UNIT III

KINETIC MOLECULAR DESCRIPTION OF THE STATES OF MATTER

→ the behavior of matter as perceived and measured on the scale of human experience to the structures and interactions of the molecules in the matter.

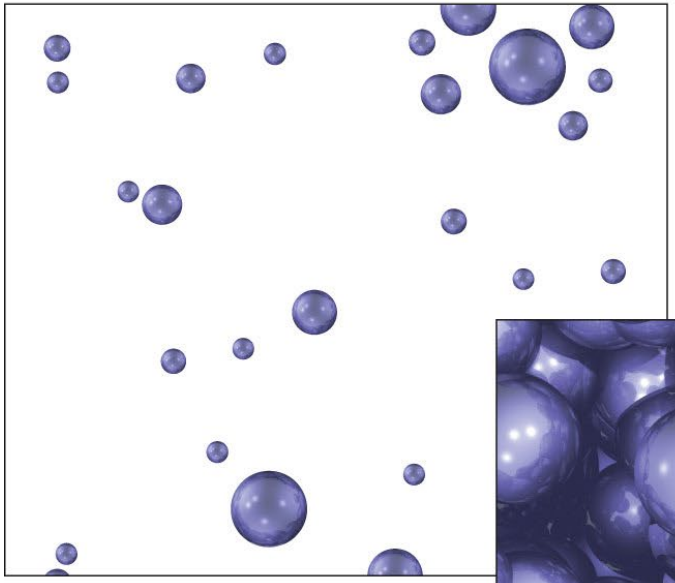
→ We see that macroscopic properties are determined by nanoscopic structures and the forces between them.

CHAPTER 9
The Gaseous State

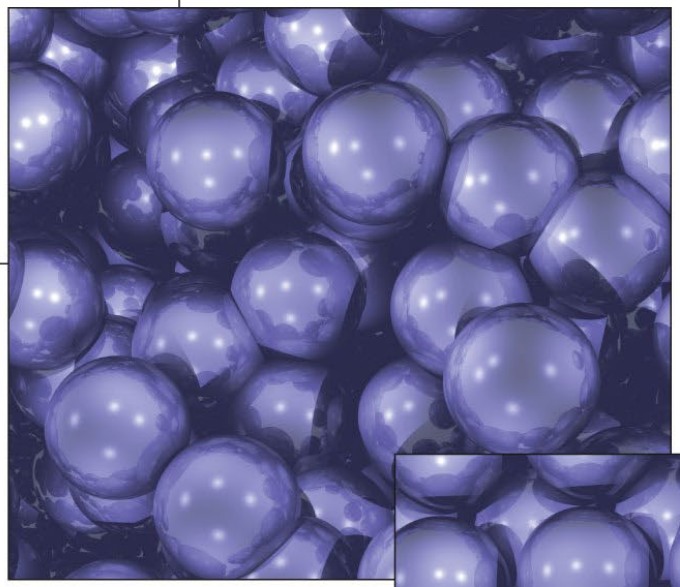
CHAPTER 10
Solids, Liquids, and Phase Transitions

CHAPTER 11
Solutions

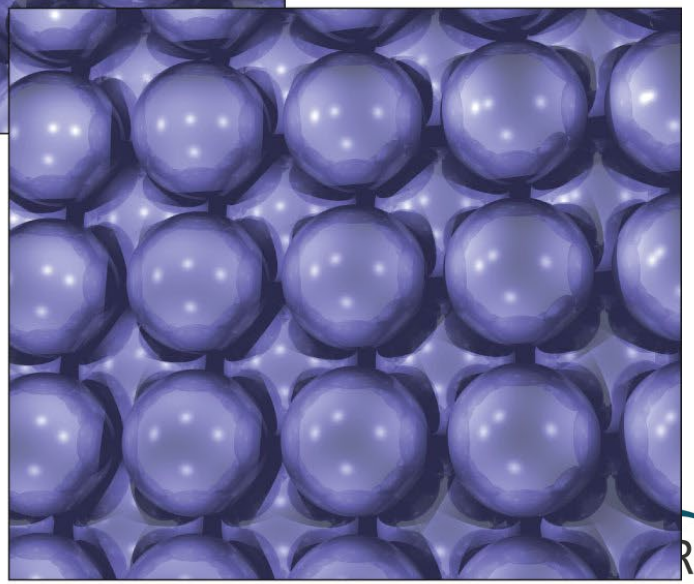
KAIST CHEMISTRY



(a) Gas



(b) Liquid



Solid

(c)

CHAPTER 9

THE GASEOUS STATE

→ Statistical mechanics to explain the connection between microscopic structure and macroscopic properties.

→ In the study of gases it is a legitimate simplification to ignore interactions between molecules until they collide and then to consider collisions between only two molecules at a time

9.2 Pressure and Temperature of Gases

9.3 The Ideal Gas Law

9.4 Mixtures of Gases

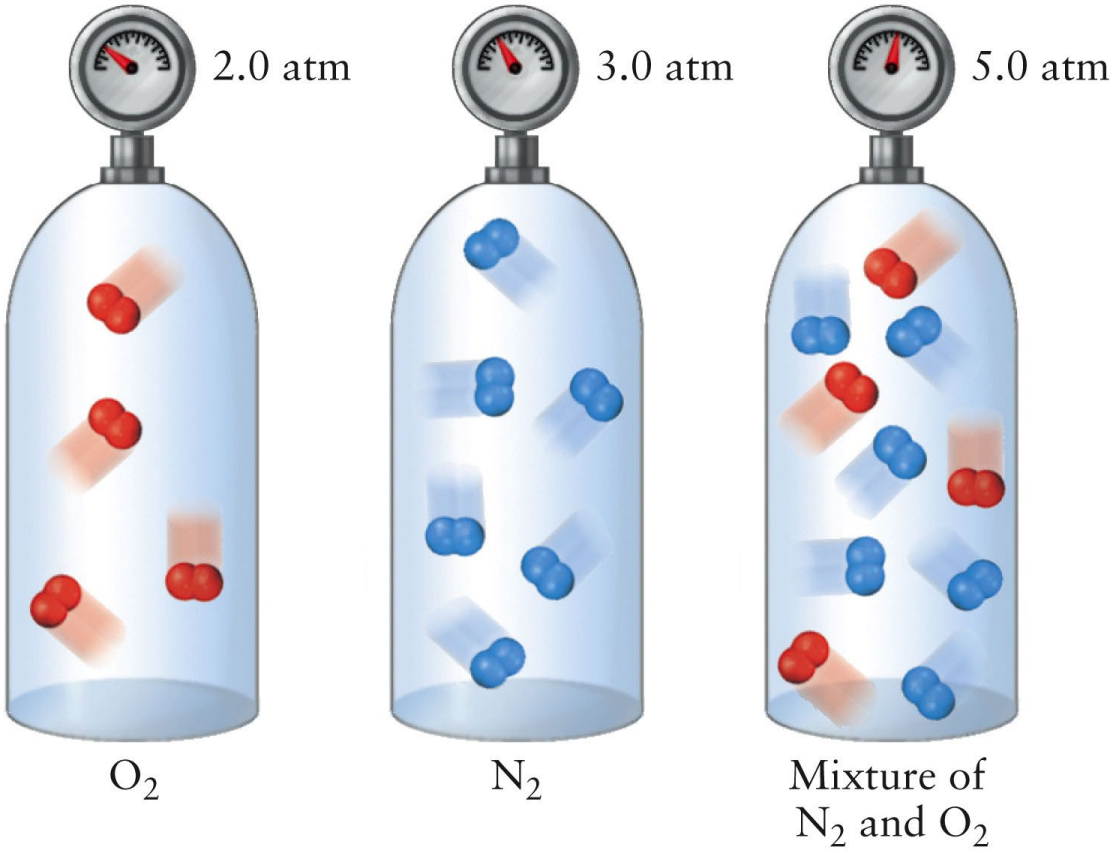
9.5 The Kinetic Theory of Gases

9.6 Real Gases: Intermolecular Forces

→ Whereas the chemical properties of gases vary significantly, their physical properties are quite similar and much simpler to understand

KAIST CHEMISTRY

Key question: how can we describe molecular behaviors in the gaseous state?



9.2 PRESSURE AND TEMPERATURE OF GASES

Macroscopic behavior of a gas can be characterized by the three properties

Volume (V): Avogadro's hypothesis: $V \propto n$

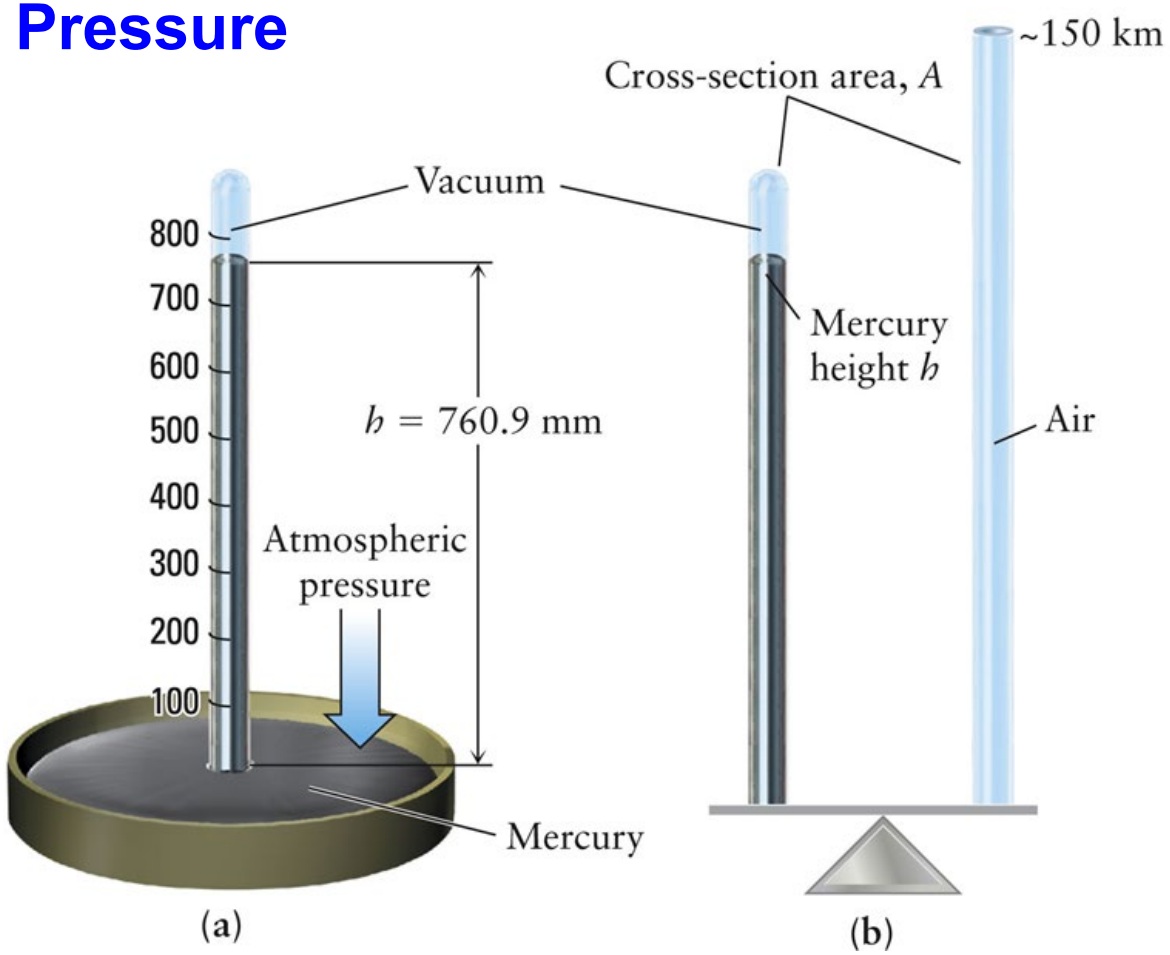
Pressure (P): P = F/A, how can we measure this?

Temperature (T): ??

What is the relation between V, P, and T?

9.2 PRESSURE AND TEMPERATURE OF GASES

◆ Pressure



Torricelli's barometer

Evangelista Torricelli
(ITA, 1608-1647)

KAIST CHEMISTRY

Force exerted by the mercury column at its base

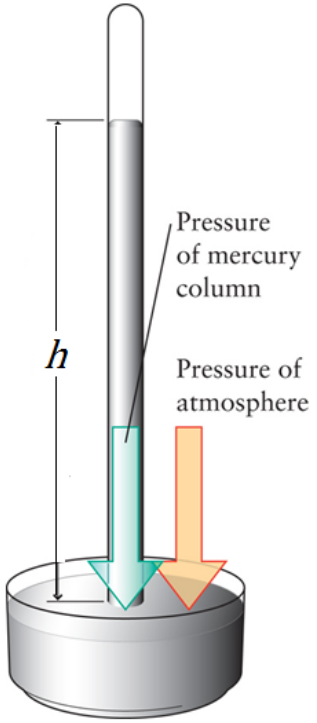
$$F = mg$$

$$\text{Pressure}: \quad P = \frac{F}{A} = \frac{mg}{A} = \frac{mg}{V/h} = \frac{m}{V}gh = \rho gh$$

ρ = 13.5951 g cm^{-3} → density of Hg(l) at 0 °C

g = 9.80665 m s^{-2} → gravitational acceleration

h = 76 cm → height of mercury column



$$\therefore \quad P = 1.01325\times10^{5} \ \text{kg m}^{-1}\text{s}^{-2}$$
$$= 1.01325\times10^{5} \ \text{Pa}$$
$$= 1.01325 \ \text{bar}$$
$$= 1 \ \text{atm}$$
$$= 760 \ \text{torr} \qquad \text{(at any temperature)}$$
$$= 760 \ \text{mmHg} \qquad \text{(at 0°C)}$$

TABLE 9.2 Units of Pressure

Unit	Definition
pascal (Pa)	1 kg m^{-1} s^{-2}
bar	1 × 10^5 Pa
atmosphere (atm)	101,325 Pa
torr	1/760 atm
760 mm Hg (at 0°C)	1 atm
14.6960 pounds per square inch (psi, lb in^{-2})	1 atm

◆ Pressure and Boyle's Law

~ Experiments on the compression and expansion of air.

"*The spring of the Air and Its Effects*" (1661).

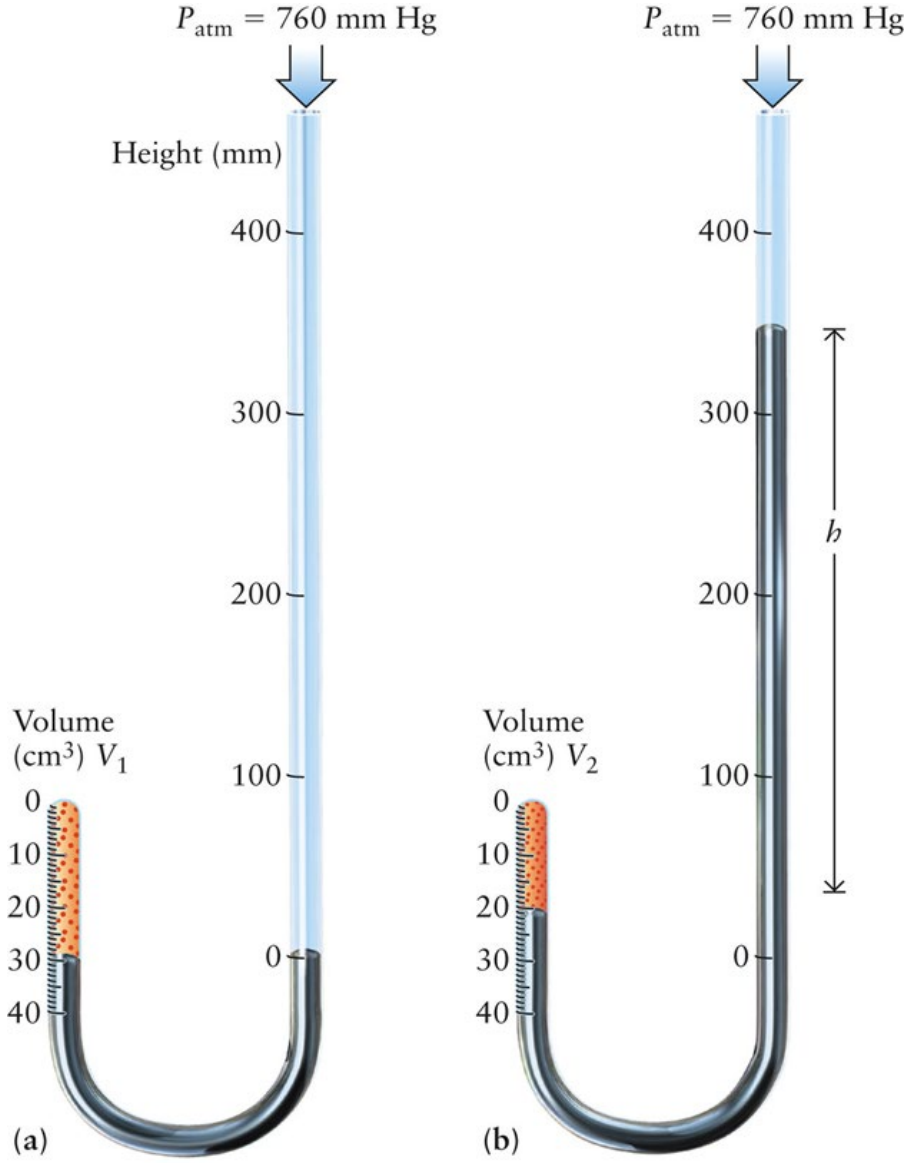


Fig. 9.3 Boyle's J-tube.

(a) Same Hg height on two sides

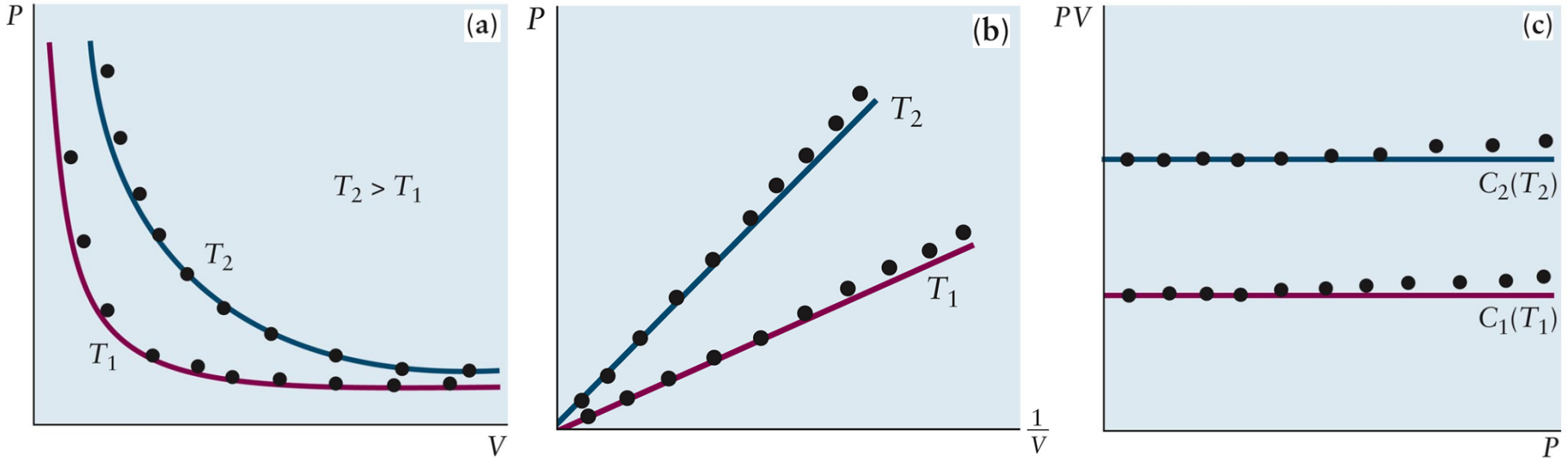
$P_{confined} = P_{air}$

(b) Hg added

→ Difference in Hg heights, h

→ $V_{confined}$ compressed

Robert Boyle
(UK, 1627-1691)



(a) *P vs. V* → hyperbola

(b) *P vs.* 1/*V* → straight line passing through the origin (slope: *C*)

(c) *PV vs. P* → straight line independent of *P*

(parallel to *P*-axis, intercept *C* on *PV*-axis)

The value of *C* at 0°C and for 1 mol of gas,

~ *good for <u>all</u> gases at very <u>low</u> pressure*

$C = PV = 22.414$ L atm

KAIST CHEMISTRY

◆ Pressure and Boyle's Law

➢ Boyle's *J*-tube experiment

Trapped air at the closed end of the *J*-tube:

$$P = 1 \text{ atm} + \frac{h \text{ (in mm)}}{760 \text{ mm atm}^{-1}}$$

Add Hg and measure the volume of air (*V*):

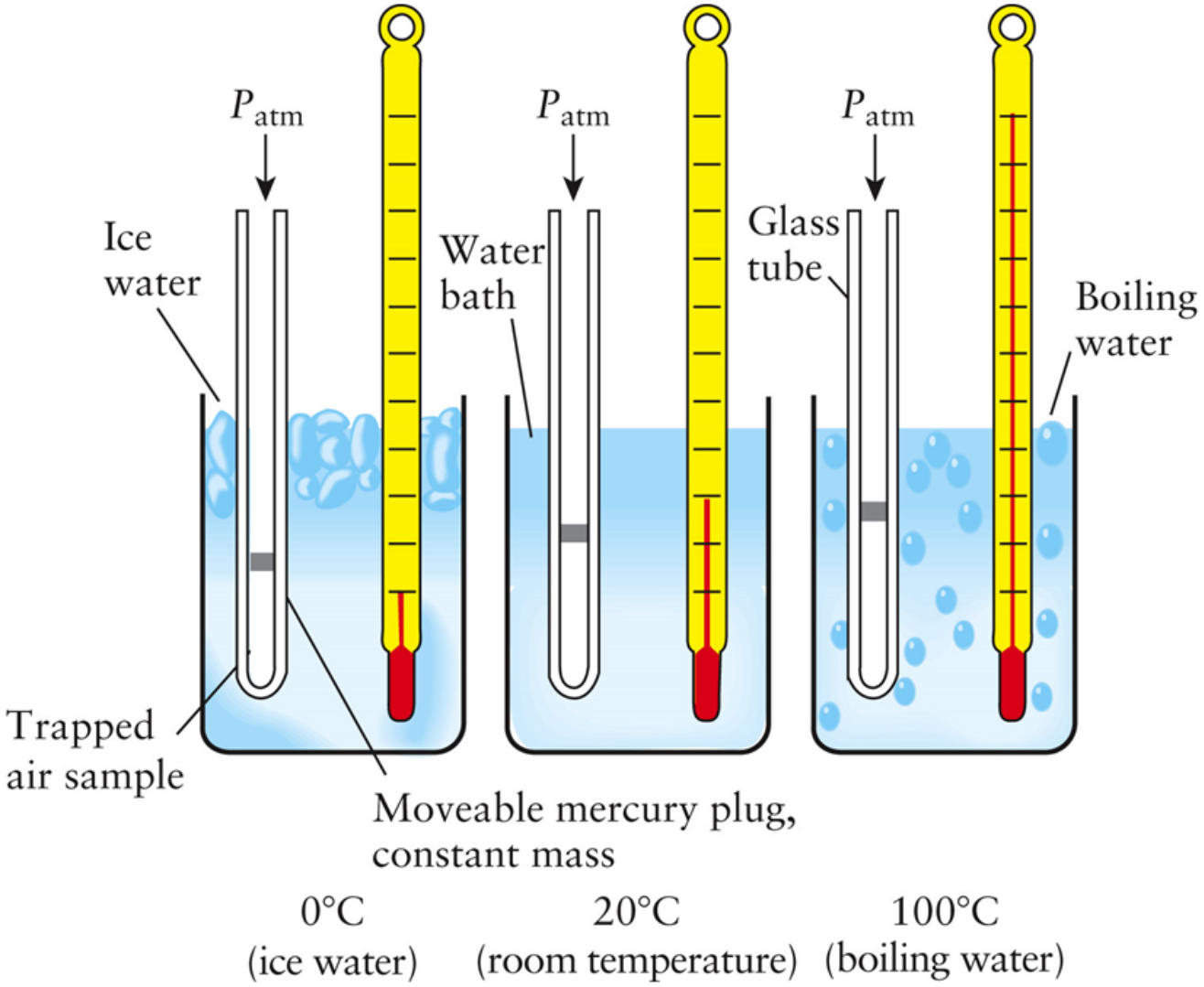
$$P = \frac{C}{V} = C\left(\frac{1}{V}\right)$$

or $\boxed{PV = C}$

C: a constant at constant *T* and fixed amount of gas

Robert Boyle
(UK, 1627-1691)

◆ Temperature and Charles's law



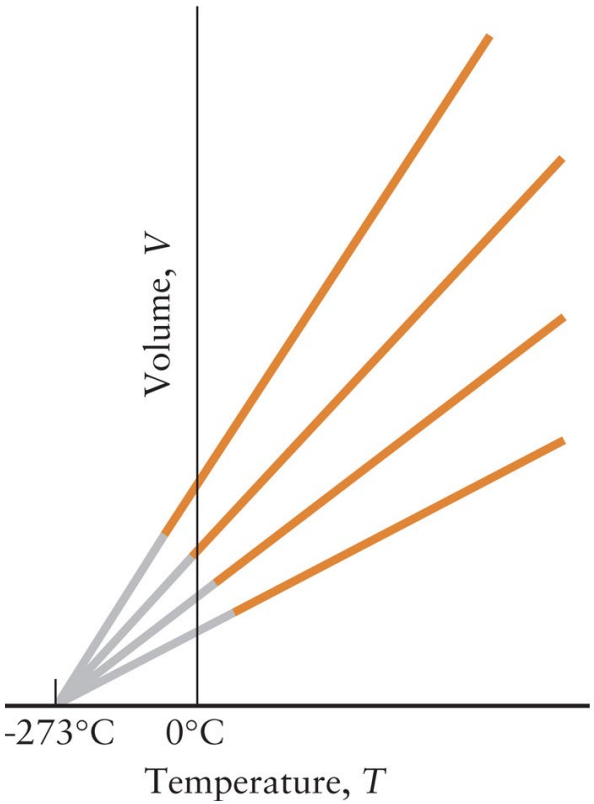


Fig. 9.5 Volume of a gas confined at constant *P* increases as *T* increases.

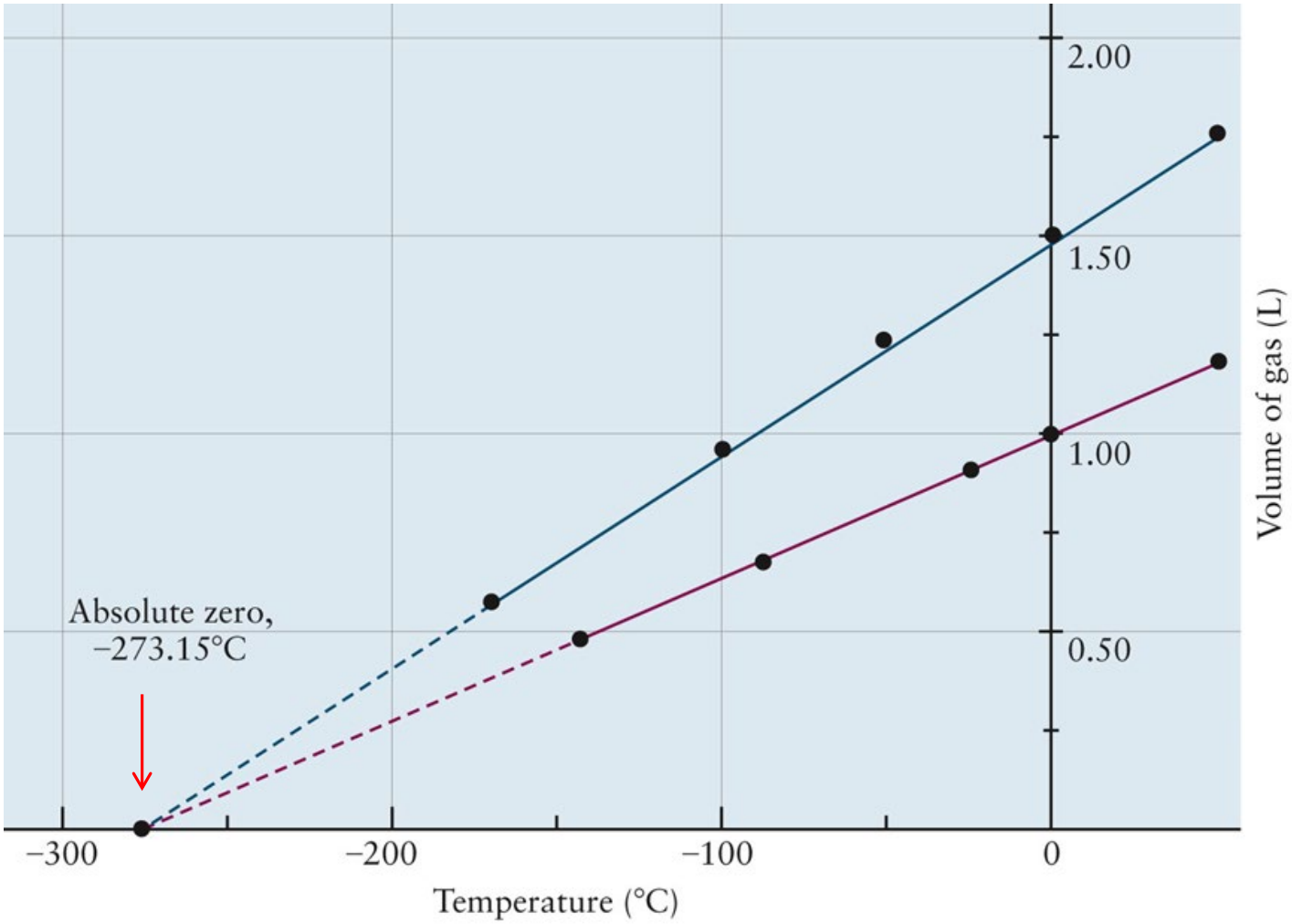


Fig. 9.6 The volume of a sample of a gas is a function of temperature at constant pressure.

◆ Temperature and Charles's law

$$V = \text{constant} \times T \ \text{(at constant } n \text{ and } P\text{)}$$

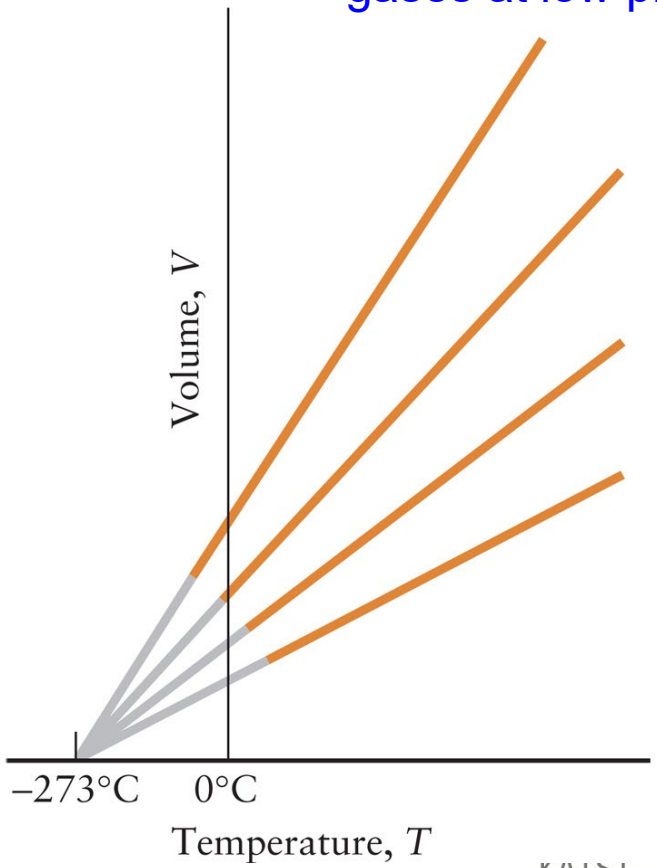
$$t = 273.15^{\circ}\text{C}\left(\frac{V}{V_0} - 1\right)$$

$$V = V_0\left(1 + \frac{t}{273.15^{\circ}\text{C}}\right) = V_0 \cdot \frac{T}{273.15}$$

$$T(\text{Kelvin}) = 273.15 + t(\text{Celsius})$$

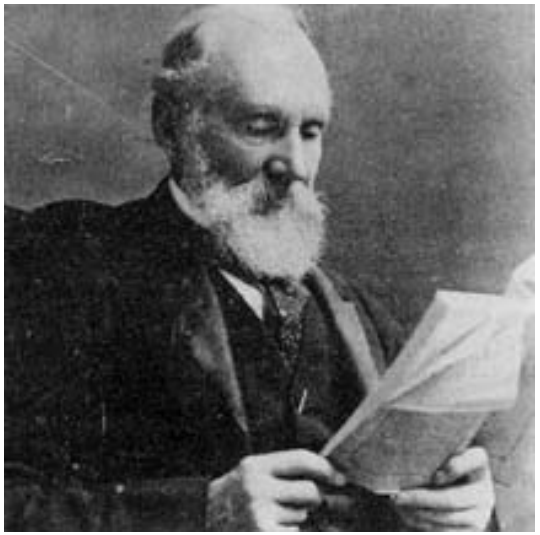
Jacques Charles
(France,1746-1823)

→ 273.15: Same for all gases at low pressures



◈ Absolute Temperature Scale, K

Kelvin, Lord William Thomson
(UK, 1824-1907)



0 K : ‘absolute zero’temperature
273.16 K : triple point of water

0 K = - 273.15 ^{o}C → 0 ^{o}C = 273.15 K

Kelvin scale: absolute, thermodynamic temperature scale
‘absolute zero’ temperature at which all thermal motion ceases in the classical description of thermodynamics.

→ a direct connection between the experimentally observed macroscopic behavior of matter and the structure and interactions of its constituent molecules.

9.3 THE IDEAL GAS LAW

Boyle's law: $V \propto 1/P$ (at constant T and n)
Charles' law: $V \propto T$ (at constant P and n)
Avogadro's hypothesis: $V \propto n$ (at constant T and P)

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

$$PV = nRT$$

√ Equation of state
√ Limiting law for real gases
as $P \rightarrow 0$
√ *Universal* gas constant, R
$R = 8.314\ \text{J·K}^{-1}\text{·mol}^{-1}$
$= 8.206 \times 10^{-2}\ \text{L·atm·K}^{-1}$

The Gas Constant, *R*

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

EXAMPLE 9.5

Concentrated nitric acid acts on copper to give nitrogen dioxide and dissolved copper ions according to the balanced chemical equation

$$Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow 2NO_2(g) + Cu^{2+}(aq) + 2H_2O(l)$$

$$Cu(s) + 4H^+(aq) + 4NO_3^-(aq) \rightarrow 2NO_2(g) + Cu(NO_3)_2(aq) + 2H_2O(l)$$

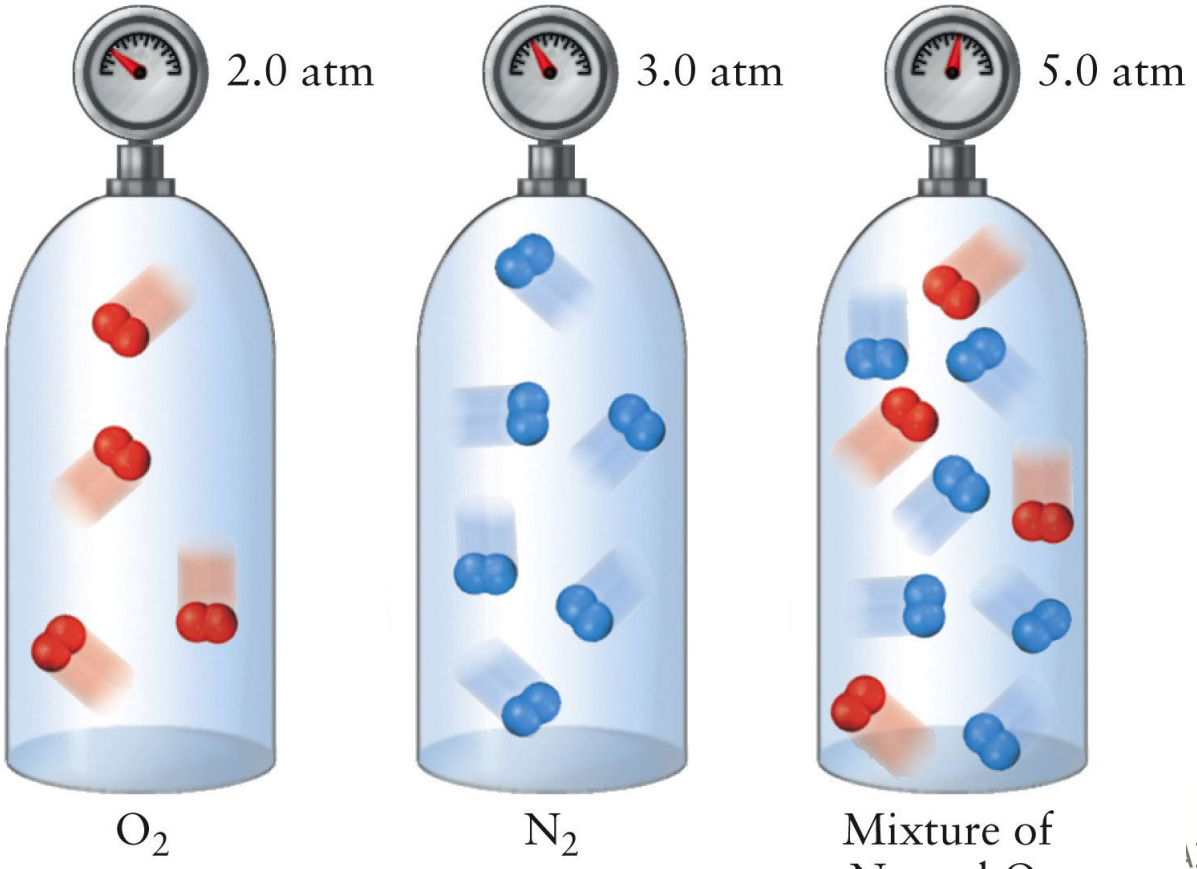
Suppose that 6.80 g copper is consumed in this reaction, and that the NO_2 is collected at a pressure of 0.970 atm and a temperature of 45°C. Calculate the volume of NO_2 produced.

$$\frac{6.80\ g\ Cu}{63.55\ g\ mol^{-1}} = 0.107\ mol\ Cu \qquad 0.107\ mol\ Cu \times \frac{2\ mol\ NO_2}{1\ mol\ Cu} = 0.214\ mol\ NO_2$$

$$V = \frac{nRT}{P} = \frac{(0.214\ mol)(0.08206\ L\ atm\ mol^{-1}K^{-1})(273.15 + 45)K}{0.970\ atm} = 5.76\ L$$

9.4 MIXTURE OF GASES

▶ **Partial pressure** (P_i) of the ith gas in a mixture of gases → pressure that the ith gas would exert if it occupied the container alone



Dalton's Law of Partial Pressures

The total pressure of a mixture of gases is the sum of the partial pressures of its component.

$$P = P_{\mathrm{A}} + P_{\mathrm{B}} + \cdots = \sum_{\mathrm{i}} P_{\mathrm{i}}$$

- **Mole fraction** of the component A, x_{A}

$$x_{\mathrm{A}} = \frac{n_{\mathrm{A}}}{n_{\mathrm{A}} + n_{\mathrm{B}} + \cdots}, \qquad x_{\mathrm{A}} + x_{\mathrm{B}} + \cdots = 1$$

$$P_{\mathrm{A}} = \frac{n_{\mathrm{A}} RT}{V}, \quad P = \frac{nRT}{V} = \left(n_{\mathrm{A}} + n_{\mathrm{B}} + \cdots\right)\frac{RT}{V} \longrightarrow P_{\mathrm{A}} = \frac{n_{\mathrm{A}} P}{n_{\mathrm{A}} + n_{\mathrm{B}} + \cdots} = x_{\mathrm{A}} P$$

$$\therefore \quad P_{\mathrm{A}} = x_{\mathrm{A}} P$$

EXAMPLE 9.6 When NO_2 is cooled to room temperature, some of it reacts to form a dimer, N_2O_4, through the reaction

$$2NO_2(g) \rightarrow N_2O_4(g)$$

Suppose 15.2 g of NO_2 is placed in a 10.0 L flask at high temperature and the Flask is cooled to 25°C. The total pressure is measured to be 0.500 atm. What partial pressures and mole fractions of NO_2 and N_2O_4 are present?

$$\frac{15.2\ g\ NO_2}{46.01\ g\ mol^{-1}} = 0.330\ mol\ NO_2 \qquad n_{NO_2} + 2n_{N_2O_4} = 0.330\ mol$$

$$P_{NO_2} + P_{N_2O_4} = \frac{RT}{V} n_{NO_2} + \frac{RT}{V} n_{N_2O_4} = 0.500\ atm$$

$$n_{NO_2} + n_{N_2O_4} = 0.500\ atm \frac{V}{RT} = \frac{(0.500\ atm)(10.0\ L)}{(0.08206\ L\ atm\ mol^{-1}\ K^{-1})(298\ K)} = 0.204\ mol$$

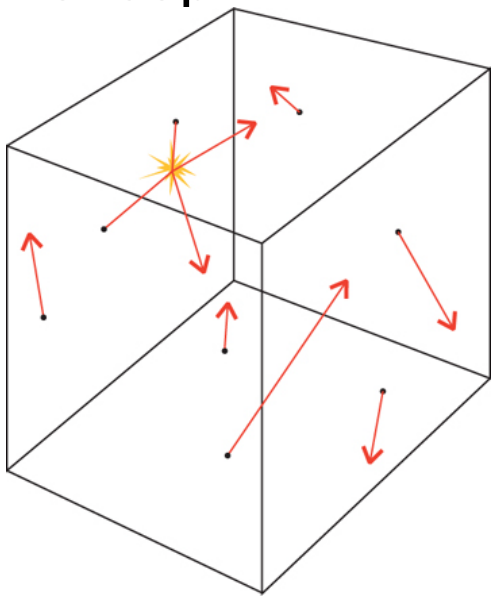
$$\therefore \boldsymbol{n_{N_2O_4} = 0.126\ mol, n_{NO_2} = 0.078\ mol}$$

KAIST CHEMISTRY

→ Microscopic explanation of empirical ideal gas law
→ Begin with a model and use the basic laws of physics with mathematical reasoning to show how this model helps explain the measured properties of gases.

9.5 THE KINETIC THEORY OF GASES

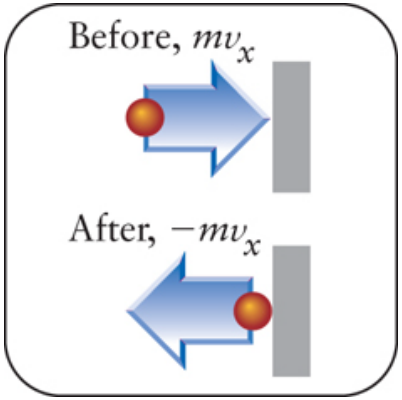
1. A gas consists of a collection of molecules in continuous random motion.
2. Gas molecules are infinitesimally small (mass) points.
3. The molecules move in straight lines until they collide.
4. The molecules do not influence one another except during collisions.



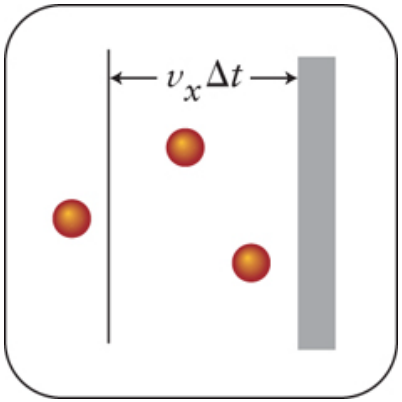
→ provides a microscopic understanding of Boyle's law and also a microscopic mechanical definition of temperature as a measure of the average kinetic energy of the molecules in a gas

- **Collision with walls**: consider molecules traveling only in one dimensional x with a velocity of v_x.

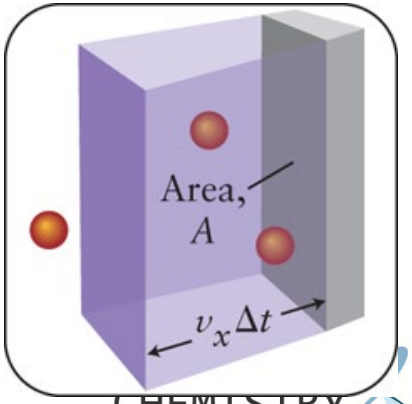
The change in momentum of one molecule: $2mv_x$



All the molecules within a distance $v_x\Delta t$ of the wall and traveling toward it will strike the wall during the interval Δt.

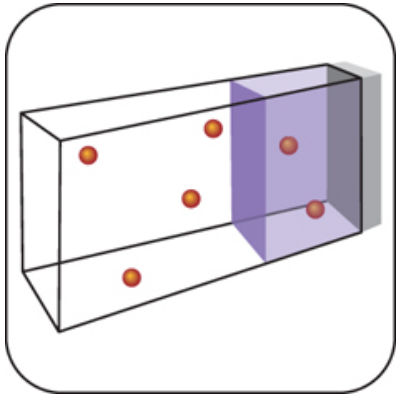


If the wall has area A, all the particles in a volume $Av_x\Delta t$ will reach the wall if they are traveling toward it.



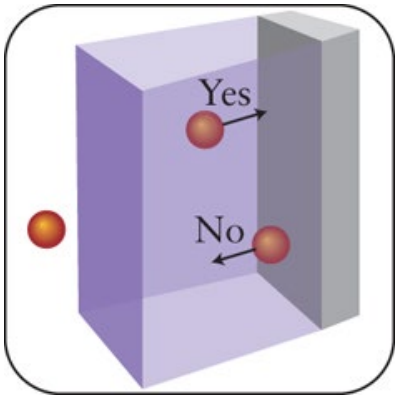
The number of molecules in the volume $Av_x\Delta t$ is that fraction of the total volume V, multiplied by the total number of molecules:

$$Number\ of\ molecules = \frac{Av_x\Delta t}{V} \times N = \frac{NAv_x\Delta t}{V}$$



The average number of collisions with the wall during the interval Δt is half the number in the volume $Av_x\Delta t$:

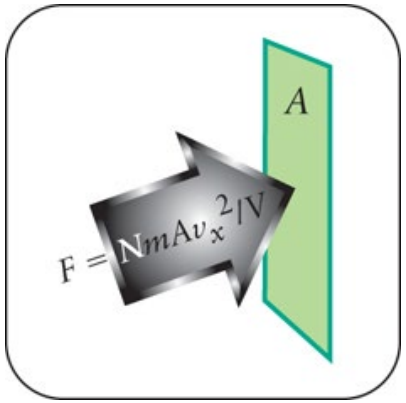
$$Number\ of\ collisions = \frac{NAv_x\Delta t}{2V}$$



The total momentum change = number of collisions × individual molecule change

$$Total\ momentum\ change = \frac{NAv_x\Delta t}{2V} \times 2mv_x = \frac{NmAv_x{}^2\Delta t}{V}$$

Force = rate of change of momentum =
(total momentum change)/Δt



$$Force = rate\ of\ change\ of\ momentum = \frac{NmAv_x{}^2}{V}$$

$$Pressure = \frac{NmAv_x{}^2}{VA} = \frac{Nmv_x{}^2}{V}$$

$$P = \frac{Nm\overline{v_x{}^2}}{V}$$ for the average value of $\overline{v_x{}^2}$

- **mean-square speed** $\overline{u^2} = \overline{v_x{}^2} + \overline{v_y{}^2} + \overline{v_z{}^2} = 3\overline{v_x{}^2}$

$$\boldsymbol{PV = \frac{1}{3}Nm\overline{u^2}} \qquad \boldsymbol{P = \frac{Nm\overline{u^2}}{3V}}$$

$$PV = \frac{1}{3}Nm\overline{u^2} = nRT \qquad \frac{1}{3}N_A m\overline{u^2} = RT$$

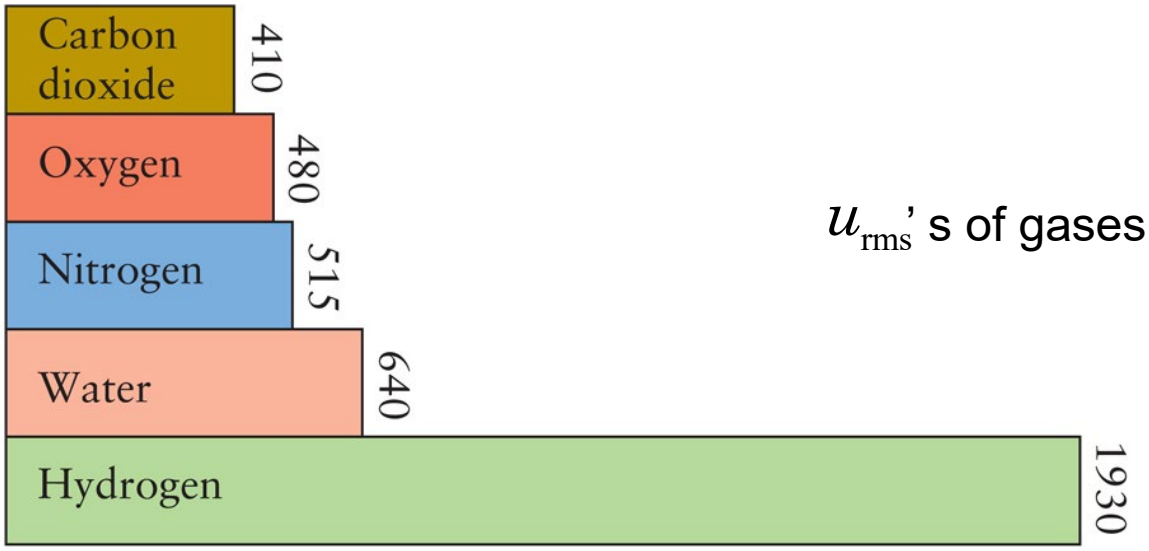
- Kinetic energy of N_A molecules, $\bar{E} = \frac{1}{2}N_A m\overline{u^2} = \frac{3}{2} \times \left(\frac{1}{3}N_A m\overline{u^2}\right) = \frac{3}{2}RT$

- **average kinetic energy per molecule**, $\bar{\varepsilon} = \frac{3}{2}k_B T$ $k_B = R/N_A$

→ Depends only on the temperature

- **root-mean-square speed** $\overline{u^2} = \frac{3RT}{M}$ $u_{rms} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$

M = molar mass = $N_A m$



u_{rms}' s of gases at 25°C

KAIST CHEMISTRY

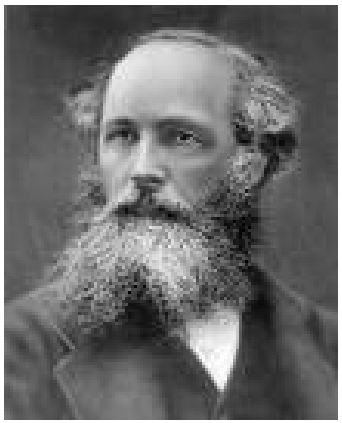
Maxwell-Boltzmann distribution of speed

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

→ the speed distribution function

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

Boltzmann constant: $k_B = R / N_A = 1.38066 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$



James Clerk Maxwell
(Scotland, 1831-1879)

Ludwig Eduard Boltzmann
(Austria, 1844-1906)

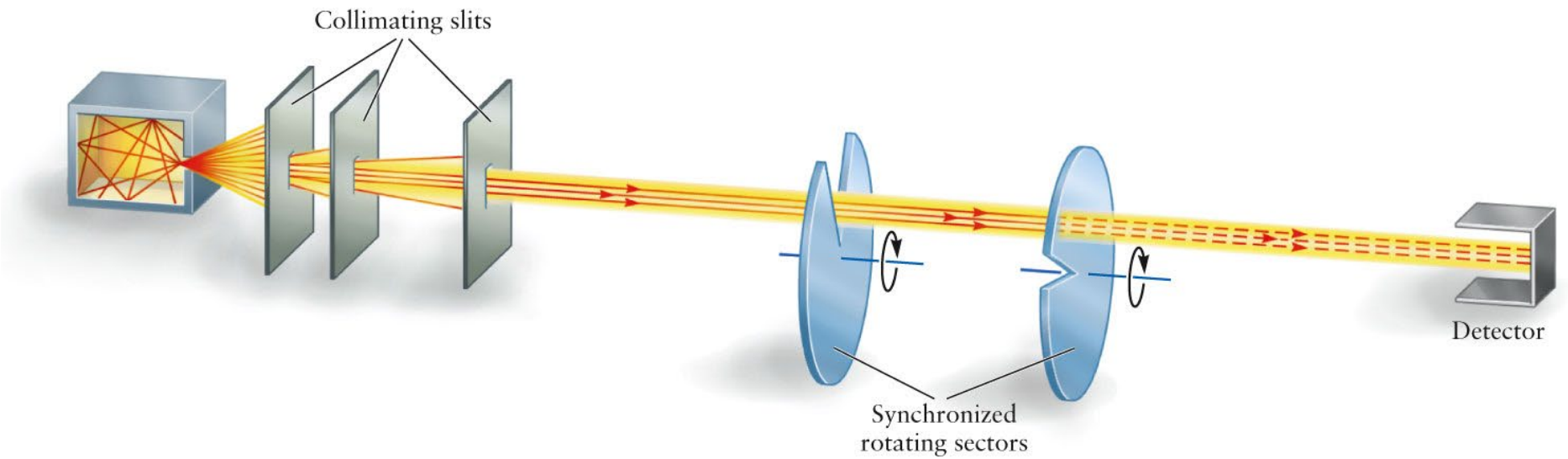
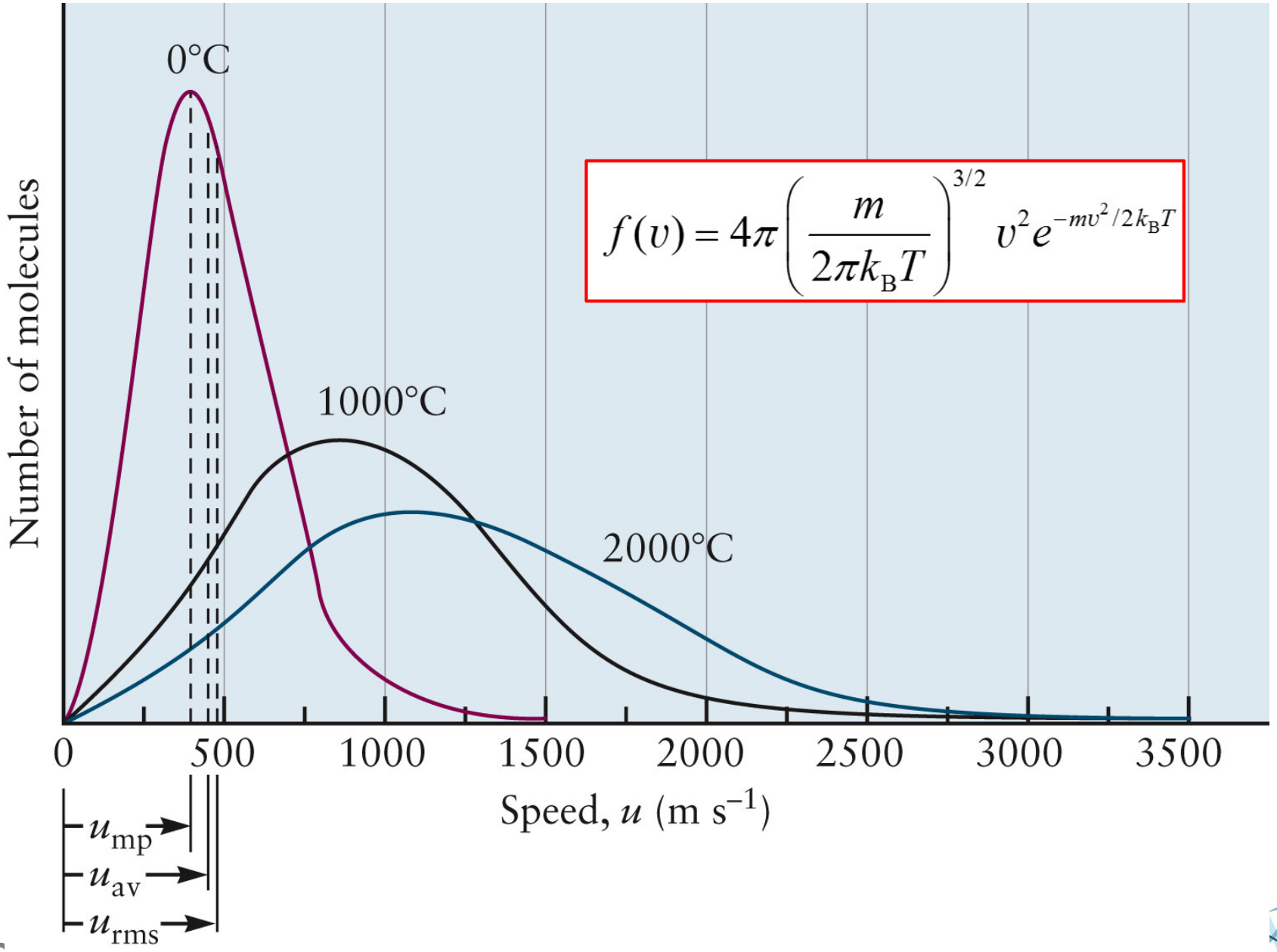


Fig. 9.13 A device for measuring the distribution of molecular speeds.


0°C
1000°C
2000°C
$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$
Number of molecules
0
500
1000
1500
2000
2500
3000
3500
Speed, u (m s^{-1})
u_{mp}
u_{av}
u_{rms}

(1) Most probable speed:

$$v_{mp} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}} \qquad \left[\frac{df(v)}{dv} = 0\right]_{v=v_{mp}}$$

(2) Average speed:

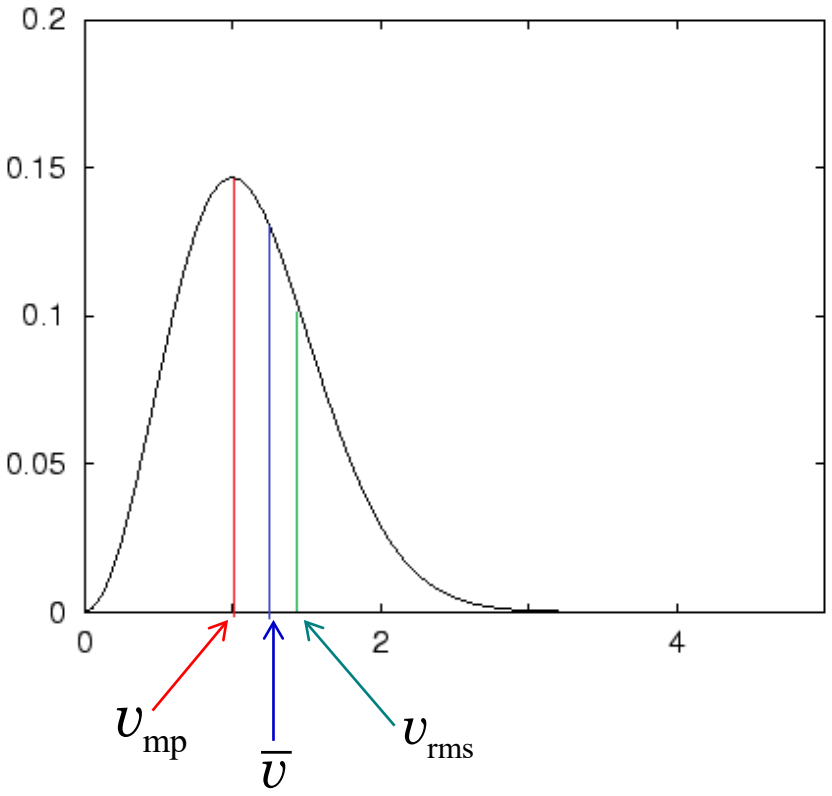
$$\bar{v} = \int_0^\infty vf(v)dv = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

(3) Mean square speed:

$$\overline{v^2} = \int_0^\infty v^2 f(v)dv = \frac{3k_BT}{m} = \frac{3RT}{M}$$

(4) Root-mean-square speed:

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



$$v_{mp} < \bar{v} < v_{rms} = 1.000 : 1.128 : 1.225$$

9.6 REAL GASES: INTERMOLECULAR FORCES

- **Compression (or Compressibility) factor, Z**

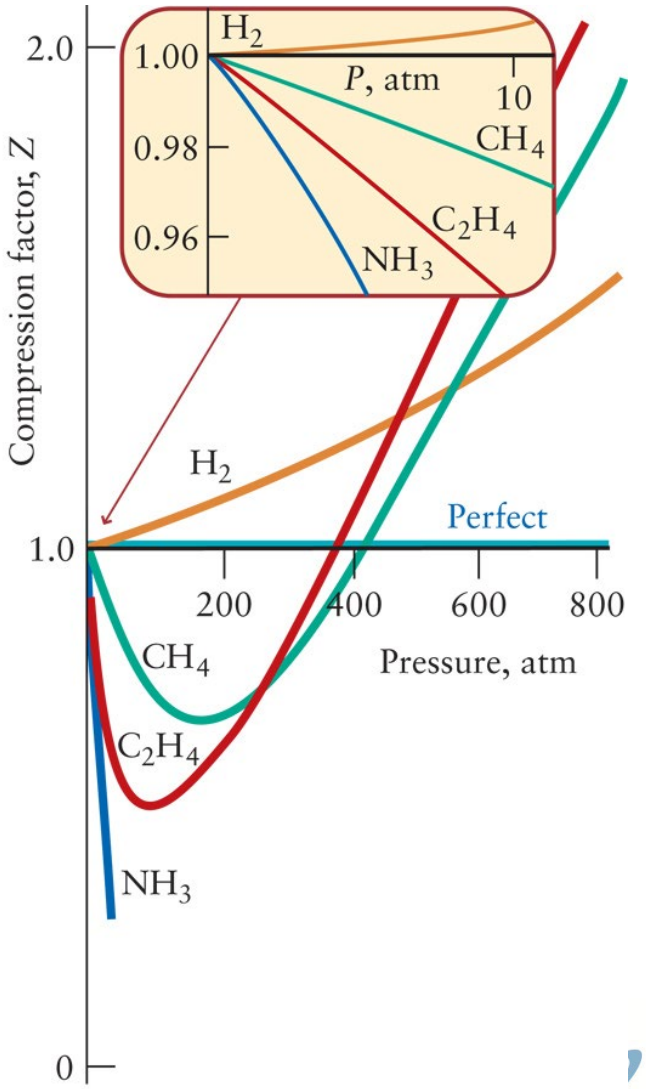
$$Z = \frac{V_m}{V_m^{ideal}} = \frac{V_m}{RT/P} = \frac{PV_m}{RT}$$

- For an ideal gas, $Z = 1$.
- Real gases,

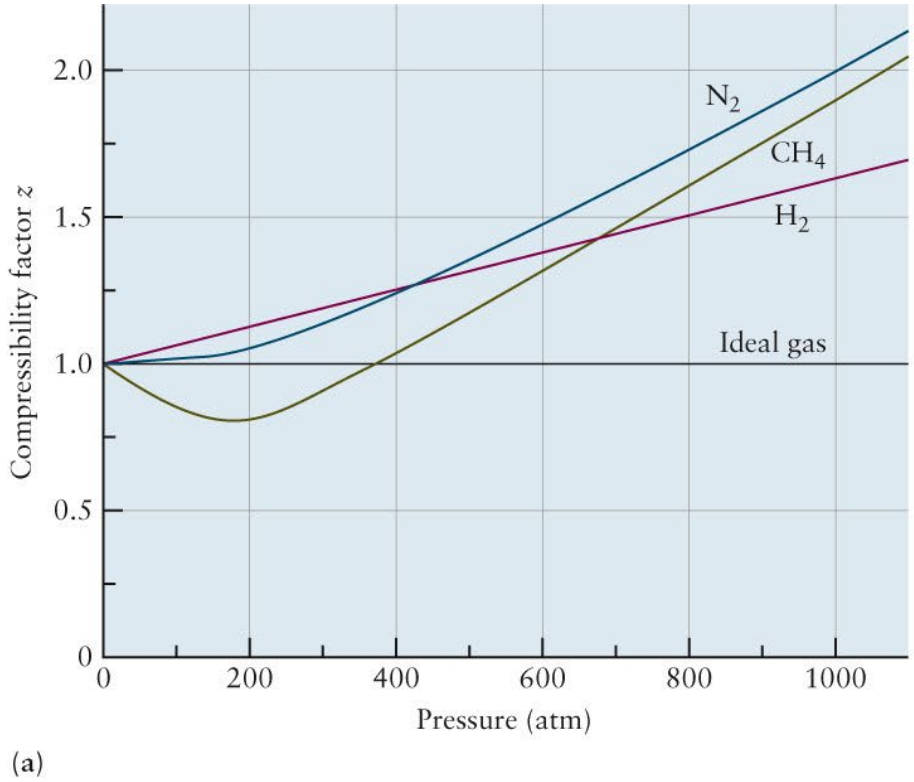
  deviation from $Z = 1$ as P ↑.

  $Z < 1$ for attractive force

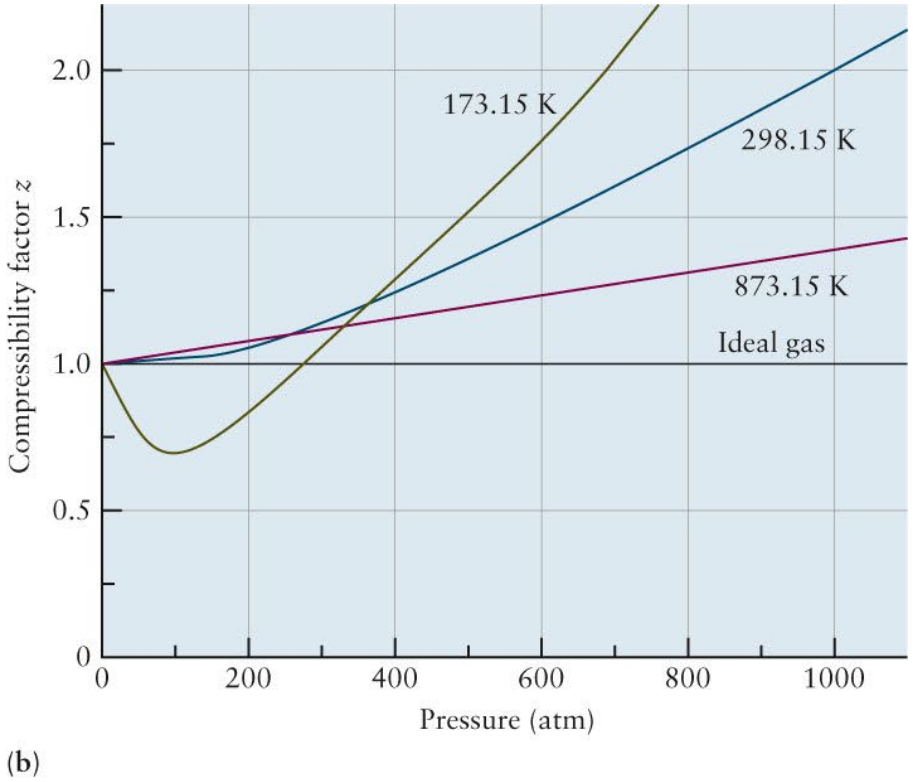
  $Z > 1$ for repulsion



z = PV/nRT


Compressibility factor z
2.0
1.5
1.0
0.5
0
0
200
400
600
800
1000
Pressure (atm)
N_2
CH_4
H_2
Ideal gas

(a)


Compressibility factor z
2.0
1.5
1.0
0.5
0
0
200
400
600
800
1000
Pressure (atm)
173.15 K
298.15 K
873.15 K
Ideal gas

(b)

The Van der Waals Equation of State

Corrections to the ideal equation of state

- Attraction at long distance:

  Reduction in collision frequency $\propto n/V$

  Reduction in intensity of collision $\propto n/V$

$$P_{\text{ideal}} = P + a\frac{n^2}{V^2}$$

- Repulsion at short distance :

  No overlap of molecules → excluded volume effect

  Reduction in free volume $\propto n$

$$V_{\text{ideal}} = V - bn$$

Van der Waals equation:

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

a: atm L^2 mol^{-2}

b: L mol^{-1}

R: L atm mol^{-1} K^{-1}

- $z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{a}{RT}\frac{n}{V} = \frac{1}{1 - \frac{bn}{V}} - \frac{a}{RT}\frac{n}{V}$

Repulsive forces (through b) increase z above 1.

Attractive forces (through a) reduce z.

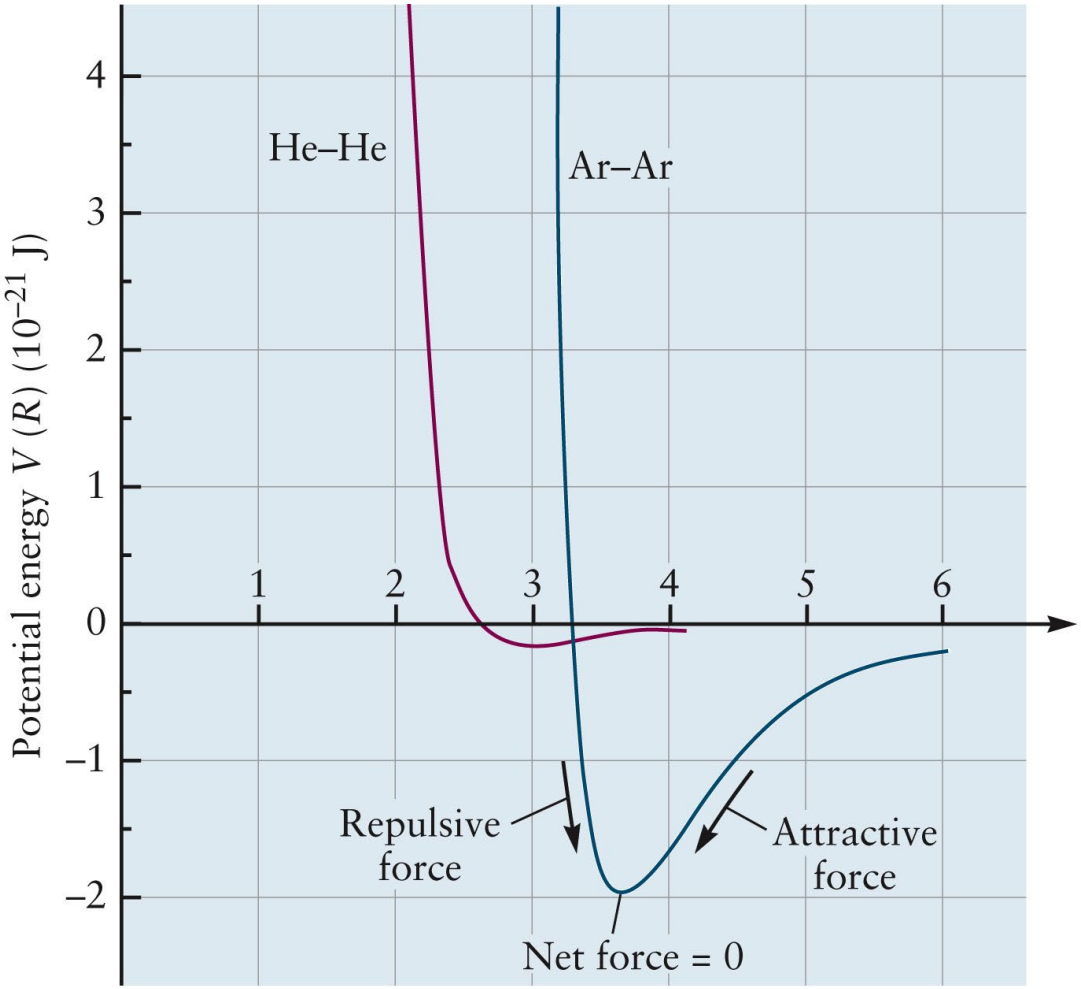
- Constant b is the volume excluded by 1 mol of molecules and should be close to V_m, the volume per mole in the liquid state.

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_2O	5.464	0.03049

◆ Intermolecular Forces



➢ Lennard-Jones Potential:

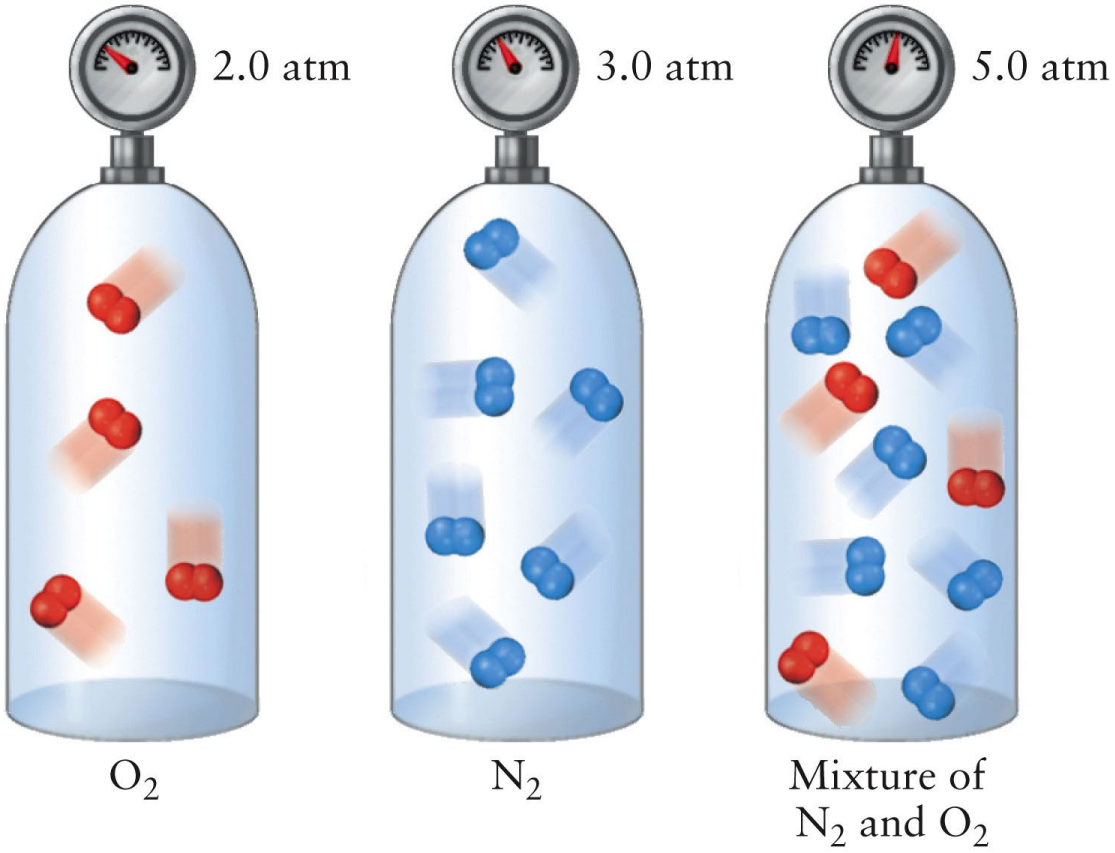
$$V_{LJ}(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$

where ε is the depth and σ is the distance at which $V(R)$ passes through zero.

→ The two parameters ε and σ in the Lennard–Jones potential, like the van der Waals parameters a and b, are simple ways of characterizing the interactions between molecules in real gases.

TABLE 9.4

Lennard–Jones Parameters for Atoms and Molecules

Substance	σ(m)	ε(J)
He	2.56×10^{-10}	1.41×10^{-22}
Ne	2.75×10^{-10}	4.92×10^{-22}
Ar	3.40×10^{-10}	1.654×10^{-21}
Kr	3.60×10^{-10}	2.36×10^{-21}
Xe	4.10×10^{-10}	3.06×10^{-21}
H_2	2.93×10^{-10}	5.11×10^{-22}
O_2	3.58×10^{-10}	1.622×10^{-21}
CO	3.76×10^{-10}	1.383×10^{-21}
N_2	3.70×10^{-10}	1.312×10^{-21}
CH_4	3.82×10^{-10}	2.045×10^{-21}

Key question: how can we describe molecular behaviors in the gaseous state?