

Chapter 2

Properties of Gases

1

Gaseous Air Emissions

- SO_2
- NO_x (NO , NO_2)
- NH_3
- CO
- CO_2
- CH_4
- Many others
- The purpose of this chapter is to provide some basics of properties of gases in general,
- applicable to gas and vapor
- Such properties are important to engineering designs.

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Gas or Vapor

- The terms gas and vapor are both used to describe the **gaseous state** of a substance.
- **Gas** is primarily for a pure substance or mixture that exists in gaseous state under normal conditions.
 - Example: Oxygen, air, SO₂,
- **Vapor** is used to describe a substance that is in gaseous state, which exists in liquid or solid state under normal conditions.
 - Example: Water vapor, “French fries”
- A gas pollutant can rise above the atmospheric pressure and even nontoxic gases can be lethal when their concentrations are high enough to displace too much oxygen in the air.
- While too much vapor will result in the phase change from gas to liquid by condensation.

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One mole of gas

Avogadro constant

$$N_A = 6.022 \times 10^{23} \text{ (1/mole)}$$

- 10, 000 billion billion
- 12 / dozen

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Molar Weight

- which is the mass of one mole of the gas

$$M = N_A m \left(\frac{g}{mol} \text{ or } \frac{kg}{kmol} \right)$$

- Example: Oxygen: O₂: 32 g/mole
- $M(\text{H}_2\text{O}) \approx 18 \text{ g/mole}$
- More at Table A-1 in **the manuscript**

It is different from molecular weight, which is the weight of a molecule

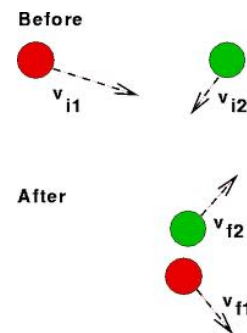
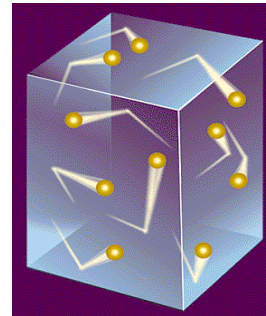
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Kinetic Theory of Gases

- Consider a cubic container, N molecules in it moving randomly

Assumptions

- Gas consists of molecules of mass, m
- Gas molecules in **random** motion
- Interaction between molecules is only through **elastic collisions**
- Elastic collision - total kinetic energy conserved

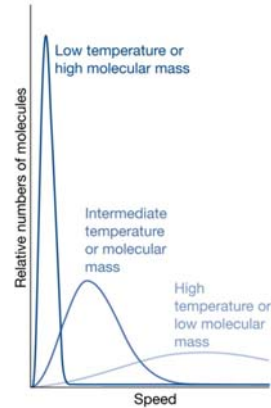
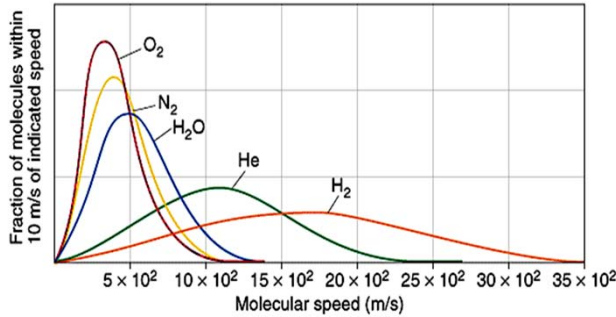


Gas molecular speed probability

Maxwell and Boltzmann Distribution

$$f(c) = 4\pi c^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mc^2}{2kT}\right)$$

- Boltzmann constant: $k = 1.3807 \times 10^{-23}$ (J/K)



Same distribution applies to aerosol particles

Mean molecular speed (\bar{c}) = $\int_0^\infty cf(c)dc = \sqrt{\frac{8kT}{\pi m}}$

$$\bar{c} = \int_0^\infty cf(c)dc = \int_0^\infty c \times 4\pi c^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} dc$$

$$= \int_0^\infty 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} c^3 e^{-mc^2/2kT} dc$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty c^3 e^{-mc^2/2kT} dc$$

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

$$\bar{c} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{1}{2(m/2kT)^2}\right)$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{2k^2T^2}{m^2}$$

$$= \left(\frac{4\pi \times 2k^2T^2}{(2\pi kT)^{1.5}}\right) \left(\frac{m^{1.5}}{m^2}\right)$$

$$= \left(\frac{2^{1.5} k^{0.5} T^{0.5}}{\pi^{0.5} m^{0.5}}\right)$$

$$= \left(\frac{8kT}{\pi m}\right)^{0.5}$$

Root mean square speed

$$c_{rms} = \sqrt{\int_0^{\infty} c^2 f(c) dc} = \sqrt{\frac{3kT}{m}}$$

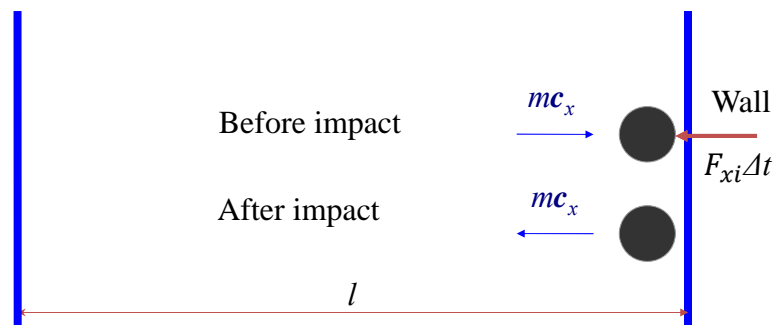
Question: How to determine the Kinetic energy of gas molecules?

Mean relative velocity

$$\bar{c}_{A/B} = \sqrt{\frac{16kT}{\pi m}}$$

See book for derivations

Molecules colliding on walls



With a constant speed of v_x , the gas molecule will impact on the same wall once every $2l/v_x$ time units (for a round trip)

$$F_{xi} = \frac{2mc_{xi}}{\Delta t} = \frac{2mc_{xi}}{2l/c_{xi}} = \frac{mc_{xi}^2}{l}$$

Effect of the *i*th single molecule

$$F_{xi} = \frac{mc_{xi}^2}{l}$$

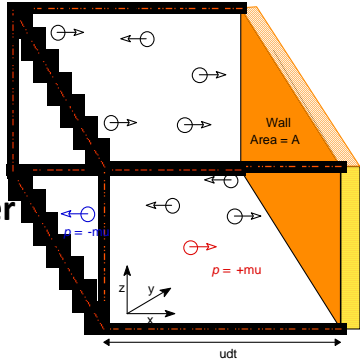
Effect of N molecules in the container

$$F = \frac{m}{l} \left(\sum_{i=1}^N c_{ix}^2 \right)$$

$$c_i^2 = c_{ix}^2 + c_{iy}^2 + c_{iz}^2$$

$$c_{ix}^2 = c_{iy}^2 = c_{iz}^2 = \frac{1}{3} c_i^2$$

$$F = \frac{m}{l} \left(\sum_{i=1}^N c_{ix}^2 \right) = \frac{m}{3l} \left(\sum_{i=1}^N c_i^2 \right)$$

$$\sum_{i=1}^N c_i^2 = N c_{rms}^2$$


Pressure:

$$P = \frac{F}{A} = \frac{Nm c_{rms}^2}{3lA} = \frac{Nm}{3V} c_{rms}^2$$

Ideal gas law

$$P = \frac{Nm}{3V} c_{rms}^2 \xrightarrow{\rho = Nm/V} P = \frac{1}{3} \rho c_{rms}^2 \xrightarrow{c_{rms} = \sqrt{\frac{3kT}{m}}} P = \frac{\rho kT}{m}$$

$$P = \frac{\rho kT}{m} \xrightarrow{R = kN_A} P = \frac{\rho RT}{mN_A}$$

$$P = \frac{\rho RT}{mN_A} \xrightarrow{\rho = nM/V} P = \frac{nRT}{V}$$

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

n = mole amount of gas
M = molar weight of a gas
N = number of molecules in the volume
 $R = 8.314 \frac{J}{mol \cdot K}$,
k = Boltzmann constant

- **Example 2.1: Estimate dry air density at 0 °C and 1 atm using ideal gas law.**

$$\rho = \frac{PM}{RT}$$

$$= \frac{101,325 \text{ (Pa)} \times 28.84 \text{ (kg/kmole)}}{8,314 \text{ J/(kmol.K)} \times 273 \text{ K}}$$

$$= 1.29 \text{ kg/m}^3$$

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Gas mixture

Mole amount: n_i

Total mole amount: $n = \sum_{i=1}^N n_i$

Molar fraction

$$y_i = \frac{n_i}{n} \text{ and } \sum_{i=1}^N y_i = 1$$

Dalton's law

$$P_i V = n_i R T \quad P_i = \frac{n_i}{n} P = y_i P$$

Dalton's Law

- For ideal gases, mole fraction of any species is equal to its volume fraction and the partial pressure of a component, P_i , in the mixture, that is

$$P_i = y_i P$$

P_i = partial pressure of the gas compound i ,

P = total pressure of the ideal gas mixture.

- This equation can also be expressed in terms of ideal gas law,

$$P_i V = n_i R T$$

- And it gives

$$P_i = \frac{n_i}{n} P$$

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Example: Table 1-1 shows the compositions of pure dry air at sea level. Using the volume percentage in this table, determine the partial pressures of nitrogen, oxygen methane, and carbon dioxide in Pascal at sea level where the atmospheric pressure is 101.325 kPa.

Gas	Percent by Volume	Molar ratio	Partial pressure (Pa)
Nitrogen	78.084 %	0.78084	79,118.61
Oxygen	20.9476 %	0.209476	21,225.16
Carbon Dioxide	0.0314 %	0.00314	318.16
Methane	0.0002 %	0.000002	0.203

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Example 2.2: Molar weight of the simplified air

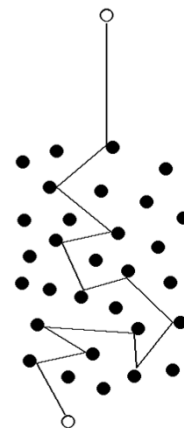
- Dry air can be approximated as a mixture of nitrogen and oxygen molecules where oxygen takes 21% by volume or mole.
- The approximate molar weights of nitrogen and oxygen gases are 28 g/mole and 32 g/mole, respectively.
- Estimate the molar weight of standard dry air.

$$\begin{aligned}
 M_{air} &= y_{N_2} M_{N_2} + y_{O_2} M_{O_2} \\
 &= 0.79 \times 28 + 0.21 \times 32 \\
 &= 28.84 \text{ (kg/kmol)}
 \end{aligned}$$

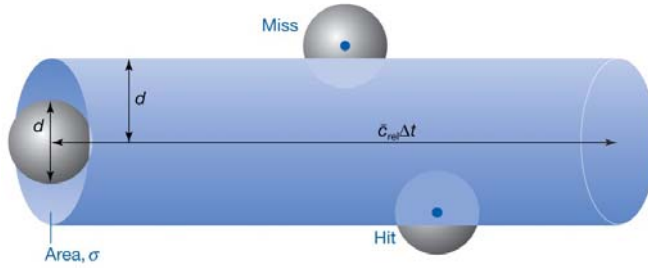
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Gas mean free path

- The mean free path of a gas is the **average** distance traveled by gas molecules between the collisions.
- Gas mean free path affects the **aerosol** dynamics and consequently air sampling and cleaning technologies.
- Gas mean free path may be estimated from kinetic theory too.



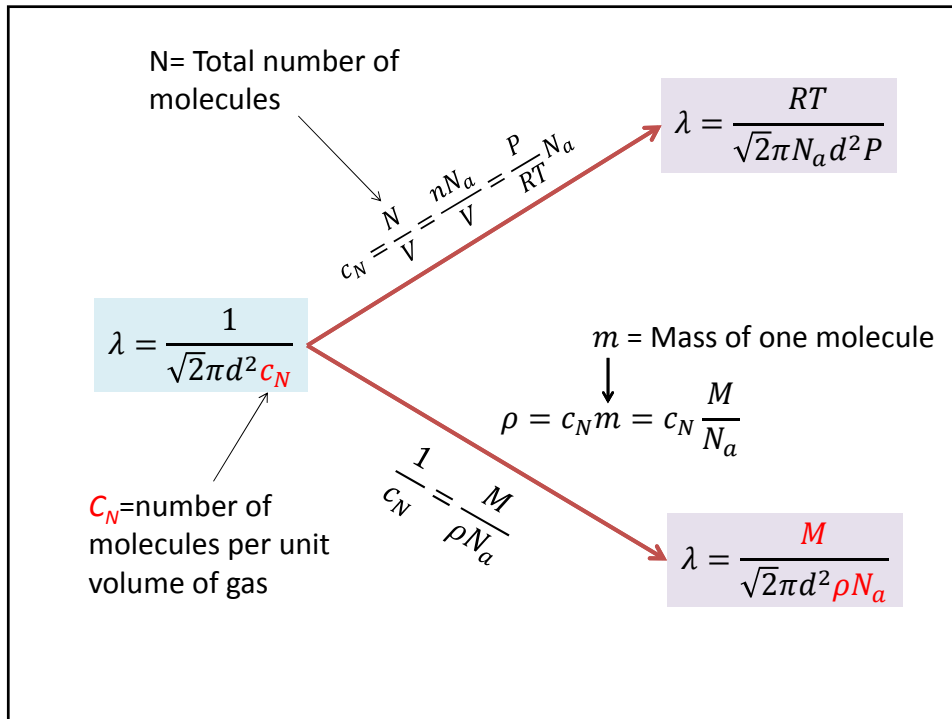
Gas mean free path



- **Collision diameter**, $d_c = 2d$; **Area swept**, $A = \pi d^2$
- **Volume swept in Δt** : $\Delta V = \pi d^2 \bar{c} \Delta t$
- Number molecules colliding with the molecule in ΔV :

$$\Delta V C_N = \pi d^2 \bar{c}_{A/B} \Delta t C_N$$
, where $\bar{c}_{A/B} = \sqrt{2} \bar{c}$
- C_N = the number of molecules per unit volume of gas
- **The mean free path**, which is the distance traveled divided by the number of collisions, can then be calculated as

$$\lambda = \frac{\bar{c} \Delta t}{\pi d^2 \bar{c}_{A/B} \Delta t C_N} = \frac{1}{\sqrt{2} \pi d^2 C_N}$$



Example: Mean Free Path of Air

For air the molecule diameter is approximately $3.7 \times 10^{-10} \text{ m}$ (0.37 nm). Determine the mean free path of air at sea level at 293 K.

$$\lambda = \frac{M}{\sqrt{2} \pi N_a d^2 \rho} \frac{1}{\rho}$$

$$= \frac{28.8 \text{ (g/mol)}}{\sqrt{2} \times \pi \times 6.0221 \times 10^{23} \text{ (#/mol)} \times (3.7 \times 10^{-10} \text{ m})^2} \times \frac{1}{1.21 (\times 1000 \text{ g/m}^3)}$$

$$= 66 \text{ nm}$$

Dynamic Viscosity

$$\mu = \frac{2\sqrt{mkT}}{3\pi^{3/2}d^2} \quad \frac{\mu}{\mu_0} = \frac{T_0 + C}{T + C} \left(\frac{T}{T_0} \right)^{3/2}$$

Gas	C (K)	T ₀ (K)	μ ₀ (10 ⁻⁶ Pa.s)
H ₂	72	293.85	8.76
N ₂	111	300.55	17.81
O ₂	127	292.25	20.18
Air	120	291.15	18.27
CO ₂	240	293.15	14.8
CO	118	288.15	17.2
NH ₃	370	293.15	9.82
SO ₂	416	293.65	12.54

Diffusivity and mass transfer by diffusion

$$D = \frac{2}{3\pi^{3/2}C_N d^2} \left(\frac{RT}{M} \right)^{1/2}$$

$$J_x = -D \frac{dC_N}{dx}$$

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Macro scale quantities

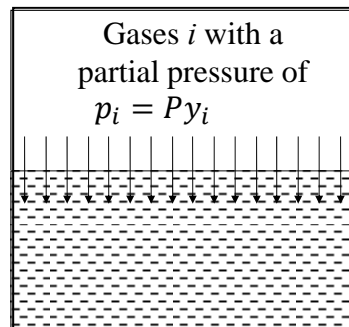
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Solubility

- Solubility of a gas in liquid affects its absorption into water
 - Absorption
 - Wet scrubbing
 - Bubble columns
- Quantified by Henry's law
 - Concentration ($C_i, kg/m^3$)
 - Mole fraction ($x_i, mol/mol$)

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Henry's Law



Liquid phase: gas i dissolved in the liquid with a amount fraction of x_i

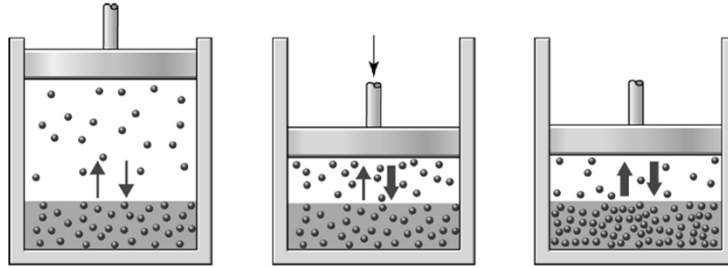
AT EQUILIBRIUM

$$Py_i = Hx_i \quad x_i = \frac{Py_i}{H}$$

- H = Henry's law constant.

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Effect of Gas Pressure



Equilibrium state 1 Changing pressure New Equilibrium state

- Henry's law constant provides a general indication of the solubilities of gases.
- Higher values for Henry's law constants indicate lower solubility.

$$x_i = \frac{P y_i}{H}$$

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T= 298.15 K Gas-water system

Gas		H with the unit of			
		$\frac{atm}{(\frac{mole\ of\ gas}{liter\ of\ water})}$	$\frac{atm}{(\frac{mole\ of\ gas}{kg\ of\ water})}$	$\frac{atm}{(\frac{mole\ of\ gas}{mole\ of\ water})}$	$\frac{Pa}{(\frac{mole\ of\ gas}{mole\ of\ water})}$
Oxygen	O ₂	769.23	769.23	4.27×10 ⁴	4.33×10 ⁸
Ozone	O ₃	83.33	83.33	4.63×10 ³	4.69×10 ⁷
Ammonia	NH ₃	0.02	0.02	0.93	9.38×10 ³
nitrogen monoxide	NO	526.32	526.32	2.92×10 ⁴	2.96×10 ⁸
nitrogen dioxide	NO ₂	83.33	83.33	4.63×10 ³	4.69×10 ⁷
hydrogen sulfide	H ₂ S	10.00	10.00	555.56	5.63×10 ⁶
sulfur dioxide	SO ₂	0.83	0.83	46.30	4.69×10 ⁵
mercury	Hg	10.75	10.75	597.37	6.05×10 ⁶
Methane	CH ₄	714.29	714.29	3.97×10 ⁴	4.02×10 ⁸
carbon monoxide	CO	1010.10	1010.10	5.61×10 ⁴	5.69×10 ⁸
Carbon dioxide	CO ₂	29.41	29.41	1633.99	1.66×10 ⁷

Henry's Law Example

- Estimate the solubility of CO_2 in water *in gram of CO_2 per kilogram of water* under standard conditions (20°C , 1 atm).

Gas		H with the following unit			
		$\frac{\text{atm}}{\left(\frac{\text{mole of gas}}{\text{liter of water}}\right)}$	$\frac{\text{atm}}{\left(\frac{\text{mole of gas}}{\text{kg of water}}\right)}$	$\frac{\text{atm}}{\left(\frac{\text{mole of gas}}{\text{mole of water}}\right)}$	$\frac{\text{Pa}}{\left(\frac{\text{mole of gas}}{\text{mole of water}}\right)}$
sulfur dioxide	SO_2	0.83	0.83	46.30	4.69×10^5
Carbon dioxide	CO_2	29.41	29.41	1633.99	1.66×10^7

Solution

- The Henry's law constant for CO_2 in water at 20°C is 29.41 atm/(mole of gas per kg of water) (Table 3-3).
- Because air is an ideal gas and CO_2 takes 0.0314% of the volume in air, the partial pressure of CO_2 is 0.0314% of the standard atmospheric pressure:

$$P_{\text{CO}_2} = 0.000314 \text{ atm}$$

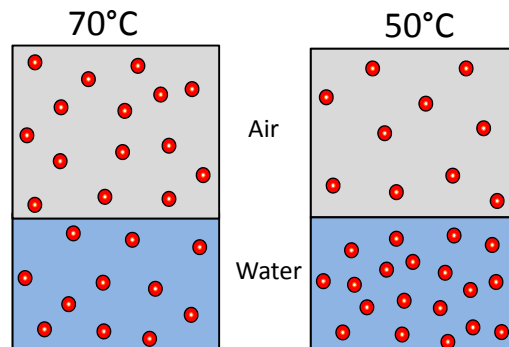
$$\begin{aligned}
 C &= \frac{P_{CO_2}}{H} \\
 &= \frac{0.000314 \text{ atm}}{29.41 \frac{\text{atm}}{\text{mole of gas per kg of water}}} \\
 &= 1.068 \times 10^{-5} \text{ moles of CO}_2/\text{kg of water}
 \end{aligned}$$

The next step is to convert the unit into gram of CO₂ per g of water with the molar weights of CO₂ being 44 g/mole.

$$\begin{aligned}
 C &= \frac{1.068 \times 10^{-5} \text{ mole}_{CO_2} \times \frac{44 \text{ g}}{\text{mole}}}{\text{kg of water}} \\
 &= 4.698 \times 10^{-4} \frac{\text{g of CO}_2}{\text{kg of water}}
 \end{aligned}$$

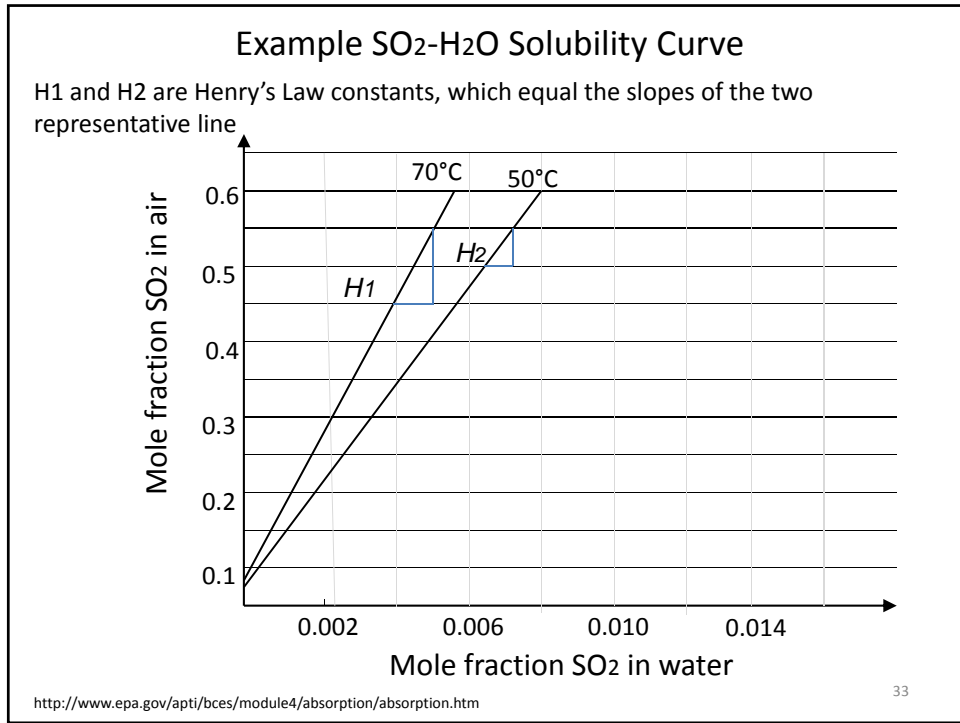
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- Liquid **temperature** affects the solubility of gases in liquids and therefore affects the value of Henry's law constant.
- Usually higher temperature, lower solubility



<http://www.epa.gov/apti/bces/module4/absorption/absorption.htm>

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Henry's law constants at for gases in water at different temperatures ($H=p/y$, unit = atm/(mole gas/mole water))

	0°C	10°C	20°C	30°C	40°C	50°C
N₂	52,900	66,800	80,400	92,400	104,000	113,000
CO	35,200	44,200	53,600	62,000	69,600	76,100
O₂	25,500	32,700	40,100	47,500	53,500	58,800
CH₄	22,400	29,700	37,600	44,900	52,000	57,700
C₂H₆	12,600	18,900	26,300	34,200	42,300	50,000
C₂H₄	5,520	7,680	10,200	12,700	-	-
CO₂	728	1,040	1,420	1,860	2,330	2,830
H₂S	268	367	483	609	745	884

- Henry's law does not apply at high concentrations
- The solubility of gases that react or dissociate must be determined empirically.

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Gas-liquid interfacial mass transfer two-film theory

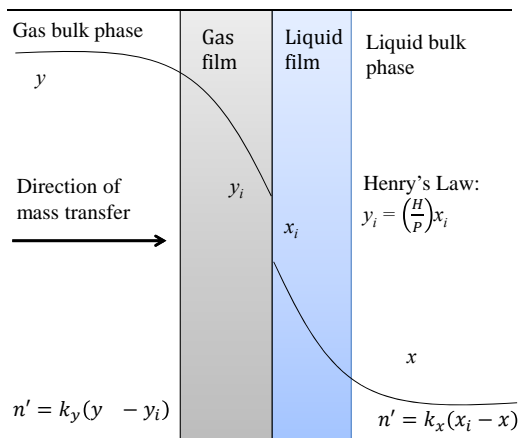


Figure 2.9.

Gas molecules are dissolved in the liquid phase by the following five steps.

1. Molecules migrate from the bulk-gas phase to the laminar gas film
2. They penetrate through the gas film by diffusion
3. These molecules cross the gas-liquid interface by diffusion
4. Diffuse through the liquid film
5. Finally they mix into the bulk liquid phase

The mass transfer per unit interface area

- Gas film: $n' = k_y(y - y_i)$
- Liquid film: $n' = k_x(x_i - x)$
- n' = mole transfer rate of gas (mole/m².s)
- k_y = gas phase mass transfer coefficient (mole/m².s)
- k_x = liquid phase mass transfer coefficient (mole/m².s)
- x, y = mole fractions in the bulk liquid and gas phases
- x_i, y_i = mole fractions at the interface

How to determine them?

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- The mass transfer equation can be described with the bulk phase parameters.

$$n' = K_y(y - y^*) \quad \text{for gas phase}$$

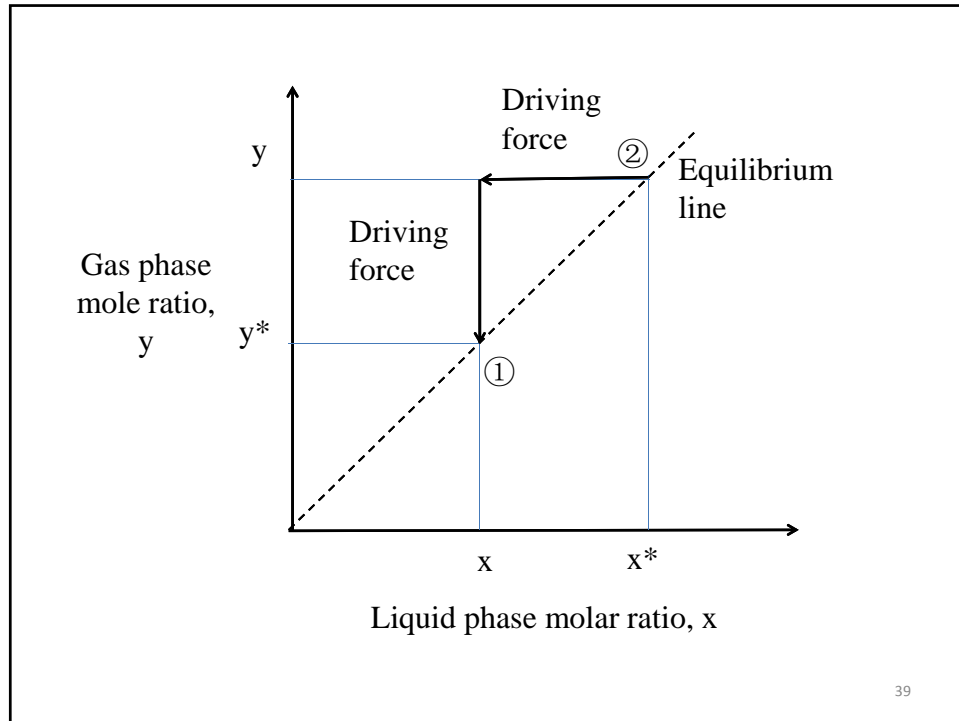
$$n' = K_x(x^* - x) \quad \text{for liquid phase}$$

- K_x, K_y = **Overall** mass transfer coefficients for the liquid and gas phases (mole/m².s).
- x^*, y^* = Hypothetical mole fraction corresponding to y, x in the bulk fluids,

$$y = Hx^*$$

$$y^* = Hx$$

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Gas Phase Equations

$$n' = K_y(y - y^*)$$

$$= K_y[(y - y_i) + (y_i - y^*)]$$

$y_i = Hx_i$

$y^* = Hx$

$$\frac{n'}{K_y} = (y - y_i) + H(x_i - x)$$

$$\frac{n'}{k_y} = y - y_i \quad \frac{n'}{k_x} = x_i - x$$

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{H}{k_x}$$

- This equation indicates that the overall mass transfer coefficient (K_y) can be calculated from the single phase mass transfer coefficients (k_y and k_x). They are usually determined experimentally.

Overall mass transfer resistance:

$$R = \frac{1}{K_y}$$

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{H}{k_x}$$

Gas phase resistance

$$R = \frac{1}{K_y}$$

Liquid phase

$$\text{resistance } R = \frac{H}{K_x}$$

- When the value of H is small, there is a great solubility of the target gas in the liquid phase; it indicates a low liquid phase film resistance and that the gas phase resistance is dominating (or gas phase mass transfer is the bottleneck). In this case, only a small amount of water is needed to hold certain amount of gases. In an engineering application, this is preferred in favor of low liquid consumption.
- On the other hand, when the value of Henry's law constant is large, it means a low solubility of the target gas in the liquid. Then the mass transfer resistance is primarily attributed to the liquid phase. A large amount of liquid is required to hold the gas.

Take Home Message

Basic Physical Properties of Gases

- Macro scale properties can be described using microscopic variables.
- Henry's Law
- Two-film Theory