## Ch. 5 Gases

5-1: Measurements on gases1. Volume, Amount, and Temperature2. Pressure
5-2: The ideal gas law1. Volume is directly proportional to amount
2. Volume is directly proportional to absolute temperature
3. Volume is inversely proportional to pressure
5-3: Gas law calculation

1. Final and initial State Problems
2. Calculation of P, V, n, or T
3. Molar Mass and Density
5-4: Stoichiometry of gaseous reactions
5-5: Gas mixtures: partial pressures and mole fractions1. Wet Gases; Partial Pressure of Water2. Partial Pressure and Mole Fraction
5-6: Kinetic theory of Gases
4. Molecular Model
5. Expression for Pressure; $P$
6. Average Kinetic Energy of Translational Motion; $\mathrm{E}_{\mathrm{t}}$
7. Average Speed; u
8. Effusion of Gases; Graham's Law
9. Distribution of Molecular Speeds

## 5-7: Real gases

1. Attractive Forces
2. Particle Volume

## Ch． 5 Gases

The Greeks：
Four fundamental element of nature：Air，earth，water and fire．

$$
V \equiv f(P, T, n) \Rightarrow P V=n R T
$$

## § 5－1 Measurements on Gases（V，n，T，P）

Volume：

$$
1 \mathrm{~L}=10^{3} \mathrm{~cm}^{3}=10^{-3} \mathrm{~m}^{3}
$$

Amount：The amount of matter in a gaseous sample is expressed in terms of the number of moles．
n：mol
$\mathrm{m}=\mathrm{MM} \times \mathrm{n} \quad \mathrm{m}$ ：mass $\quad$ MM：molar mass
Temperature：in any calculation involving the physical behavior of gases， temperatures must be expressed on the Kelvin scale．

$$
\begin{aligned}
T_{K} & =T_{\mathrm{C}}+273.15 \\
\Rightarrow T_{K} & =T_{\mathrm{C}}+273 \quad \text { 所有計算中之 } \mathrm{T} \text { 一律以 } \mathrm{K} \text { 爲單位 } \\
& \rightarrow \text { absolute temperature }
\end{aligned}
$$

Pressure：
Force per unit area．單位： $\mathrm{lb} / \mathrm{in}^{2} \Rightarrow \mathrm{psi} \quad$（pound per square inch）
Mercury barometer：
Constructed by E．Torricelli 托里切利 in 17th century．
$\longrightarrow$ 測大氣壓力 Fig．5．1 atmospheric pressure
At or near sea level，atmospheric pressure： $740-760 \mathrm{mmHg}$
$1 \mathrm{~atm}=760 \mathrm{mmHg}=760$ torr

$$
\Rightarrow 1 \mathrm{mmHg}=1 \text { torr }
$$

International system P 之單位：Pascal（Pa）

$$
1 \mathrm{~Pa}=1 \mathrm{~N} / \mathrm{m}^{2}
$$

單位換算：

$$
1 \mathrm{~atm}=760 \mathrm{mmHg}=1.013 \mathrm{bar}=1.013 \times 10^{5} \mathrm{~Pa}=14.7 \mathrm{psi}
$$

$1 \mathrm{bar}=10^{5} \mathrm{~Pa}=0.987 \mathrm{~atm}$

Ex 5.1 ：At room temperature，dry ice（solid $\mathrm{CO}_{2}$ ）becomes a gas．At $77^{\circ} \mathrm{F}, 13.6 \mathrm{oz}$ of dry ice are put into a steel tank with a volume of $10.00 \mathrm{ft}^{3}$ ．The tank＇s pressure gauge registers 11.2 psi．Express（a）．the volume（V）of the tank in liters，（b）．the amount of in $\mathrm{CO}_{2}$ in grams and moles（n），（c）．the temperature（T）in ${ }^{\circ} \mathrm{C}$ and K and（d）．the pressure（ P ）in bars， mmHg ，and atmospheres．
Ans：
a）．$\quad V=10.00 \mathrm{ft}^{3} \times \frac{28.32 \mathrm{~L}}{1 \mathrm{ft}^{3}}=283.2 \mathrm{~L}$
b）．$m=13.6 \mathrm{oz} \times \frac{28.35 \mathrm{~g}}{1 \mathrm{oz}}=386 \mathrm{~g}$
$n_{\mathrm{CO}_{2}}=\frac{386}{44.01}=8.77 \mathrm{~mol}$
c）． $\mathrm{T}_{{ }^{\circ} \mathrm{C}}=\frac{77-32}{1.8}=25^{\circ} \mathrm{C}$
$\mathrm{T}_{K}=25+273=298 \mathrm{~K}$
d）． $\mathrm{P}=11.2 \mathrm{psi} \times \frac{1 \mathrm{~atm}}{14.7 \mathrm{psi}}=0.762 \mathrm{~atm}$
$\mathrm{P}=0.762 \mathrm{~atm} \times \frac{760 \mathrm{mmHg}}{1 \mathrm{~atm}}=579 \mathrm{mmHg}$
$\mathrm{P}=0.762 \mathrm{~atm} \times \frac{1.013 \mathrm{bar}}{1 \mathrm{~atm}}=0.772 \mathrm{bar}$

## § 5－2 The ideal gas law

$$
V \equiv f(n, T, P)
$$

1．Volume is directly proportional to amount．

$$
V=k_{1} n \quad(\text { constant T, P) } \quad \text { 給呂薩克定律 (Gay-Lussac law) }
$$

P． 106 Fig 5.3 （a）
Notice that the graph is straight line passing through the origin．
2．Volume is directly proportional to absolute temperature

$$
V=k_{2} T \quad(\text { constant } \mathrm{n}, \mathrm{P}) \quad \text { 查理定律 (Charles law) }
$$

3．Volume is inversely proportional to pressure

$$
\begin{aligned}
V=\frac{k_{3}}{P} \quad(\text { constant } \mathrm{n}, \mathrm{~T}) \quad \text { 波以耳定律 (Boyle law) } \\
V=k_{1} n ; \quad V=k_{2} T ; \quad V=\frac{k_{3}}{P}
\end{aligned}
$$

$\Rightarrow \quad V=$ constant $\times \frac{n \times \mathrm{T}}{P}$
Avogadro＇s law：equal volumes of all gases at the same temperature and pressure contain the same number of moles．
$\Downarrow$
$\therefore$ The constant must be the same for all gases．
$\therefore \quad P V=n R T \quad$ Ideal gas law
$\mathrm{R}: \quad 0^{\circ} \mathrm{C} 1 \mathrm{~atm} \Rightarrow$ STP：standard temperature and pressure

$$
\begin{array}{rlrl} 
& \mathrm{n}=1 \quad \mathrm{~V}=22.4 \mathrm{~L} \\
\Rightarrow \quad & R=\frac{P V}{n T}=\frac{1 \times 22.4}{1 \times(0+273)}=0.0821 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{~K} \rightarrow \text { 單位改變 } \mathrm{R} \text { 値改變 } \\
R= & 0.0821 \mathrm{~L} \cdot \mathrm{~atm} / \mathrm{mol} \cdot \mathrm{~K} \\
= & 0.08314 \mathrm{bar} / \mathrm{mol} \cdot \mathrm{~K} \\
= & 8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K} & & \\
= & 8.314 \times 10^{3} \mathrm{~g} \cdot \mathrm{~m}^{2} / \mathrm{S}^{2} \cdot \mathrm{~mol} \cdot \mathrm{~K} \cdot \mathrm{~atm}=101.3 \mathrm{~J} \\
& & 1 \mathrm{~J}=10^{3} \mathrm{~g} \cdot \mathrm{~m}^{2} / \mathrm{S}^{2}
\end{array}
$$

## § 5－3 Gas law calculations

1．The final state of a gas．Knowing its initial state and the changes in $\mathrm{P}, \mathrm{V}, \mathrm{n}$ or T．
2．Calculate one of the four variables， $\mathrm{P}, \mathrm{V}$ ， n or $\mathrm{T} . \quad \mathrm{PV}=\mathrm{nRT}$
3．The molar mass or density of a gas．$\quad \mathrm{PMM}=\mathrm{DRT}$

## § Final and initial state problems．

Starting a gas at $25^{\circ} \mathrm{C}, 1 \mathrm{~atm}$ ，when the gas is heated to $95^{\circ} \mathrm{C}$ at constant volume．$\Rightarrow$ final $P=$ ？

$$
\begin{aligned}
\frac{P_{1} V}{P_{2} V} & =\frac{n R T_{1}}{n R T_{2}} \quad \mathrm{n}, \mathrm{~V}=\mathrm{constant} \\
\Rightarrow \quad \frac{P_{1}}{P_{2}} & =\frac{T_{1}}{T_{2}} \\
\frac{1}{P_{2}} & =\frac{25+273}{95+273} \\
P_{2} & =\frac{368}{298}=1.23 \mathrm{~atm}
\end{aligned}
$$

Ex 5.2 ：A sealed 15.0 L steel tank is used to deliver propane $\left(\mathrm{C}_{3} \mathrm{H}_{8}\right)$ gas．It is filled with 24.6 g of propane at $27{ }^{\circ} \mathrm{C}$ ．The pressure gauge registers 0.915 atm ．
(Assume that the expansion of steel from an increase in temperature is negligible.)
(a) If the tank is heated to $58^{\circ} \mathrm{C}$, what is the pressure of propane in the tank?
(b) The tank is fitted with a valve to open and release propane to maintain the pressure at 1.200 atm . Will heating the tank to $58^{\circ} \mathrm{C}$ release propane?
(c) At $200{ }^{\circ} \mathrm{C}$, the pressure exceeds 1.200 atm . How much propane is release to maintain 1.200 atm pressure ?
Ans:
(a). $\frac{P_{1}}{T_{1}}=\frac{P_{2}}{T_{2}} \quad \mathrm{P}_{1}=0.915 \mathrm{~atm} ; \mathrm{T}_{1}=273+27=300 \mathrm{~K}$

$$
\mathrm{T}_{2}=273+58=331 \mathrm{~K}
$$

$$
\begin{aligned}
\frac{0.915}{300} & =\frac{P_{2}}{331} \\
\mathrm{P}_{2} & =1.01 \mathrm{~atm}
\end{aligned}
$$

(b). $\mathrm{Q} \mathrm{P}_{2}<1.200 \mathrm{~atm} \quad \therefore$ the valve will not open.
(c). $\frac{P_{1}}{n_{1} T_{1}}=\frac{P_{2}}{n_{2} T_{2}} \quad P_{1}=0.915 \mathrm{~atm} ; n_{1}=\frac{24.6}{12.01 \times 3+1.008 \times 8}=\frac{24.6}{44.09}=0.558 \mathrm{~mol}$ $\mathrm{T}_{1}=300 \mathrm{~K} ; \mathrm{P}_{2}=1.200 \mathrm{~atm} ; \mathrm{T}_{2}=200+273=473 \mathrm{~K}$
$\frac{0.915}{0.558 \times 300}=\frac{1.200}{n_{2} \times 473}$
$\mathrm{n}_{2}=0.464 \mathrm{~mol}$
$\mathrm{m}_{2}=0.464 \times 44.09=20.5 \mathrm{~g} \quad \mathrm{MM}_{C_{3} H_{8}}=12.01 \times 2+1.008 \times 8=44.09$
$\Delta \mathrm{m}=24.6-20.5=4.1 \mathrm{~g}$

## § Calculation of P, V, n or T

Ex 5-3: Sulfur hexafluoride, $S F_{6}(g)$ is a gas used as a long-term tamponade (plug) for a retinal hole to repair detached retinas in the eye. If 2.50 g of this compound is introduced into an evacuated 500.0 mL at $83^{\circ} \mathrm{C}$, what pressure in atmospheres is developed?
Ans : $\quad M M_{S F_{6}}=32.07+6 \times 19.00=146.07 \mathrm{~g} / \mathrm{mol}$

$$
\begin{aligned}
& \mathrm{P} \mathrm{~V}=\mathrm{n} \mathrm{R} \mathrm{~T} \quad \mathrm{~V}=500 \mathrm{~mL}=0.500 \mathrm{~L} \\
& \mathrm{P} \times 0.5000=\frac{2.50}{146.07} \times 0.0821 \times(83+273) \\
& 0.5000 \mathrm{P}=0.0171 \times 0.0821 \times 356 \\
& \mathrm{P}=1.00 \mathrm{~atm}
\end{aligned}
$$

## § Molar mass and density

All you need to know is the mass of a sample confined to a container of fixed volume at a particular temperature and pressure．

Ex 5－4：Acetone is widely used as a nail polish remover．A sample of liquid acetone is placed in 3.00 L flask and vaporized by heating to $95^{\circ} \mathrm{C}$ at 1.02 atm．The vapor filling the flask at this temperature and pressure，the vapor weight is 5.87 g ．
a）What is the density of acetone vapor under these conditions？
b）Calculate the molar mass of acetone？
c）Acetone contains the three elements，C，H and O．When 1.000 g of acetone is burned， $2.27 \mathrm{~g} \mathrm{CO}_{2}(\mathrm{~g})$ and $0.932 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ are formed．What is the molecular formula of acetone？
Ans：
a） Density $=\frac{\text { mass }}{V}=\frac{5.87}{3.00}=1.96 \mathrm{~g} / \mathrm{L}$
b）

$$
\mathrm{PV}=\mathrm{nRT}
$$

$$
\begin{aligned}
& 1.02 \times 3.00=\mathrm{n} \times 0.0821 \times(95+273) \\
& \mathrm{n}=0.101 \mathrm{~mol} \\
& \mathrm{n}=\frac{\mathrm{m}}{M M} \quad \Rightarrow \quad 0.101=\frac{5.87}{M M} \Rightarrow \mathrm{MM}=58.1 \mathrm{~g} / \mathrm{mol}
\end{aligned}
$$

c）

$$
\begin{aligned}
& \mathrm{C} \xrightarrow{\Delta} \mathrm{CO}_{2}(\mathrm{~g}) \\
& \mathrm{H} \xrightarrow{\Delta} \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
& m_{C}=2.27 \times \frac{12.01 \mathrm{~g} \mathrm{C}}{44.01 \mathrm{~g} \mathrm{CO}_{2}}=0.619 \mathrm{~g} \\
& \mathrm{~m}_{\mathrm{H}}=0.932 \times \frac{2.016 \mathrm{~g} \mathrm{H}}{18.02 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}}=0.104 \mathrm{~g} \\
& \mathrm{~m}_{o}=1.000-0.619-0.104=0.277 \mathrm{~g} \\
& \mathrm{C}: \mathrm{H}: \mathrm{O}=\frac{0.619}{12.01}: \frac{0.104}{1.008}: \frac{0.277}{16.00} \\
& =0.0515: 0.103: 0.0173 \\
& =3: \quad 6 \quad: \quad 1 \\
& \therefore \mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O} \Rightarrow \stackrel{\mathrm{CH}_{3}-\mathrm{C}-\mathrm{CH}_{3}}{\circ} \text { 示性式 }
\end{aligned}
$$

## § Density

$$
\begin{aligned}
& P V=n R T \\
& P V=\frac{m}{(M M)} R T \\
& P(M M)=\frac{m}{V} R T \\
& P(M M)=D R T \\
& D=\frac{P(M M)}{R T}
\end{aligned}
$$

| $\therefore$ | $\mathrm{P} \uparrow$ | $\mathrm{D} \uparrow$ |
| :---: | :---: | :---: |
|  | $\mathrm{T} \uparrow$ | $\mathrm{D} \downarrow$ |
|  | $\mathrm{MM} \uparrow$ | $\mathrm{D} \uparrow$ |

## § 5-4 Stoichiometry of gaseous reactions.

Ex 5-5: Hydrogen peroxide, $\mathrm{H}_{2} \mathrm{O}_{2}$, is a common bleaching agent. It decomposes quickly to water and oxygen gas at high temperatures.

$$
2 \mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{I}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{O}_{2}(\mathrm{~g})
$$

How many liters of oxygen are produced at $78{ }^{\circ} \mathrm{C}$ and 0.934 atm when $1.27 \mathrm{~L}^{\text {of }} \mathrm{H}_{2} \mathrm{O}_{2}(\mathrm{~d}=1.00 \mathrm{~g} / \mathrm{mL})$ decompose?
Ans :

$$
\begin{aligned}
& m_{H_{2} O_{2}}=1.27 \mathrm{~L} \times \frac{1000 \mathrm{~mL}}{1 \mathrm{~L}} \times 1.00 \mathrm{~g} / \mathrm{mL}=1270 \mathrm{~g} \\
& n_{H_{2} O_{2}}=\frac{1270}{1.008 \times 2+16.00 \times 2}=37.3 \mathrm{~mol} \\
& n_{H_{2} O_{2}}: n_{O_{2}}=2: 1 \\
& 37.3: n_{O_{2}}=2: 1 \\
& \quad n_{O_{2}}=18.7 \mathrm{~mol} \\
& \mathrm{~V}_{O_{2}}=\frac{n R T}{P}=\frac{18.7 \times 0.0821 \times(78+273)}{0.934}=577 \mathrm{~L}
\end{aligned}
$$

Ex 5-6: Sodium bicarbonate (baking soda) is widely used to absorb odors inside refrigerators. When acid is added to baking soda, the following reaction occurs:

$$
\mathrm{NaHCO}_{3}(s)+\mathrm{H}^{+}(a q) \rightarrow \mathrm{Na}^{+}(a q)+\mathrm{CO}_{2}(g)+\mathrm{H}_{2} \mathrm{O}
$$

All experiments here are performed with 2.45 M HCl and 12.75 g of $\mathrm{NaHCO}_{3}$ at 732 mmHg and $38^{\circ} \mathrm{C}$.
(a) If an excess of HCl is used, what volume of $\mathrm{CO}_{2}$ is obtained?
(b) If $\mathrm{NaHCO}_{3}$ is in excess, what volume of HCl is required to produce $2.65 \mathrm{~L}^{\text {of } \mathrm{CO}_{2}}$ ?
(c) What volume of $\mathrm{CO}_{2}$ is produced when all the $\mathrm{NaHCO}_{3}$ is made to react with 50.0 mL of HCl ?
Ans:
（a）． $\mathrm{n}_{\mathrm{NaHCO}_{3}}=\frac{12.75 \mathrm{~g}}{22.99+1.008+12.01+16.00 \times 3}=\frac{12.75}{84.01}=0.1518 \mathrm{~mol}$

$$
\mathrm{n}_{\mathrm{NaHCO}_{3}}: \mathrm{n}_{\mathrm{CO}_{2}}=1: 1
$$

$$
0.1518: \mathrm{n}_{C O_{2}}=1: 1
$$

$$
\mathrm{n}_{C O_{2}}=0.1518 \mathrm{~mol}
$$

$$
\mathrm{V}_{C O_{2}}=\frac{n R T}{P}=\frac{0.1518 \times 0.0821 \times(38+273)}{732 / 760}=4.02 \mathrm{~L}
$$

$$
\text { (b). } \mathrm{n}_{\mathrm{CO}_{2}}=\frac{P V}{R T}=\frac{732 / 760 \times 2.65}{0.0821 \times(38+273)}=0.100 \mathrm{~mol}
$$

$$
\mathrm{n}_{H^{+}}: \mathrm{n}_{C O_{2}}=1: 1
$$

$$
\mathrm{n}_{H^{+}}: 0.100=1: 1
$$

$$
\mathrm{n}_{H^{+}}=0.100 \mathrm{~mol}
$$

$$
\mathrm{V}_{H^{+}}=\frac{n_{H^{+}}}{M_{H^{+}}}=\frac{0.100}{2.45}=0.0408 \mathrm{~L}=40.8 \mathrm{~mL}
$$

（c）． $\mathrm{n}_{\mathrm{CO}_{2}}=\mathrm{n}_{\mathrm{H}^{+}}=\mathrm{V}_{H^{+}} \cdot \mathrm{M}_{\mathrm{H}^{+}}=\frac{50.0}{1000} \times 2.45=0.123 \mathrm{~mol}$

$$
\mathrm{n}_{H^{+}}: \mathrm{n}_{C O_{2}}=1: 1
$$

$$
0.123: \mathrm{n}_{\mathrm{CO}_{2}}=1: 1
$$

$$
\mathrm{n}_{C O_{2}}=0.123 \mathrm{~mol}
$$

$$
\mathrm{V}_{C O_{2}}=\frac{n R T}{P}=\frac{0.123 \times 0.0821 \times 311}{732 / 760}=3.26 \mathrm{~L}
$$

## § Law of combining volumes 結合體積定律

The first stoichiometric relationship to be discovered was the law of combining volumes，by Gay－Lussac in 1808.

The volume ratio of any two gases in a reaction at constant T and P is the same as the reacting mole ratio．

T， $\mathrm{P}=$ constant

$$
\begin{gathered}
n \quad \alpha \quad \mathrm{~V} \\
V=k \times n
\end{gathered}
$$

Ex 5－7：Consider the reaction

$$
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

（a）What volume of $\mathrm{H}_{2}(\mathrm{~g})$ at $25^{\circ} \mathrm{C}$ and 1.00 atm is required to react with $1.00 \mathrm{~L}^{\text {of }} \mathrm{O}_{2}(\mathrm{~g})$ at the same temperature and pressure ？
（b）What volume of $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ at $25{ }^{\circ} \mathrm{C} 1.00 \mathrm{~atm}(\mathrm{~d}=0.997 \mathrm{~g} / \mathrm{mL})$ is formed from the reaction（a）？
（c）What mass of $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ is formed from the reaction in（a），assuming a

$$
\text { yield of } 85.2 \% ?
$$

Ans：
（a）．$\quad \mathrm{T}, \mathrm{P}=\mathrm{constant} \quad n \propto \mathrm{~V}$

$$
\begin{aligned}
\therefore V_{O_{2}}: & V_{H_{2}}=1: 2 \\
1.00: & V_{H_{2}}=1: 2 \\
& V_{H_{2}}=2.00 \mathrm{~L}
\end{aligned}
$$

（b）．

$$
\begin{gathered}
2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \\
1.00 \mathrm{~L} \\
n_{O_{2}}= \\
\frac{P V}{R T} \\
=\frac{1.00 \times 1.00}{0.0821 \times(273+25)}=0.0409 \mathrm{~mol} \\
n_{O_{2}}: n_{H_{2} \mathrm{O}}=1: \text { 氣態, 以 } \mathrm{n} \text { 計算之 } \\
0.0409: n_{H_{2} \mathrm{O}}=1: 2 \\
n_{H_{2} \mathrm{O}}=0.0818 \mathrm{~mol} \\
m_{\mathrm{H}_{2} \mathrm{O}}=0.0818 \times 18.02=1.47 \mathrm{~g} \\
V_{\mathrm{H}_{2} \mathrm{O}}=\frac{1.47}{0.997}=1.47 \mathrm{~mL} \\
\text { (c). } m_{\mathrm{H}_{2} \mathrm{O}}=0.0818 \times 18.02 \times 85.2 \%=1.26 \mathrm{~g}
\end{gathered}
$$

## § 5－5 Gas mixtures：Partial pressures and mole fractions

The ideal gas law applies to all gases，you might expect it to apply to gas mixtures．For a mixture of two gases A and B ，the total pressure is given by the expression

$$
\begin{aligned}
P_{\text {tot }} & =n_{\text {tot }} \times \frac{R T}{V}=\left(n_{A}+n_{B}\right) \times \frac{R T}{V} \\
& =n_{A} \times \frac{R T}{V}+n_{B} \frac{R T}{V} \\
& P_{A}=n_{A} \times \frac{R T}{V}=\text { partial pressure A } \\
& P_{B}=n_{B} \times \frac{R T}{V}=\text { partial pressure B } \\
P_{\text {tot }}= & P_{A}+P_{B} \quad \text { Dalton's law of partial pressure }
\end{aligned}
$$

§ Dalton＇s law of partial pressure：
The total pressure of a gas mixture is the sum of the partial pressures of the components of the mixture．

## § Wet Gases；Partial pressure of water

某氣體如 $H_{2}$ ，藉由排水集氣法收集

$$
P_{\text {tot }}=P_{H_{2} O}^{P_{2}}+P_{H_{2}}
$$

Ex 5－8：A student prepare a sample of hydrogen gas by electrolyzing water at $25^{\circ} \mathrm{C}$ ． She collects 152 mL of $\mathrm{H}_{2}$ at a total pressure of 758 mmHg ．Using Appendix 1 to find the vapor pressure of water，calculate
（a）．the partial pressure of hydrogen？
（b）．the number of moles of hydrogen collected？
（From Appendix $1 \Rightarrow$ find vapor pressure of water $P_{H_{2} \mathrm{O}}$ at $25^{\circ} \mathrm{C}=23.76$

$$
\left.\mathrm{mmHg} \Rightarrow P_{604}\right)
$$

Ans ：

$$
\begin{aligned}
& \text { a) } P_{\text {tot }}=P_{H_{2}}+P_{H_{2} O} \\
& 758=P_{H_{2}}+23.76 \quad \Rightarrow P_{H_{2}}=734 \mathrm{mmHg} \\
& \text { b) } n_{H_{2}}=\frac{P_{H_{2}} V}{R T}=\frac{734 / 760 \times 0.152}{0.0821 \times(25+273)}=6.00 \times 10^{-3} \mathrm{~mol}
\end{aligned}
$$

Vapor pressure of water：

$$
\begin{aligned}
25^{\circ} \mathrm{C} & P_{\mathrm{H}_{2} \mathrm{O}}=23.76 \mathrm{mmHg} ; & 40^{\circ} \mathrm{C} & P_{\mathrm{H}_{2} \mathrm{O}}=55.3 \mathrm{mmHg} \\
70^{\circ} \mathrm{C} & P_{H_{2} \mathrm{O}}=233.7 \mathrm{mmHg} ; & 100^{\circ} \mathrm{C} & P_{\mathrm{H}_{2} \mathrm{O}}=760.0 \mathrm{mmHg}
\end{aligned}
$$

## § Partial Pressure and mole fraction

$$
P_{A}=X_{A} P_{\text {tot }} \quad X_{A}=\frac{n_{A}}{n_{A}+n_{B}}
$$

$$
X_{A}: \text { mole fraction }
$$

Ex 5－9：When one mole of methane， $\mathrm{CH}_{4}$ ，is heated with four moles of oxygen，the following reaction occurs ：

$$
\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

a）．Assuming all of the methane is converted to $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ ，what are the mole fractions of $\mathrm{O}_{2}, \mathrm{CO}_{2}$ ，and $\mathrm{H}_{2} \mathrm{O}$ in the resulting mixture？
b）．If the total pressure of the mixture is 1.26 atm ，What are the partial pressures？

Ans：

$$
\mathrm{CH}_{4(\mathrm{~g})}+2 \mathrm{O}_{2(\mathrm{~g})} \longrightarrow \mathrm{CO}_{2(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}
$$

$$
\begin{aligned}
& \text { 開始 } 1.00 \quad 4.00 \\
& \text { 平衡 } 0.00 \text { (4.00-2.00) } 1.00 \quad 2.00 \\
& n_{\mathrm{O}_{2}}+n_{\mathrm{CO}_{2}}+n_{\mathrm{H}_{2} \mathrm{O}}=2.00+1.00+2.00=5.00 \mathrm{~mol} \\
& X_{O_{2}}=\frac{2.00}{5.00}=0.400 ; \quad X_{C O_{2}}=\frac{1.00}{5.00}=0.200 ; X_{H_{2} \mathrm{O}}=\frac{2.00}{5.00}=0.400 \text {; } \\
& P_{O_{2}}=1.26 \times 0.400=0.504 \mathrm{~atm} \\
& P_{\mathrm{CO}_{2}}=1.26 \times 0.200=0.252 \mathrm{~atm} \\
& P_{H_{2} \mathrm{O}}=1.26 \times 0.400=0.504 \mathrm{~atm}
\end{aligned}
$$

## § 5－6 Kinetic theory of gases 氣體動力論

## 1880，James Maxwell，Rudolf Clausius，Ludwig Boltzmann，and others developed the Kinetic theory of gases．

## Molecular Model

1．Gases are mostly empty space．The total volume of gas molecules is negligible． （氣體分子實際體積小到可忽略）
2．Gas molecules are in constant，chaotic motion．
3．Collisions are $100 \%$ elastic．（完全彈性體）
4．Gas pressure is caused by collisions of molecules with the walls of the container． （氣體分子撞擊器壁產生壓力）
5．The interaction between gas particles is negligible．（氣體分子與分子間作用力可忽略）．
6．Kinetic energy（動能），K．E．$\alpha$ T，At the same temperature，all gases have the same kinetic energy．（同 T 下所有氣體動能相同．）
符合以上 6 點者 $\rightarrow$ Ideal gas

## § Expression for pressure， $\mathbf{P}$

$$
\begin{aligned}
& P= \frac{N m u^{2}}{3 V} \\
& \mathrm{~N}: \text { 分子數目 } \\
& \mathrm{m}: \text { 一個分子之質量 } \\
& \mathrm{u}: \text { 平均速度 }
\end{aligned}
$$

每次磀撞動量變化：mu $-(-\mathrm{mu})=2 \mathrm{mu}$
第二次碰撞行徑 21 之長度需時間 $t=\frac{2 l}{u}$
分子每秒內碰撞之動能變化 $=\mathrm{f}$

$$
f=\frac{2 m u}{t}=2 m u \times \frac{u}{2 l}=\frac{m u^{2}}{\mathrm{l}}
$$

占 $1 / 3$ 機會 $Q^{2 \text { 面 } / 6 \text { 面 }}$

$$
\begin{aligned}
F= & \frac{N}{3} \times \frac{m u^{2}}{\mathrm{I}} \\
P= & \frac{F}{\mathrm{I}^{2}}=\frac{N}{3} \times \frac{m u^{2}}{\mathrm{I}^{2} \times \mathrm{I}} \\
& \therefore P=\frac{N m u^{2}}{3 V}
\end{aligned}
$$

1．The ratio $N / V$ expresses the concentration of gas molecules in the container．
2．The product $m u^{2}$ is a measure of the energy of collision ；Hence as this equation predicts，pressure is directly related to $m u^{2}$ ．

## § Average kinetic energy of translational motion，Et

$$
\begin{array}{rlr}
E_{t} & =\frac{1}{2} m u^{2} & P=\frac{N m u^{2}}{3 V} \Rightarrow m u^{2}=\frac{3 P V}{N} \\
& =\frac{3}{2} \frac{P V}{N} & \mathrm{PV}=\mathrm{nRT} \\
& =\frac{3 n R T}{2 N} & N=\mathrm{n} \times \mathrm{N}_{A} \\
\mathrm{E}_{\mathrm{t}}=\frac{3 R T}{2 N_{A}} & \mathrm{R} ; \mathrm{N}_{A} \Rightarrow \text { constant } \\
\Rightarrow E_{t} \alpha \mathrm{~T} & \\
\therefore E_{t}=\frac{1}{2} m u^{2} \alpha \mathrm{~T} &
\end{array}
$$

$\therefore 1$ ．At a given T，molecules of different gases must all have the same average kinetic energy of translational motion．
2．The average translational kinetic energy of a gas molecule is directly proportional to the Kelvin temperature，T．

## § Average speed．u

$$
\begin{aligned}
E_{t} & =\frac{1}{2} m u^{2}=\frac{3 R T}{2 N_{A}} \\
u^{2} & =\frac{3 R T}{m N_{A}} \quad m N_{A}=\mathrm{MM} \\
u & =\sqrt{\frac{3 R T}{M M}} \quad \text { (average speed) }
\end{aligned}
$$

1. Average speed is directly proportional to the square root of the absolute temperature, for a given gas at different temperatures, $\mathrm{T}_{2}$ and $\mathrm{T}_{1}$, the quantity MM is constant.
2. Average speed is inversely proportional to the square root of molar mass (MM)

$$
\frac{u_{2}}{u_{1}}=\sqrt{\frac{T_{2}}{T_{1}}}=\sqrt{\frac{M M_{1}}{M M_{2}}}=\sqrt{\frac{m_{1}}{m_{2}}}=\sqrt{\frac{D_{1}}{D_{2}}}=\frac{t_{1}}{t_{2}}
$$

Ex 5-10: Calculate the average speed, u , of an $N_{2}$ molecule at $25^{\circ} \mathrm{C}$.
Ans:

$$
\begin{aligned}
& \begin{aligned}
u & =\sqrt{\frac{3 R T}{M M}} \quad R=8.31 \times 10^{3} \mathrm{~g} \cdot \mathrm{~m}^{2} / \mathrm{S}^{2} \cdot \mathrm{~mol} \cdot \mathrm{~K} \\
& =\sqrt{\frac{3 \times 8.31 \times 10^{3} \times 298}{28.02}}=515 \mathrm{~m} / \mathrm{s}
\end{aligned} \\
& u \text { in mil/h } \Rightarrow 515 \times 3600 \div 1609=1.15 \times 10^{3} \mathrm{mile} / \mathrm{h} \\
& (1 \text { mile }=1609 \mathrm{~m})
\end{aligned}
$$

## § Effusion of Gases: Graham's law

1. High concentration diffuse to one of low concentration.
2. The relative rates of effusion of different gases depend on two factors: the pressures of the gases and the relative speeds of their particles. If two different gases A and B are compared at the same pressure, only their speeds are of concern, and

$$
\begin{equation*}
\frac{u_{B}}{u_{A}}=\sqrt{\frac{M M_{A}}{M M_{B}}} \tag{5-7}
\end{equation*}
$$

## 3. Graham's law : At a given temperature and pressure, the rate of effusion of a gas. In moles per unit time, is inversely proportional to the square root of its molar mass.

Ex 5-11: In an effusion experiment, argon gas is allowed to expand through a tiny opening into an evacuated flask of volume 120 mL for 32.0 s , at which point the pressure in the flask is found to be 12.5 mmHg . This experiment is repeated with a gas X of unknown molar mass at the same T and P . It is found that the pressure in the flask builds up to 12.5 mmHg after 48.0 s. Calculate the molar mass of X ?
120 mL Argon $\quad \mathrm{MM}=39.95 \mathrm{~g} / \mathrm{mL} ; \mathrm{t}_{\mathrm{Ar}}=32.0 \mathrm{~s} ; \mathrm{P}=12.5 \mathrm{mmHg}$ gas X at same T. $\mathrm{P}, \mathrm{t}_{\mathrm{X}}=48.0 \mathrm{~s} \Rightarrow$ molar mass of X .
Ans:

$$
\begin{aligned}
\sqrt{\frac{M M_{A r}}{M M_{X}}}=\frac{t_{A r}}{t_{X}} \Rightarrow \sqrt{\frac{39.95}{M M_{X}}} & =\frac{32.0}{48.0}=0.667 \\
\frac{39.95}{M M_{x}} & =0.445 \\
M M_{x} & =89.8 \mathrm{~g} / \mathrm{mol}
\end{aligned}
$$

## § Distribution of Molecular speeds



## § 5－7 Real gases

1．Table5．2 低溫高壓時其與理想氣體偏差大因氣體越緊密，越接近液體所以偏差大。
2．故真實氣體與理想氣體較接近的條件是在高溫低壓下，低極性分子。 Real gases behave close to ideal gas．

Deviations between real gas and ideal gas are caused by：
1．Attractive forces between gas particles．
2．The finite volume of gas particles．

