

General Chemistry

Chapter 5

Chapter 5 Gases

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- 5.1 Pressure
- 5.2 Gas Laws
- 5.3 The Ideal Gas Law
- 5.4 Gas stoichiometry
- 5.5 Dalton's Law
- 5.6 Kinetic molecular Theory
- 5.7 Effusion and Diffusion
- 5.8 Real Gases
- 5.9 Chemistry in the atmosphere

§ 5.1 Pressure

barometer: 氣壓計 a device to measure atmosphere pressure

units of pressure: mm Hg = torr

standard atmosphere (atm)

$$1 \text{ standard atmosphere} = 1 \text{ atm} = 760 \text{ mm Hg} \\ = 760 \text{ torr}$$

SI unit: (Newton/m²), 又稱 **Pascal (Pa)**

$$1 \text{ atm} = 101,325 \text{ Pa} \doteq 10^5 \text{ Pa} = 10^2 \text{ kPa}$$

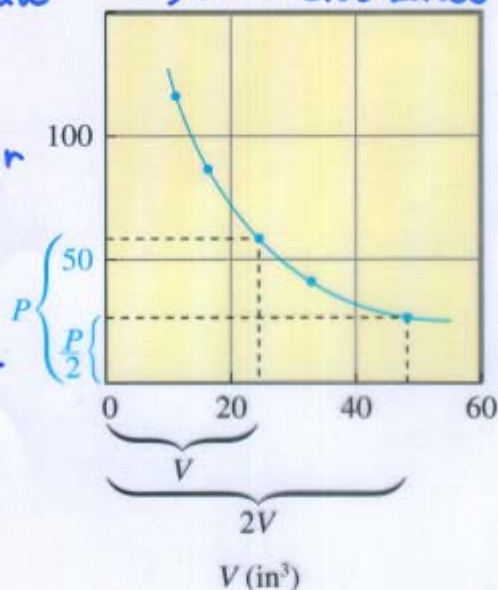
§ Boyle's Law
 $PV = k$

§ 5-2 Gas Laws

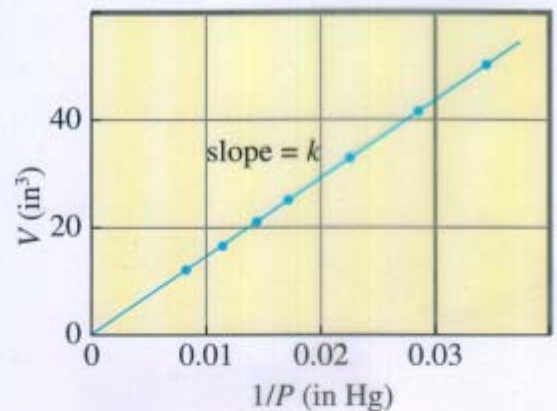
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k : a const for
 a given
 sample of air
 at a specific
 temperature



(a)



(b)

Figure 5.5
Plotting Boyle's data

§ The Gas Laws of Boyle, Charles,
and Avogadro

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Boyle's law: (-1650 AD)

$$PV = k$$

Charles' law (1787 AD)

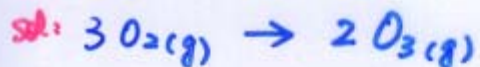
$$V = bT \quad (T \text{ in Kelvins})$$

see page 194, Fig 5.8 & 5.9 K

Avogadro's law (1811 AD)

$$V = an$$

Sample Ex. 5.5



0.50 mol O_2

0

0.33 mol O_3

$$V = an$$

$$\therefore \frac{V_1}{V_2} = \frac{n_1}{n_2}$$

$$\frac{12.2 L}{V_2} = \frac{0.50 \text{ mol}}{0.33 \text{ mol}}$$

$$\therefore V_2 (O_3) = 8.1 L$$

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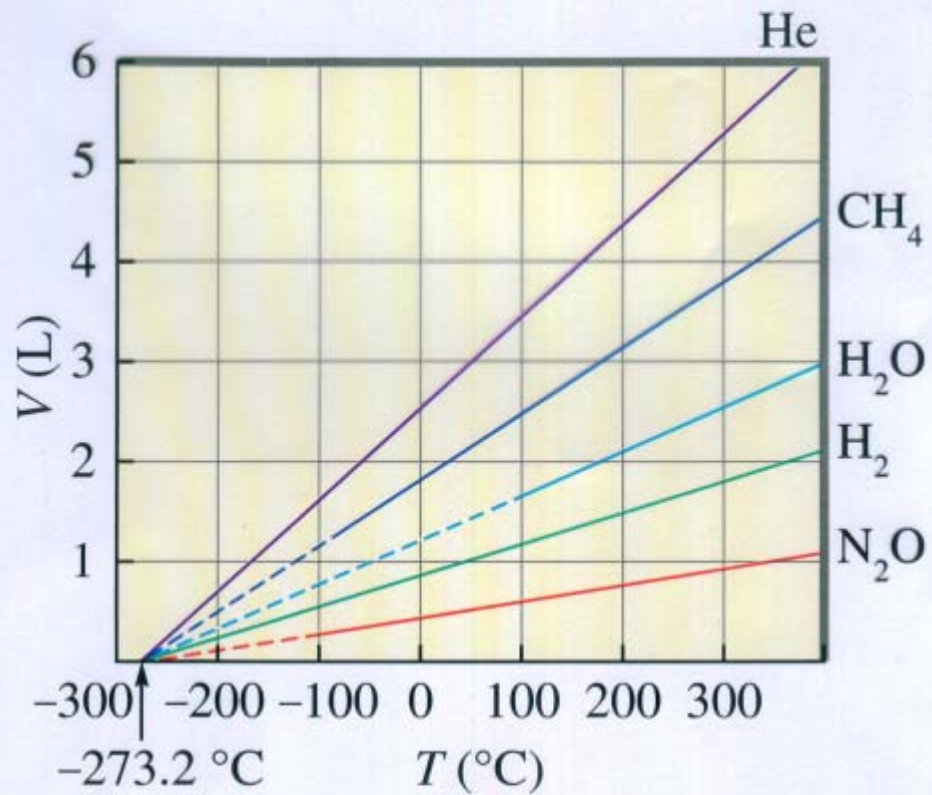


Figure 5.8
Plots of V versus T

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§§ The Ideal Gas Law

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$$PV = nRT$$

R = universal gas const

$$0.08206 \text{ L} \cdot \text{atm} / \text{K} \cdot \text{mol}$$

at low pressure, high temperature
real gas can be expressed by ~~this~~
ideal gas law.

Ex. 5.6 - 5.10

5.4 Gas Stoichiometry

Molar volume: 1 mole of an ideal gas at 0°C (273K) and 1atm . the volume of gas (≈ 22.42 liters) is the molar volume.

Standard Temperature and Pressure (STP)

The conditions 0°C and 1atm

Ex. 5.11

Question: $\text{N}_2(\text{g})$ has a volume of 1.75L at STP
How many moles are present?

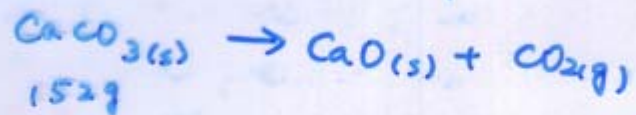
sol:

$$\frac{1.75\text{ L N}_2}{22.42 \frac{\text{L}}{\text{mole}}} = 7.81 \times 10^{-2} \text{ mol N}_2$$

See Table 5.2

He , H_2 are the gases which are closest to the definition of 'ideal gas'

Ex 5.12 Thermal decomposition of calcium carbonate ⁵⁻⁷
-ate



$$\frac{152g}{100.09 \frac{g}{\text{mol}}} = 1.52 \text{ mol CaCO}_3$$

$$1.52 \text{ mol} \times 22.42 \frac{\text{L}}{\text{mol}} = 34.1 \text{ L CO}_2 \neq$$

Molar ~~gas~~ Mass of a Gas

$$PV = nRT$$
$$= \left(\frac{\text{mass}}{\text{molar mass}} \right) RT$$

$$\text{Molar mass} = \frac{(\text{mass}) RT}{PV}$$
$$= \frac{\left(\frac{\text{mass}}{V} \right) RT}{P} = \frac{dRT}{P}$$

Ex 5.14

§ 5.5 Dalton's Law of Partial Pressures 5-8

For a mixture of gases in a container, the total pressure exerted is the **sum** of the pressures that each gas would exert if it were alone.

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$$

The symbols P_1, P_2, P_3 : **partial pressure** of individual gas 1, gas 2, ...

$$P_{\text{total}} = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \dots$$
$$= \underline{n_{\text{total}}} \left(\frac{RT}{V} \right)$$

total mole # of particles

mole fraction : the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

$$X_1 = \frac{n_1}{n_{\text{total}}} = \frac{P_1 \left(\frac{V}{RT} \right)}{P_1 \left(\frac{V}{RT} \right) + P_2 \left(\frac{V}{RT} \right) + P_3 \left(\frac{V}{RT} \right) \dots}$$
$$= \frac{P_1}{P_1 + P_2 + \dots} = \frac{P_1}{P_{\text{total}}}$$

Ex. 5.15 - 5.17

Fig 5.13

Ex 5.18

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§ 5.6 The Kinetic Molecular Theory of Gases
Kinetic molecular theory (KMT): a simple model that attempts to explain the properties of an ideal gas. This model is based on speculations about the behavior of individual gas particles

1. The particles are so small
2. in const motion,

The ~~gas~~ particles' collisions w/ the walls of the container are the cause of the pressure.

3. The particles are assumed to exert no force to each other
4. The average kinetic energy of a collection of gas particles is assumed to be directly proportional to the Kelvin temp of the gas.

How to use KMT to explain the laws of gases ?

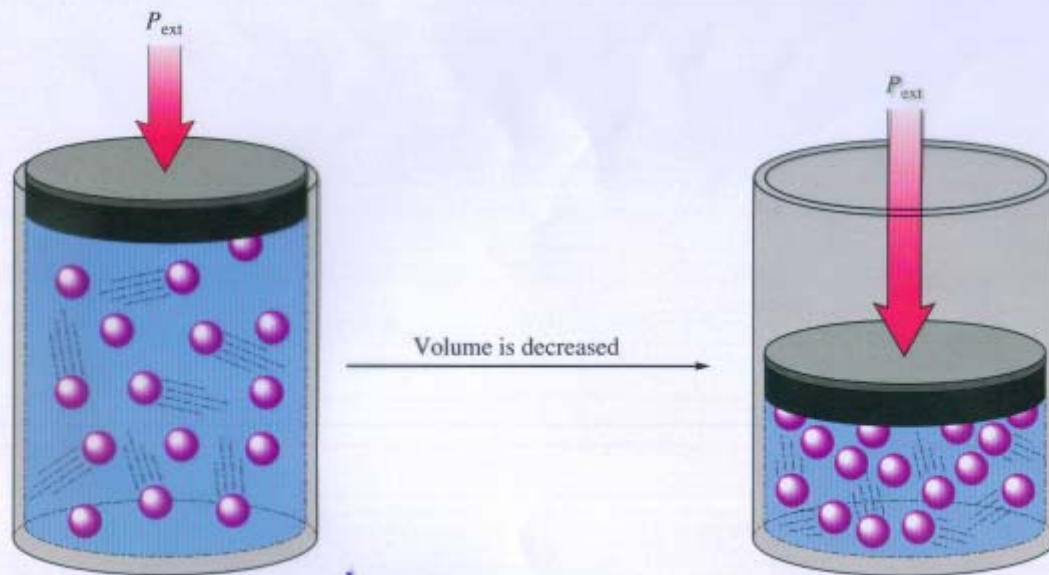


Figure 5.14
Decreasing V of a sample of gas at constant T

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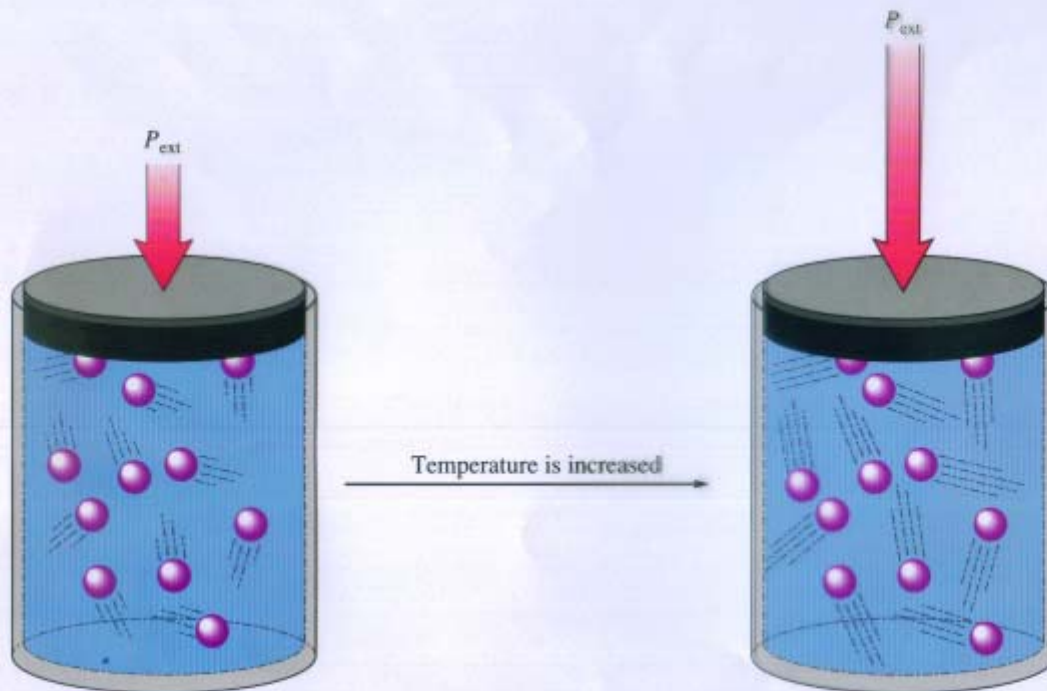


Figure 5.15
Increasing T of a sample of gas at constant V

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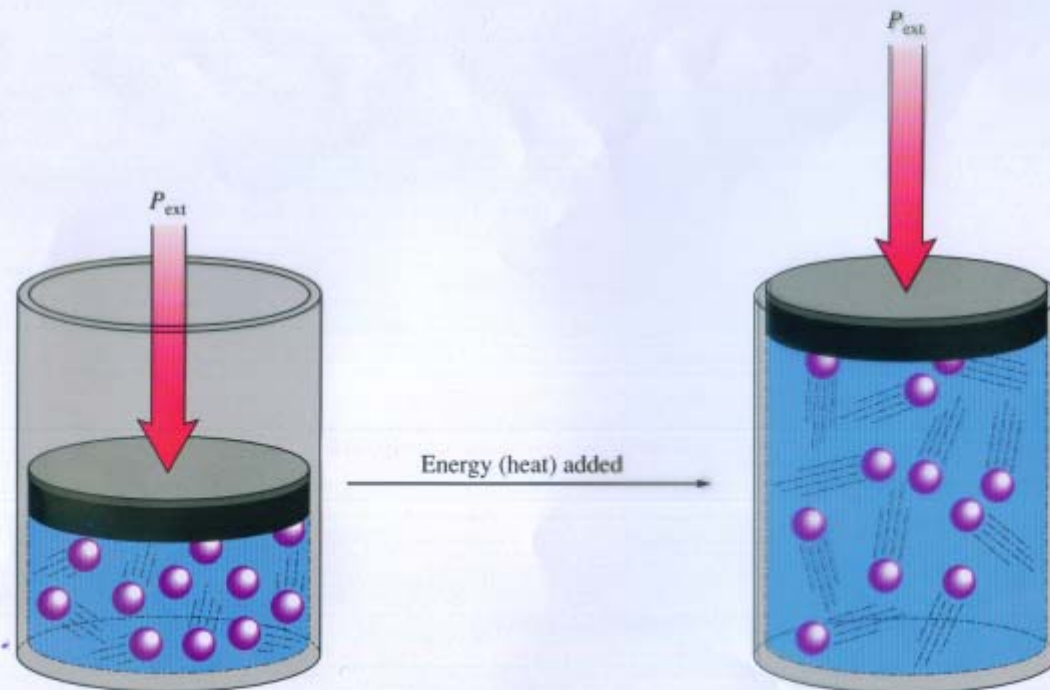


Figure 5.16
Increasing T of a sample of gas at constant P

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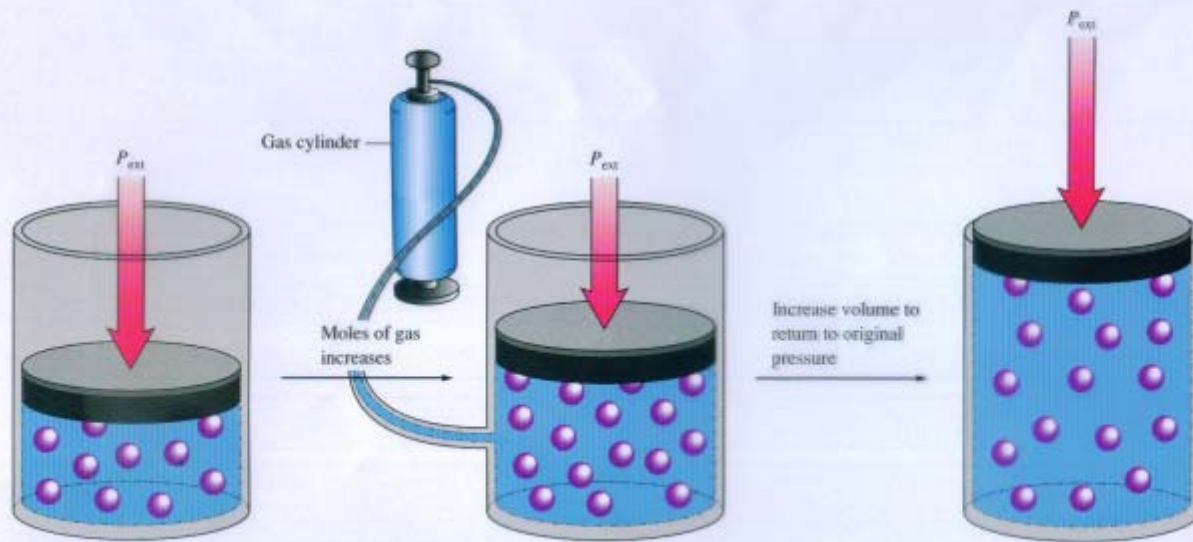


Figure 5.17
Increasing the number of moles of gas particles at constant P and T

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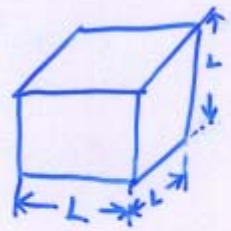
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- P7
5-14
- a. Pressure v.s volume (Boyle's law)
 - b. Pressure and temp
 - c. volume and temp (Charles' law)
 - d. volume and number of moles (Avogadro's law)
 - e. mixture of gases (Dalton's law)

Deriving the Ideal Gas Law

$$P = \frac{2}{3} \left[\frac{\overset{\text{\# of moles}}{n} N_A \left(\frac{1}{2} m \overline{u^2} \right)}{V} \right]$$

↑ pressure
 ↓ Avogadro's number
 → Average kinetic energy of a gas particle



Assume n moles of particles
in a cubical container

elastic collision: no loss of Kinetic energy

velocity of a gas particle (u)

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

(collision frequency)_x = $\frac{\text{velocity in the x direction}}{\text{distance between the wall}}$

↑
collisions per unit of time = $\frac{u_x}{L}$

the force of a collision (F)

$$F = ma = m \left(\frac{\Delta u}{\Delta t} \right) = \frac{\Delta m u}{\Delta t} = \frac{\text{change in momentum}}{\text{unit time}}$$

$$F_x = \frac{(\Delta m u)_x}{\Delta t} ; F_y = \frac{(\Delta m u)_y}{\Delta t} ; F_z = \frac{(\Delta m u)_z}{\Delta t}$$

弹性碰撞是 elastic collision

$$\begin{aligned} F_x &= \frac{(\Delta m u)_x}{\Delta t} = \frac{(-m u_x) - (m u_x)}{\Delta t} \\ &= - \frac{2m u_x}{\Delta t} \quad (\text{方向是相对的}) \\ &= \frac{2m u_x}{\left(\frac{L}{u_x}\right)} = \frac{2m u_x^2}{L} \end{aligned}$$



$$\begin{aligned}
 \text{Force total} &= F_x + F_y + F_z \\
 &= \frac{2m u_x^2}{L} + \frac{2m u_y^2}{L} + \frac{2m u_z^2}{L} \\
 &= \frac{2m}{L} (u_x^2 + u_y^2 + u_z^2) \\
 &= \frac{2m}{L} (u^2) \quad (\text{for a gas particle w/ velocity } u)
 \end{aligned}$$

Average force:

$$\overline{\text{Force total}} = \frac{2m}{L} (\overline{u^2})$$

$\overline{u^2}$: the average of the square of the velocity

Pressure due to "average" particle

$$= \frac{\text{Force total}}{\text{area total}} = \frac{2m \overline{u^2} / L}{6L^2} = \frac{m \overline{u^2}}{3L^3}$$

$$\therefore \text{Pressure} = \frac{m \overline{u^2}}{3L^3} = \frac{m \overline{u^2}}{3V} \quad (\text{for an "average" particle})$$

$$\begin{aligned}
 \text{Pressure} &= \overset{\substack{\uparrow \\ \text{Avogadro's } N_A}}{(n N_A)} \frac{m \overline{u^2}}{3V} \\
 &= \left(\frac{2}{3}\right) (n N_A) \frac{\frac{1}{2} m \overline{u^2}}{V}
 \end{aligned}$$

$$\begin{aligned}
 PV &= \left(\frac{2}{3}\right) (n N_A) \left(\frac{1}{2} m \overline{u^2}\right) \\
 &\quad \quad \quad \uparrow \\
 &\quad \quad \quad \text{kinetic energy}
 \end{aligned}$$

Deriving the Ideal Gas Law

$$P = \frac{2}{3} \left[\frac{n N_A \left(\frac{1}{2} m \bar{u}^2 \right)}{V} \right]$$

P : pressure of the gas

n : number of moles of gas

N_A : Avogadro's number

m : mass of each particle

\bar{u}^2 : the average of the squares of the velocities of the particles.

V : the volume of the container

$\frac{1}{2} m \bar{u}^2$: average kinetic energy of a gas particle.

$N_A \left(\frac{1}{2} m \bar{u}^2 \right) = (K.E.)_{avg}$: average kinetic energy of a mole of gas particles

$$\therefore PV = \frac{2}{3} n (K.E.)_{avg}$$

$$\frac{PV}{n} = \frac{2}{3} (\text{K.E.})_{\text{avg}} \quad \text{--- (1)}$$

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(1) From the fourth postulate of KMT:

$$(\text{K.E.})_{\text{avg}} \propto T \quad \text{理論假說得到 --- (2)}$$

Kelvin temp

(2) From ideal gas law

$$\frac{PV}{n} = RT \quad \text{實驗得到 --- (3)}$$

將式 (1), (3) 合起來

$$\frac{PV}{n} = RT = \frac{2}{3} (\text{K.E.})_{\text{avg}}$$

$$\therefore (\text{K.E.})_{\text{avg}} = \frac{3}{2} RT \quad \text{--- (4)}$$

#

$$\therefore (\text{K.E.})_{\text{avg}} = N_A \left(\frac{1}{2} m \bar{u}^2 \right)$$

式(4)代入

$$\frac{3}{2} RT = N_A \left(\frac{1}{2} m \bar{u}^2 \right)$$

$$\therefore \frac{3RT}{N_A \cdot m} = \bar{u}^2 \quad N_A \cdot m = M$$

$$\sqrt{\frac{3RT}{M}} = \sqrt{\bar{u}^2} = \bar{u}_{\text{rms}}$$

Root mean square velocity

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

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K}}$$

$$8.3145 \text{ J/K}$$

$$\text{J (joule)}: \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

Ex: 5.19:

Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C.

Sol:

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

$$= \sqrt{\frac{3 \cdot 8.3145 \cdot (273+25)}{(4.00 \times 10^{-3} \text{ kg})}}$$

$$= \sqrt{1.86 \times 10^6} = 1.36 \times 10^3 \text{ m/s}$$

Root Mean Square velocity of helium

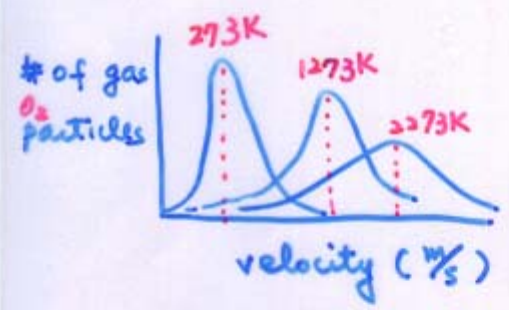
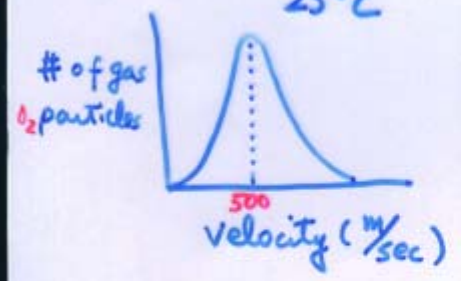
$$\text{單位: } \sqrt{\frac{\frac{\text{J}}{\text{K}} \cdot \text{K}}{\text{kg}}} = \sqrt{\frac{\text{J}}{\text{kg}}} = \sqrt{\frac{\frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}{\text{kg}}} = \sqrt{\frac{\text{m}^2}{\text{s}^2}} = \frac{\text{m}}{\text{s}}$$

Root mean square velocity of O₂

$$\sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \cdot 8.314 \cdot (273+25)}{32.00 \times 10^{-3}}}$$

$$\doteq \sqrt{\frac{3 \cdot 8.314 \cdot 298}{32 \times 10^{-3}}} \doteq \sqrt{\frac{900 \cdot 298}{32 \times 10^{-3}}} \doteq \sqrt{225 \cdot 10^3} \doteq 500 \text{ m/s}$$

实际速度分佈：(∵ 会碰撞其它 O₂ 分子 将动能交换)
25°C



Mean Free Path: The average distance a particle travels between collisions in a gas sample. (1×10^{-7} m for O₂ at STP)

very small

Effusion:

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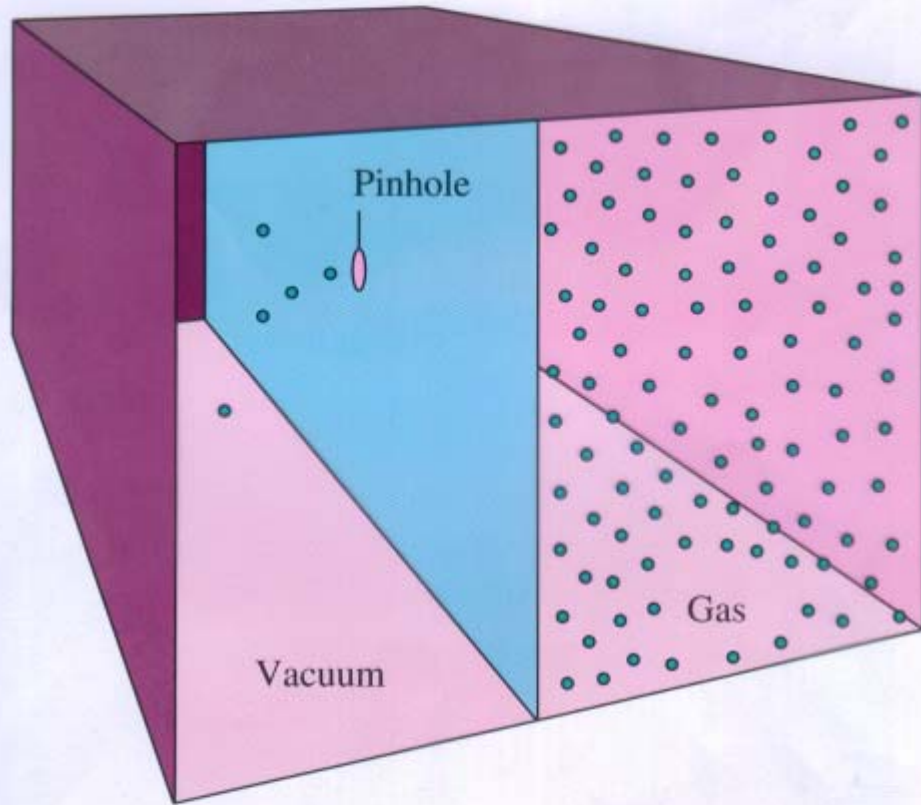


Figure 5.21
Effusion of a gas



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§ 5.7 Effusion and Diffusion

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Effusion: the passage of a gas through a tiny orifice into an evacuated chamber. see Fig. 5.21

Diffusion: describe the mixing of gases

Graham's law of effusion:

$$\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \quad \begin{array}{l} M: \text{molar} \\ \text{mass} \end{array}$$

— 实验式

From KMT:

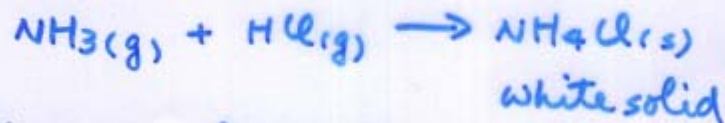
$$\frac{u_{\text{rms for gas 1}}}{u_{\text{rms for gas 2}}} = \frac{\sqrt{\frac{3RT}{M_1}}}{\sqrt{\frac{3RT}{M_2}}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

— 理论式

∴ Kinetic molecular Theory (KMT) does fit the experimental data for the effusion of gases.

Diffusion (Describing The mixing of gases)

§ 5.23 (page 224)



$$\frac{\text{Distance traveled by NH}_3}{\text{Distance traveled by HCl}} = \frac{u_{\text{rms for NH}_3}}{u_{\text{rms for HCl}}}$$

from KMT 理論

$$= \frac{\sqrt{M_{\text{HCl}}}}{\sqrt{M_{\text{NH}_3}}} = \frac{\sqrt{36.5}}{\sqrt{17}} \doteq 1.5$$

However, KMT doesn't fit the diffusion experiment data.

$$\left(\begin{array}{l} \text{HCl} \quad 450 \text{ m/s} \\ \text{NH}_3 \quad 660 \text{ m/s} \end{array} \right) \text{ from KMT })$$

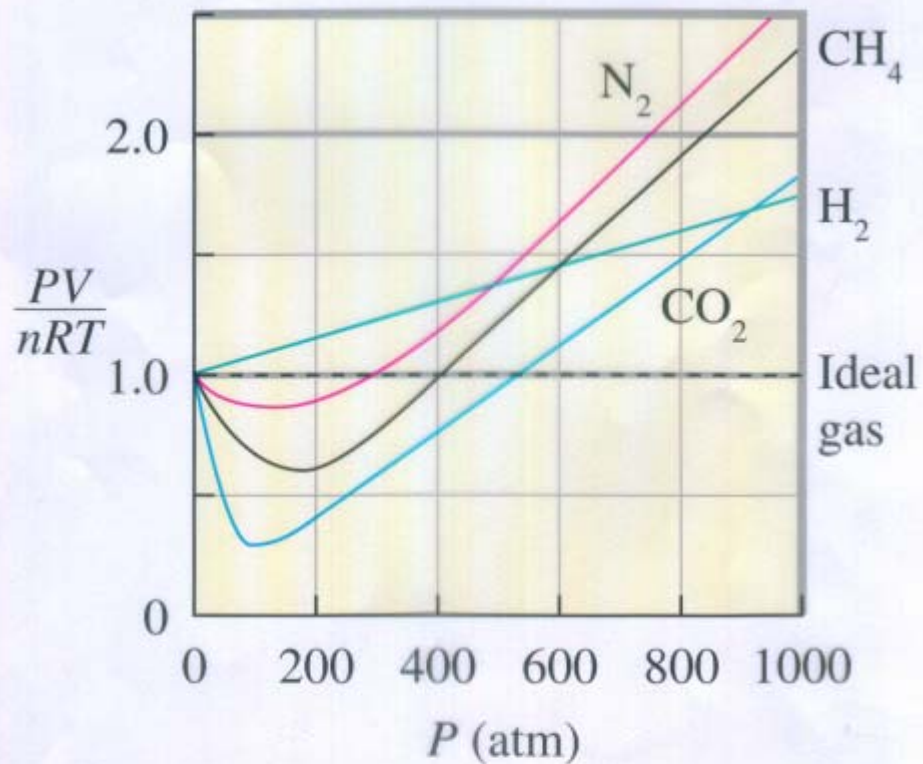
但需花數分鐘 for HCl . NH₃ to mix)

§ 5.8 Real Gases

"Ideal" Gas Law : $PV = nRT$

No gas follows the ideal gas law exactly

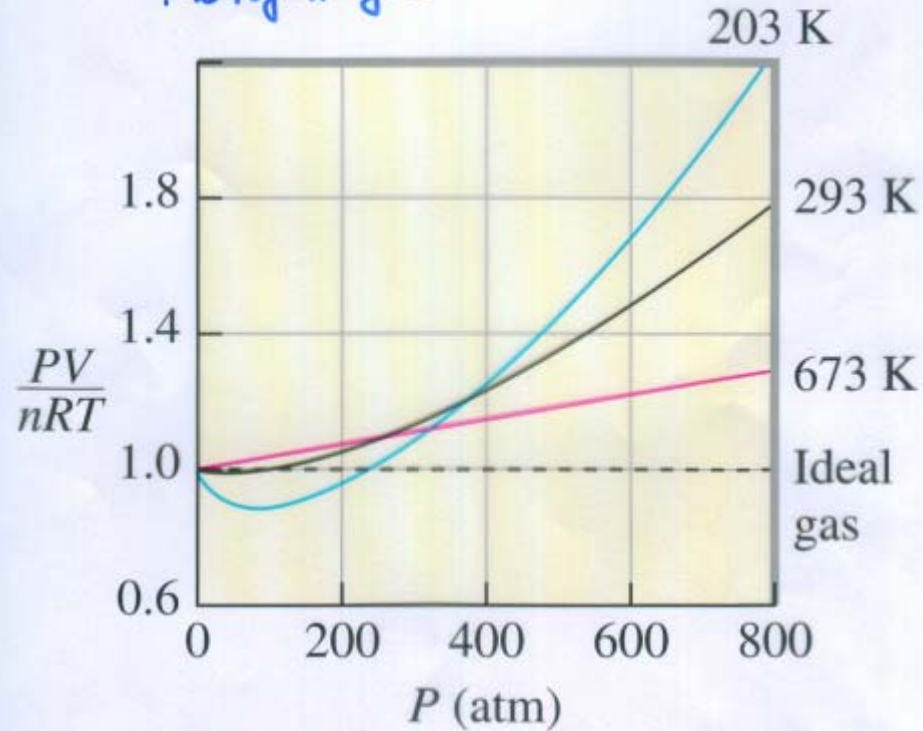
(∴ ideal gas : no interparticle interaction
zero volume for the gas particles)



very low pressure (< 1 atm)
approaches "ideal" gas

Figure 5.24
Plots of PV/nRT versus P

Nitrogen gas



very high temperature
approaches 'ideal' gas

Figure 5.25
Plots of PV/nRT versus P for N_2 gas

Real gas approaches ideal gas

only at low pressure

high temperature

Van der Waals (1910 Nobel prize)

↑ } ideal gas law to fit real gas

(I) ↓ } volume:

$$V_{obs} - nb$$

↑
of mol

empirical const
(实验得到)

(The volume actually available to a given gas molecule)

(II) ↓ } pressure:

$$P_{obs} + a \left(\frac{n}{V}\right)^2$$

see Fig 5.26 & 5.27

the # of interaction pairs of particles

$$\propto \left(\frac{n}{V}\right)^2$$

(假设 N particles)

$$\Rightarrow \text{interaction pairs} = \frac{N(N-1)}{2} \approx \frac{N^2}{2}$$

a: correction const
empirical const
(实验得到)

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

ideal pressure

ideal volume

see Table 5.3

Ex. 85 (page 235) calculate the pressure
0.5000 mol N_2 in a 1.0000-L container
at $25^\circ C$

(a) use ideal gas law

(b) use van der Waals equation

(c) compare the results

Sol:

(a) $PV = nRT$

$$P = \frac{nRT}{V} = \frac{0.5000 \cdot 0.08206 \cdot (273.15 + 25)}{1.0000} = 12.24 \text{ atm}$$

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

$$\left[P + 1.39 \left(\frac{0.5000}{1.0000} \right)^2 \right] \left[1.0000 - 0.5000 \times 0.0391 \right] = 12.24 \text{ atm} \cdot L$$

$$\therefore (P + 0.348) (0.9805 L) = 12.24 \text{ atm} \cdot L$$

$$\therefore P = 12.13 \text{ atm}$$