-molecule distance gets smaller

→ molecules interact each other

→ Changes the pressure exerted by molecules on the walls.



$$P \rightarrow P + a (n/V)^2$$

Correction due to particle-particle interaction

Why $a(n/V)^2$ correction?

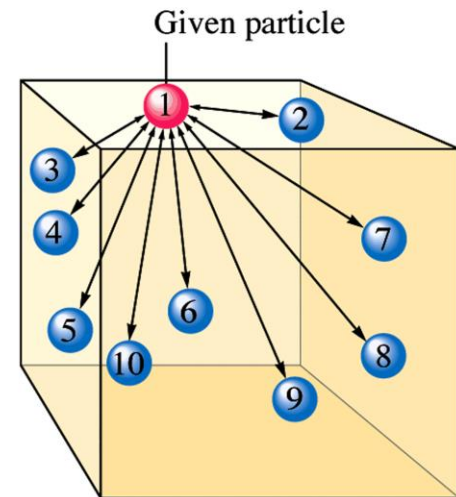
Assume only two-particle interaction.

N particles ($N = nN_{\text{avogadro}}$) in volume V .

Number of particles in volume $\rightarrow N_0 = N/V$

Number of ways to choose two particles among N_0 -particles in unit volume

$$= {}_{N_0}C_2 = (N_0)(N_0 - 1)/2 \sim (N/V)^2/2 \quad \text{if } N/V \gg 1.$$



Gas sample with ten particles

van der Waals equation

$$\underbrace{\text{corrected pressure}}_{P_{\text{ideal}}} \quad \underbrace{\text{corrected volume}}_{V_{\text{ideal}}}$$

TABLE 9.3 van der Waals Constants of Several Gases

Name	Formula	a (atm L ² mol ⁻²)	b (L mol ⁻¹)
Ammonia	NH ₃	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO ₂	3.592	0.04267
Hydrogen	H ₂	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH ₄	2.253	0.04278
Nitrogen	N ₂	1.390	0.03913
Nitrogen dioxide	NO ₂	5.284	0.04424
Oxygen	O ₂	1.360	0.03183
Sulfur dioxide	SO ₂	6.714	0.05636
Water	H ₂ O	5.464	0.03049

4.14. Equation of State of Real Gas

van der Waals Equation of State

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

a: a positive const. that depends on the attractive forces

b: excluded volume per mole

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

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

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

For ideal gas, $a=b=0$, $Z=1$

When attraction between molecules becomes significant, $a > 0$, and $Z < 1$.

When repulsion becomes significant, $b > 0$, and $Z > 1$.

Example

Estimate the pressure for 1.50 mol of a gas ($a = 16.2 \text{ L}^2 \cdot \text{atm} \cdot \text{mol}^{-2}$, $b = 0.084 \text{ L} \cdot \text{mol}^{-1}$) at 273 K in 5.00L

