Chapter 2
Basic Properties of Gases

The purpose of this chapter is to describe some basic properties of gases, which are applicable to not only air but also gaseous air emissions.

The terms gas and vapor are both used to describe the gaseous state of a substance. However, gas is primarily for a pure substance or mixture that exists in gaseous state under normal conditions. Vapor is used to describe a substance that is in gaseous state, which exists in liquid or solid state under normal conditions. A gas can be compressed 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.

Gaseous air emissions can be divided into organic and inorganic types. Organic compound includes most chemicals based on a structure of carbon atoms. Organic air emissions include such gases as methane, but the majorities are vapors under normal conditions. Inorganic gaseous air emissions are primarily gases, except for mercury.

Despite the differences in gas and vapor, they also share some common properties. Therefore, within this text, gas is used to include vapor unless otherwise stated.

2.1 Gas Kinetics

Kinetic theory is also known as kinetic molecular theory or collision theory. Kinetic theory of gases attempts to explain macroscopic properties of gases, such as pressure, temperature, or volume, by considering their microscopic compositions and motion. In the kinetic theory of gases, the following assumptions are made

- Gas molecules are considered uniform spherical particles, each of which has a mass but negligible volume compared to the gas container.
- The number of molecules is large and thus their behaviors can be analyzed statistically.
- Gas molecules move rapidly, constantly, and randomly. The collision between the molecules and the wall is considered perfectly elastic and instantaneous.
- The average distance between the gas molecules is large compared to their size.

2.1.1 Speeds of Gas Molecules

An understanding of the gas properties requires a good understanding of the molecular velocities. In engineering dynamics analysis, we describe a particle velocity with its magnitude and its direction. Similarly, a gas molecule velocity vector $\vec{c}$ is described using its three directional components in a rectangular x-y-z coordinate system as

$$\vec{c} = c_x\hat{i} + c_y\hat{j} + c_z\hat{k} \tag{2.1}$$

Maxwell-Boltzmann distribution is the most commonly used for molecular speed distribution. The distribution of one-dimensional velocity $-\infty < c_i < \infty$ is

$$f(c_i) = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mc_i^2}{2kT}\right) \quad i = x, y, z \tag{2.2}$$

This is a normal distribution with a mean of 0 and a variance of kT/m. It also applies to the other two velocity components.

In engineering applications, total speeds of molecules are of more interest than their components. The Maxwell-Boltzmann distribution describes the probability of molecular speed [16].

$$f(c) = 4\pi c^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mc^2}{2kT}\right) \tag{2.3}$$

where the Boltzmann constant $k = 1.3807 \times 10^{-23}(\text{J/K})$, c is the molecular speed of a molecule, m is the mass of the molecule, and T is the temperature of the gas.

In air pollution, we are interested in the distributions of the molecular mean speed, root-mean-square speed and mean relative speed. As to be seen shortly, they are useful parameters in molecular kinetics that lead us to microscopic properties like pressure, viscosity, diffusivity, and so on. These speeds can be computed from the Maxwell–Boltzmann distribution of molecular speed described in Eq. (2.3).

The *mean molecular speed* ($\bar{c}$) is the mathematical average of the speed distribution and it can be calculated by integration

$$\bar{c} = \int_0^\infty cf(c)\mathrm{d}c = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty\left[c^3\exp\left(-\frac{mc^2}{2kT}\right)\right]\mathrm{d}c \tag{2.4}$$

In order to complete the integration, we need to know that

$$\int_0^\infty \left[x^3 \exp\left(-ax^2\right) \right] dx = \frac{1}{2a^2} \tag{2.5}$$

For this specific problem, $a = -m/2kT$, and the integration term can be determined as

$$\int_0^\infty \left[c^3 \exp\left(-\frac{mc^2}{2kT} \right) \right] dc = \frac{1}{2(-m/2kT)^2} = 2\left(\frac{kT}{m} \right)^2 \tag{2.6}$$

Substituting Eq. (2.6) into Eq. (2.4) leads to

$$\bar{c} = \left(\frac{8kT}{\pi m} \right)^{1/2} \tag{2.7}$$

By similar approaches, we can get the root-mean-square speed (v_{rms}), which is the square root of the average squared speed:

$$c_{rms} = \sqrt{\int_0^\infty c^2 f(c) dc} = \sqrt{\frac{3kT}{m}} \tag{2.8}$$

Comparison between Eqs. (2.7) and (2.8) shows that $c_{rms} > \bar{c}$ because c_{rms} contains a factor of 3 and $\bar{c}$ contains a factor of $8/\pi \approx 2.55$. This is resulted from the fact that greater speeds are weighted more heavily in the integration based on c^2.

Average relative velocity is another molecular speed needed in our analysis that follows. From engineering dynamics, we have learned that the relative velocity of any two molecules A and B which behave like particles is

$$\vec{c}_{A/B} = \vec{c}_A - \vec{c}_B \tag{2.9}$$

where $\vec{c}_{A/B}$ is the velocity of molecule A relative to molecule B (m/s), and the magnitude of the relative velocity is the square root of the scale product of itself:

$$\vec{c}_{A/B}^2 = \vec{c}_{A/B} \times \vec{c}_{A/B} = (\vec{c}_A - \vec{c}_B) \times (\vec{c}_A - \vec{c}_B) = \vec{c}_A \times \vec{c}_A - 2\vec{c}_A \times \vec{c}_B + \vec{c}_B \times \vec{c}_B \tag{2.10}$$

Replacing the speeds in the above equation with the average speeds gives

$$\vec{c}_{A/B}^2 = (\vec{c}_A \times \vec{c}_A)_{ave} - 2(\vec{c}_A \times \vec{c}_B)_{ave} + (\vec{c}_B \times \vec{c}_B)_{ave} \tag{2.11}$$

Since A and B are randomly selected and they are independent on each other, the term $(\vec{c}_A \times \vec{c}_B)_{\mathrm{ave}}$ results in a quantity of zero. Meanwhile, since A and B are randomly selected from the same population, where the molecules behave statistically the same, we also have $\bar{c}_A = \bar{c}_B = \bar{c}$. Then Eq. (2.11) becomes

$$\bar{c}^2_{A/B} = \bar{c}^2_A + \bar{c}^2_B = 2\bar{c}^2 \tag{2.12}$$

The relation between the magnitudes of the average relative speed and mean speed is

$$\bar{c}_{A/B} = \sqrt{2}\bar{c} = \left(\frac{16kT}{\pi m}\right)^{1/2}. \tag{2.13}$$

2.1.2 Avogadro Constant and Molar Weight

A gas volume contains a large number of molecules, which are treated as particles, in rapid motions. Mole amount is used to quantify the amount of molecules. In 1 mol of gas there are 6.022×10^{23} molecules. This is described using the Avogadro number or Avogadro constant

$$N_A = 6.022 \times 10^{23} \quad (1/\mathrm{mol}) \tag{2.14}$$

Any gas can be characterized with its molar weight, which is the mass of 1 mol of the gas

$$M = N_A m \tag{2.15}$$

where m is the mass of a single molecule, and M is the molar weight of a gas with a unit of g/mol or kg/kmol. Molar weights of typical gases with known molecular formula can be determined by the corresponding number of atoms. For example, the molar weight of O_2 is 32 because there are two oxygen atoms in one oxygen molecule and each of the atom weight is 16 g/mol.

2.1.3 Gas Pressure

The pressure of a gas is resulted from the force exerted by gas molecules on the walls of the container due to the collision between the wall and molecules. Consider a cubic container having N gas molecules and the length of the container is l.

The linear momentum before and after the impact is $m\vec{c}_1$ and $m\vec{c}_2$, respectively, when a gas molecule collides with the wall of the container that is normal to the x coordinate axis and bounces back in the opposite direction. From the principle of impulse and linear momentum one has,
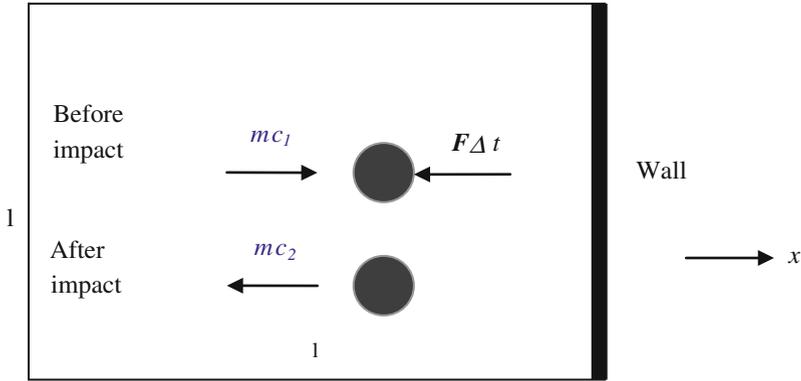
Fig. 2.1 Principle of impulse and linear momentum analysis on a single molecule

$$m\vec{c_1} + \vec{F}\Delta t = m\vec{c_2} \tag{2.16}$$

where the term $\vec{F}\Delta t$ is the impulse during the collision [9]. Both force and velocity are vector quantities defined by their magnitudes and directions. Along one of the rectangular coordinates, say x direction as depicted in Fig. 2.1, the above equation can be written in terms of magnitudes,

$$mc_{1x} - F_x\Delta t = -mc_{2x} \tag{2.17}$$

Reorganize it and one gets,

$$F_x\Delta t = m(c_{1x} + c_{2x}) \tag{2.18}$$

Since the impact between the surface and the gas molecules is elastic, we have $c_{1x} = c_{2x} = c_x$ and the above equation becomes

$$F_x\Delta t = 2mc_x \tag{2.19}$$

With a constant speed of c_x, the molecule will impact on the same wall once every $2l/c_x$ time units (for a round trip), where l is the distance between two opposite walls of the container. Then, the force on the wall produced by the same molecule along x direction is:

$$F_x = \frac{2mc_x}{2l/c_x} = \frac{mc_x^2}{l} \tag{2.20}$$

Now, consider all the N molecules in the container. The total force acting on the wall due to N molecules with the same mass of m is

$$F = \frac{m}{l}\left(\sum_{i=1}^{N} c_{ix}^2\right) \tag{2.21}$$

Recall the assumptions of kinetic theory, there are a large number of molecules moving randomly and constantly, therefore, Eq. (2.21) is applicable to any directions in the container. And the force on each wall can be considered same in magnitude. Consider the force acting only on one wall and the magnitude of the velocity can be calculated using

$$c_i^2 = c_{ix}^2 + c_{iy}^2 + c_{iz}^2 \tag{2.22}$$

Since x, y, and z are randomly chosen and the molecular motion is random and uniform along any direction, we get

$$c_{ix}^2 = c_{iy}^2 = c_{iz}^2 = \frac{1}{3}c_i^2 \tag{2.23}$$

Now, the total force exerted by the molecules on one wall described in Eq. (2.21) can be expressed in terms of the total speed instead of a single component of the velocity,

$$F = \frac{m}{3l}\left(\sum_{i=1}^{N} c_i^2\right) \tag{2.24}$$

According to the definition of root-mean-square speed described in Eq. (2.8),

$$Nc_{\text{rms}}^2 = \sum_{i=1}^{N} c_i^2 \tag{2.25}$$

Then the total force on the wall of the container can be written as:

$$F = \frac{Nmc_{\text{rms}}^2}{3l} \tag{2.26}$$

The resultant pressure, which is force per unit area of the wall, of the gas can then be written as

$$P = \frac{F}{A} = \frac{Nmc_{\text{rms}}^2}{3lA} = \frac{Nm}{3V}c_{\text{rms}}^2 \tag{2.27}$$

where A = the area of the wall on which force is exerted, and V = the volume of the container. Since Nm stands for the total mass of the gas, then the density of the gas is

$$\rho = Nm/V \tag{2.28}$$

Equation (2.27) can be further rewritten as

$$P = \frac{1}{3}\rho c_{rms}^2 \tag{2.29}$$

This formula demonstrates the relationship between a macroscopic property (pressure) and a microscopic property (the root-mean-square speed). For example, the pressure of a gas is due to collisions between molecules and the wall.

2.1.4 Density and Specific Volume of a Gas

In an engineering practice, we hardly use or even care about the exact number of molecules in a volume. Rather we use the mole amount of gases, which is denoted as n and

$$n = N/N_A = Nm/M \tag{2.30}$$

Then, the gas density is described as

$$\rho = nN_A m/V = nM/V \tag{2.31}$$

The equation allows us to estimate the density of a gas with known molar weight by comparing with another gas with known density.

A term related to density is specific volume, which is the inverse of density

$$v = 1/\rho \tag{2.32}$$

It has a unit of volume per mass, for example, m^3/kg.

2.1.5 Ideal Gas Law and Dalton's Law

Air and typical gases of interest in air emissions are often considered as ideal gases. The ideal gas law governs the relationship between the pressure P, the volume V, and the temperature T of an ideal gas. It can be derived by continuing with the gas molecular kinetics.

Substituting Eq. (2.8) into Eq. (2.27) we can get, with Eq. (2.25 below),

$$PV = nRT \tag{2.33}$$

With $\rho = Nm/V$, Eq. (2.33) becomes

$$P = \frac{\rho RT}{M} \tag{2.34}$$

This is the so called ideal gas law, where n is the mole amount of the gas, and $R =$ the universal gas constant and $R = 8314 \frac{J}{\text{kmol K}}$ or $8.314 \frac{J}{\text{mol}}$ K.

Example 2.1: Gas density calculation
Estimate dry air density at 0 °C and 1 atm using Eq. (2.34)

Solution
From Eq. (2.34) we have

$$\rho = \frac{PM}{RT} = \frac{101,325(\text{Pa}) \times 28.84(\text{kg/kmol})}{8,314 \text{J}/(\text{kmol K}) \times 273\text{K}} = 1.29 \,\text{kg/m}^3$$

The universal ideal gas constant is related to the Boltzmann constant k as,

$$R = kN_A \tag{2.35}$$

As such, the ideal gas law can be rewritten in terms of the Boltzmann constants

$$PV = nN_A kT = NkT \tag{2.36}$$

where $(N = nN_A)$ is the total number of molecules in the subject gas.

Dalton's law is an empirical law that was observed by John Dalton in 1801 and it is related to the ideal gas law. It is important to air emission studies in that gases in air emission engineering are often mixtures of multiple compounds.

Consider a mixture of gases, the mole number n of a gas mixture equals to the sum of the mole numbers of all its components.

$$n = \sum_{i=1}^{N} n_i \tag{2.37}$$

and the mole fraction, denoted as y_i, of any given species is

$$y_i = \frac{n_i}{n} \quad \text{and} \quad \sum_{i=1}^{N} y_i = 1 \tag{2.38}$$

For ideal gases under some conditions, mole fraction of any species is equal to its volume fraction. The molar weight of a mixture of ideal gases can be determined from the mole fraction of each compound and the corresponding molar weight using Eq. (2.39):

$$M = \sum_{i=1}^{N} y_i M_i \tag{2.39}$$

where M_i is the molar weight of each substance in the gas mixture.

Example 2.2: Molar weight of simplified air
Dry air can be approximated as a mixture of nitrogen and oxygen molecules where oxygen takes 21 % by volume. The approximate molar weights of nitrogen and oxygen molecules are 28 and 32 g/mol, respectively. Estimate the molar weight of standard dry air.

Solution
Using Eq. (2.39) we can get

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

Assuming the gases are nonreactive, each individual gas in the mixture is also governed by the ideal gas law:

$$P_i V = n_i RT \tag{2.40}$$

where P_i is partial pressure of the gas compound i. Combining Eqs. (2.33) and (2.40) gives,

$$P_i = \frac{n_i}{n} P = y_i P \tag{2.41}$$

This relationship is also referred to as *Dalton's law*. It states that the total pressure of a mixture of nonreactive gases is equal to the sum of the partial pressures of all individual gases.

The partial pressure of a gas in a mixture is an important property that affects many engineering practices, for example, the solubility of a gas in liquid depends on the partial pressure of the gas (see Sect. 2.3).

Example 2.3: Partial pressure of an ideal gas
Table 2.1 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.

Table 2.1 Mean free paths for ideal gases

Pressure (atm)	Temperature (K)	Mean free path (m)
1	300	7×10^{-8}
10^{-4}	300	7×10^{-4}
10^{-8}	300	7

Solution

Gas	Percent by volume (%)	Mole 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

Sometimes, we need to determine the amount of moisture or water vapor in the air. It is useful in air emission monitoring, characterization of the air cleaning efficiency, or simply quantification of indoor air quality. It can be expressed by either specific humidity or relative humidity of the air. Specific humidity quantifies the mass ratio of water molecules to dry air. The specific humidity, w, of air can be calculated using

$$w = \frac{m_w}{m_{air}} = \frac{n_w M_w}{n_{air} M_{air}} \tag{2.42}$$

Relative humidity of air is expressed as the ratio of the vapor partial pressure of the air to the saturation vapor partial pressure of the air at the actual dry bulb temperature.

$$RH = \frac{P_w}{P_{sat}} \tag{2.43}$$

where P_w = vapor partial pressure and P_{sat} = saturation vapor partial pressure at the actual dry bulb temperature. They shall carry the same unit to make RH dimensionless. Since vapor partial pressure is less than the saturation vapor partial pressure, we have $0 < RH < 1$. More practically, relative humidity can also be expressed as the ratio of actual mass of water vapor in a given air volume to the mass of water vapor required to saturate at this air.

$$RH = \frac{m_w}{m_{w,s}} \tag{2.44}$$

where m_w = mass of water vapor in the given air volume and $\mathrm{m}_{w,s}$ = mass of water vapor required to saturate at this volume

Example 2.4: Vapor pressure
Relative humidity of air in a typical cool summer day in Canada is about 40 % and it is known that the saturation pressure at 21°C is 25 mbar. What is the corresponding vapor pressure in the air.

Solution
From Eq (2.43), we have

$$P_w = P_{\text{sat}} \times RH = 25.0 \, \text{mbar} \times \ 40 \ \% = 10 \, \text{mbar}$$

2.1.6 Kinetic Energy of Gas Molecules

Combining Eqs. (2.35) and (2.8) leads to the root-mean-square speed of an ideal gas in terms of microscopic variables, molecular weight M and temperature T.

$$c_{\text{rms}} = \left(\frac{3RT}{N_a m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2} \tag{2.45}$$

This equation can be used to determine c_{rms} of a known ideal gas at a certain temperature. This formula shows that root-mean-square speed of a gas is proportional to the square root of the temperature, so it increases with the increase in gas temperature.

The molecular kinetic energy can be determined from root-mean-square speed. Usually, it is quantified on a per mole base. The kinetic energy for 1 mol of ideal gas can be calculated as,

$$e_k = \frac{1}{2} N_a m c_{\text{rms}}^2 = \frac{3}{2} RT \tag{2.46}$$

This equation shows that the kinetic energy of an ideal gas depends only on its temperature. This implies that the molar kinetic energy of different gases is the same at the same temperature.

Example 2.5: Gas kinetic energy
Compute root-mean-square speeds and the kinetic energy of 1 mol of the following gases H_2, H_2O vapor, air, and CO_2 at standard temperature of 293 K.

Solution

Step 1. Determine the molar weight of the gases

Gas or Vapor	Molar weight (g/mol)
H_2	2
H_2O	18
Air	29
CO_2	44

Step 2. Compute the root-mean-square speed of the gas molecules using Eq. (2.45) and the kinetic energy of 1 mol of the gas using Eq. (2.46)

| Gas or Vapor	Molecular weight (g/mol)	Equation (2.45) c_{rms} (m/s)	Equation (2.46) (J/mol)
H_2	2	1911.54	3654.0
H_2O	18	637.18	3654.0
Air	29	501.99	3654.0
CO_2	44	407.54	3654.0

It is apparent that the lighter molecules have the greater root-mean-square speeds to maintain the equal kinetic energy at the same temperature.

2.1.7 Gas Mean Free Path

The mean free path of a gas is the average distance traveled by gas molecule 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.

Consider a gas with molecules with a uniform diameter of d. As shown in Fig. 2.2, the effective cross section for collision is $d_c = 2d$, and the cross section area can be calculated as $A = 4\pi d^2$.

Fig. 2.2 Collision diameter of gas molecules
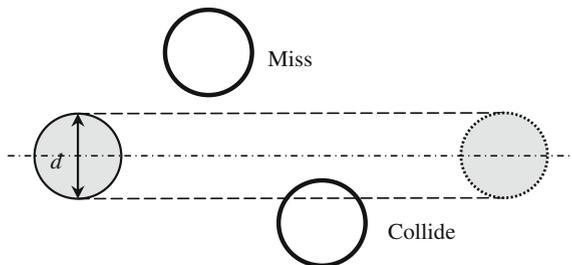
The number of collisions this molecule experiences during the time interval of Δt is determined by the number molecules colliding with the molecule in the swept volume, ΔV, which is

$$\Delta V C_N = \pi d^2 \bar{c}_{A/B} \Delta t C_N \tag{2.47}$$

where C_N is the number of molecules per unit volume of the gas ($\#/m^3$). The relative velocity is used because other molecules are also traveling within the space; it is described in Eq. (2.13):

$$\bar{c}_{A/B} = \sqrt{2}\bar{c}$$

The distance it travels in Δt is $\bar{c}\Delta t$, then the mean free path, which is the distance traveled divided by the number of collisions, can then be calculated as

$$\lambda = \frac{\bar{c}\Delta t}{\pi d^2 \bar{c}_{A/B} \Delta t C_N} = \frac{1}{\sqrt{2}\pi d^2 C_N} \tag{2.48}$$

There is no need to correct the average speed in the numerator for the calculation of distance traveled, which is supposed to be calculated using the average speed of the molecules.

Assuming ideal gas, the number concentration of the gas molecules can be calculated as

$$C_N = \frac{N}{V} = \frac{nN_a}{V} = \frac{P}{RT}N_a \tag{2.49}$$

where N is the total number of molecules in the container with a volume V. There is a simple relationship between the gas density and molecule number concentration as

$$\rho = C_N m \tag{2.50}$$

With Eq. (2.49) and Eq. (2.50), Eq. (2.48) becomes

$$\lambda = \frac{RT}{\sqrt{2}\pi N_a d^2 P} = \frac{M}{\sqrt{2}\pi N_a d^2 \rho} \tag{2.51}$$

Molar weight (M) and gas molecule diameter (d) are fixed for a gas at stable state, therefore, the mean free path depends only on the density of the gas (ρ), which depends on the pressure and temperature of the gas. For ambient conditions, the mean free path increases with increasing temperature or decreasing pressure.

Example 2.6: Air mean free path

For air, the molecule diameter is approximately 3.7×10^{-10} m. Determine the mean free path of air at sea level at 293 K. What is the value for air mean free path at an elevation of 2,000 m by assuming same temperature?

Solution

Air density at the sea level is $\rho_0 = 1.21$ kg/m^3. At the elevation of 2,000 m, air density becomes $\rho_{2000} = 0.95$ kg/m^3. The corresponding mean free paths are calculated using Eq. (2.51).

At sea level,

$$\lambda_0 = \frac{0.02884}{\sqrt{2}\pi \times 6.0221 \times 10^{23} \times (3.7 \times 10^{-10})^2} \times \frac{1}{1.21}$$
$$= 0.066 \times 10^{-6}\,\text{m} = 0.066\,\mu\text{m}$$

At 2,000 m above the sea level,

$$\lambda_{2000} = \frac{0.02884}{\sqrt{2}\pi \times 6.0221 \times 10^{23} \times (3.7 \times 10^{-10})^2} \times \frac{1}{0.95}$$
$$= 0.083 \times 10^{-6}\,\text{m} = 0.083\,\mu\text{m}$$

Conversion between the mean free paths under different conditions was given by Allen and Raabe [1], Cited by [14]

$$\frac{\lambda}{\lambda_0} = \frac{p_0}{p}\left(\frac{T}{T_0}\right)^2\left(\frac{T_0 + T_s}{T + T_s}\right) \tag{2.52}$$

where the parameters with subscript of 0 is for the standard condition and those without subscripts are for any other conditions. Examples of values of mean free path for air are given in Table 2.1.

2.1.8 Number of Collisions with Wall/Surface

By applying the kinetic theory, one can also calculate the number of collisions on the walls of a container. The quantitative analysis of the collision on the wall of the container is important for the study of the kinetic molecular theory of transport properties such as diffusion and viscosity.

Again, consider the scenario in Fig. 2.1, a cubic container with a wall area, A, and assume elastic impact between the molecules and the wall. During a small time interval of Δt, the distance that the molecule with the moving speed of c_x travel is $\Delta x = c_x \Delta t$ in the +x-direction if they do not collide with the wall. In another word, the molecules will collide with the wall if they are within a distance $\Delta x = c_x \Delta t$ from the wall.

Assume one molecule collides with the wall only once during Δt, then the number of collisions is the same as the number of molecules within the volume formed by Δx and A. Then, the number of collisions is expressed as the corresponding number of molecules that collide with the wall during Δt

$$n_c = C_N c_x A \Delta t \tag{2.53}$$

where C_N is the number of molecules per unit volume of gas, which is defined in Eq. (2.49). From this equation, we can get the number of molecules colliding with the wall per unit area per unit time $(1/s\ m^2)$

$$j_x = \frac{n_c}{A \Delta t} = C_N c_x \tag{2.54}$$

Then, the total number of collisions considering the molecule speed distribution is determined by integration, assuming constant molecule number concentration C_N at steady state,

$$J_x = \int_0^\infty j_x f(c_x) dc_x = C_N \int_0^\infty c_x f(c_x) dc_x \tag{2.55}$$

Using the Maxwell-Boltzmann distribution described in Eq. (2.2), the integration part in Eq. (2.55) can be manipulated following

$$\int_0^\infty c_x f(c_x) dc_x = \frac{1}{2} \int_{-\infty}^\infty |c_x| f(c_x) dc_x = \frac{1}{2} \bar{c}_x \tag{2.56}$$

where $|\bar{c}_x|$ is the average of the absolute value of c_x. Then Eq. (2.55) becomes

$$J_x = \frac{1}{2} C_N \bar{c}_x \tag{2.57}$$

A step further from the Boltzmann distribution, we can relate $|\bar{c}_x|$ with average molecular speed that can be calculated from Eq. (2.2)

$$\bar{c}_x = \int_0^\infty c_x f(c_x) dc_x = \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mc_x^2}{2kT}\right) c_x dc_x = \frac{1}{2} \bar{c} \tag{2.58}$$

Thus, the collision per unit time per unit area along x direction in terms of average molecular speed is

$$J_x = \frac{1}{4} C_N \bar{c} \tag{2.59}$$

Substitute Eq. (2.7) into this equation and we can get

$$J_x = C_N \sqrt{\frac{kT}{2\pi m}} \tag{2.60}$$

Considering the relationship between gas density and the molecule number concentration described in Eq. (2.50), the total number of collisions per unit time per unit area can also be expressed in terms of gas density as

$$J_x = \rho \sqrt{\frac{kT}{2\pi m^2}}. \tag{2.61}$$

2.1.9 Diffusivity of Gases

We can derive the diffusivity of a single gas by applying the preceding analysis of molecule collision on a surface to an imaginary cubic container that is formed by a distance of mean free path, 2λ. We can apply finite element analysis from $(x - \lambda)$ to $(x + \lambda)$. The concentration at x is C_N. Assuming a constant gas concentration gradient of $\frac{dC_N}{dx}$ from $(x - \lambda)$ to $(x + \lambda)$; the concentrations at $(x + \lambda)$ and $(x - \lambda)$ are $\left(C_N + \frac{dC_N}{dx}\lambda \right)$ and $\left(C_N - \frac{dC_N}{dx}\lambda \right)$, respectively.

Considerations of symmetry lead us to assert that the average number of particles traveling in a given direction $(\pm x, \pm y$ or $\pm z)$ will be one-sixth of the total, and thus the mean rate at which molecules crosses a plane is $N\bar{c}/6$ per unit area in unit time. N is the total number of molecules in the container. This differs slightly from the exact result, although it is suitable for some simplified argument.

Statistically, 1/6 of the molecules at $(x + \lambda)$ will move along $-x$ direction. According to the definition of mean free path, these molecules leaving the plane $(x + \lambda)$ along $-x$ direction will reach plane x. Therefore, the number of molecules leaving plane $(x + \lambda)$ per second per unit area is

$$J_{\leftarrow x} = \frac{1}{6}\left(C_N + \frac{dC_N}{dx}\lambda \right)\bar{c}$$

Similarly, the number of molecules per second per unit area leaving plane $(x - \lambda)$ to plane x is

$$J_{\rightarrow x} = \frac{1}{6}\left(C_N - \frac{dC_N}{dx}\lambda \right)\bar{c}$$

Then, the net flux of molecules in the positive x direction (#/s m^2) is

$$J_x = J_{\to x} - J_{\leftarrow x} = -\frac{1}{3}\frac{dC_N}{dx}\lambda\bar{c} \tag{2.62}$$

Comparing this equation with the Fick's law of diffusion

$$J_x = -D\frac{dC_N}{dx} \tag{2.63}$$

gives the diffusivity or diffusion coefficient of gas in m^2/s:

$$D = \frac{1}{3}\lambda\bar{c} \tag{2.64}$$

Combining with Eqs. (2.7) and (2.51), we can get leads to

$$D = \frac{1}{3}\frac{RT}{\sqrt{2}\pi N_a d^2 P}\sqrt{\frac{8kT}{\pi m}} = \frac{2}{3\pi^{1.5}d^2}\frac{RT}{PN_a}\sqrt{\frac{RT}{M}}. \tag{2.65}$$

2.1.10 Viscosity of a Gas

Viscosity is a measure of the resistance of a fluid being deformed by either shear or extensional stress. Viscosity in gases arises principally from the molecular diffusion that transports momentum between layers of flow. The kinetic theory of gases allows accurate prediction of the viscosity of a gas.

Similar to the analysis for diffusivity, consider a laminar flow of gas above a horizontal plate. We can apply finite element analysis from $(x - \lambda)$ to $(x + \lambda)$. The concentration at x is C_N. Assuming a constant gas velocity gradient of $\frac{du}{dx}$ from $(x - \lambda)$ to $(x + \lambda)$; the velocities at $(x + \lambda)$ and $(x - \lambda)$ are $\left(u + \frac{du}{dx}\lambda\right)$ and $\left(u - \frac{du}{dx}\lambda\right)$, respectively. The gas may be treated as layers perpendicular to the moving direction (say x axis). Also assume a constant gas molecule concentration C_N. In each layer, the steady flow gas velocity is also constant. Then, the rate of transport of momentum per unit area in the $+x$ and $-x$ directions, respectively, are

$$M_{\to x} = \frac{1}{6}C_N m\bar{c}\left(u - \frac{\partial u}{\partial x}\lambda\right)$$

$$M_{\leftarrow x} = \frac{1}{6}C_N m\bar{c}\left(u + \frac{\partial u}{\partial x}\lambda\right)$$

Table 2.2 Sutherland's constants and reference temperatures

Gas	Formula	T_s (K)	T_0 (K)	μ_0 (10^{-6} Pa s)
Hydrogen	H_2	72	293.85	8.76
Nitrogen	N_2	111	300.55	17.81
Oxygen	O_2	127	292.25	20.18
Air	–	120	291.15	18.27
Carbon dioxide	CO_2	240	293.15	14.8
Carbon monoxide	CO	118	288.15	17.2
Ammonia	NH_3	370	293.15	9.82
Sulfur dioxide	SO_2	416	293.65	12.54

where m is the mass of a single molecule. C_N is the molecule number concentration. The term $\left(\frac{1}{6}C_N m\bar{c}\right)$ stands for the average mass flow rate per unit area through plane x. This leads to a net flux of momentum in the $+x$ direction through the plane x as

$$M_x = -\frac{1}{3}C_N m\bar{c}\frac{\partial u}{\partial x}\lambda \tag{2.66}$$

Comparing with the definition of shear stress

$$\tau = -\mu\frac{\partial u}{\partial x} \tag{2.67}$$

we can get the kinetic viscosity of the gas as

$$\mu = \frac{1}{3}C_N m\bar{c}\lambda = \frac{1}{3}\rho\bar{c}\lambda \tag{2.68}$$

Combining this equation with Eqs. (2.7) and (2.51), we can get

$$\mu = \frac{1}{3}\rho\sqrt{\frac{8kT}{\pi m}}\frac{RT}{\sqrt{2}\pi N_a d^2 P} = \frac{2}{3}\frac{\sqrt{mkT}}{\pi^{1.5}d^2} \tag{2.69}$$

where μ = kinetic viscosity in Pa s or N s/m^2.

The effect of temperature on the dynamic viscosity of an ideal gas can also be calculated using the Sutherland's equation (Licht and Stechert 1944 cited by [12]).

$$\frac{\mu}{\mu_0} = \frac{T_0 + T_s}{T + T_s}\left(\frac{T}{T_0}\right)^{3/2} \tag{2.70}$$

where μ = viscosity in Pa.s at input temperature T, μ_0 = reference viscosity at reference temperature T_0, T = input temperature, T_0 = reference temperature, T_s = Sutherland's constant. Values of Sutherland's constant T_s are taken from Crane [4].

The viscosities at different reference temperatures can be found in the handbook of CRC [5]; and some examples are listed Table 2.2. For temperatures between $0 < T < 555$ K, the Sutherland's constants and reference temperatures for some gases are listed. The maximum error is 10 %.

2.2 Gas Fluid Dynamics

2.2.1 Reynolds Number

Reynolds number of a fluid quantifies the relative importance of inertial forces (ρu) and viscous forces (μ/L) for a flow. Mathematically, it is described by

$$\text{Re} = \frac{\rho u D}{\mu} = \frac{4\dot{m}}{\mu \pi D} \tag{2.71}$$

where u = magnitude of the mean fluid velocity in m/s, D = characteristic length in m, μ = dynamic viscosity of the fluid in $(N.s/m^2)$ or Pa.s, ρ = density of the fluid in kg/m^3, and $\dot{m}$ is the mass flow rate of the fluid.

The characteristic length depends on the flow condition, internal or external, and the cross section of the pipe for internal flow. For flow in a pipe, it is the hydraulic diameter of the pipe, and for flow over a body, the characteristic length is usually the length of the body. The flow is likely laminar if Re < 2,000 and turbulent for Re > 4,000 for either internal or external flows. In a boundary layer analysis (Sect. 2.2.3), the characteristic length is the distance measured from the leading edge where the boundary layer starts to develop.

2.2.2 Bernoulli's Equation

Bernoulli's equation is important to air emission analysis too. It is derived from the basic concept of conservation of mass and conservation of energy. Very briefly, consider a streamline of a moving fluid without heat transfer; Bernoulli's equation describes the relationship between the static pressure of the fluid, fluid velocity, and the elevation for a steady flow,

$$\frac{v^2}{2} + \int \frac{\Delta P}{\rho} + gz = \text{constant} \tag{2.72}$$

where v is the local velocity on the streamline (m/s), P is the absolute static pressure $(Pa, \text{N/m}^2)$, ρ is the density of the fluid (kg/m^3), g is gravitational acceleration (9.81 m/s^2) and z is the elevation (m).

Assuming constant fluid density for the incompressible fluid, Eq. (2.72) becomes

$$P + \frac{1}{2}\rho v^2 + \rho g z = \text{constant} \tag{2.73}$$

where P represents the static pressure and $\rho v^2/2$ the velocity pressure. The consequent total pressure is $P + \frac{1}{2}\rho v^2$. This equation is applicable to most air emission related to analysis.

When $z_1 = z_2$, the pressure difference between two points along a streamline is related to the speeds at these points

$$P_1 - P_2 = \frac{1}{2}\rho\left(v_2^2 - v_1^2\right) \tag{2.74}$$

This simple equation finds important applications in air emission analysis such as the estimation of the resistance to airflow (pressure drop) in an air cleaning device. It is also the principle behind the design of a Pitot tube, which will be introduced later in Chap. 15.

2.2.3 Boundary Layer and Drag

When a gas flows around outside of a body, it produces a force on the body that tends to drag the body in the direction of the gas flow. There are two mechanisms behind this drag effect, one is the skin friction drag and another is form drag. To illustrate the skin drag, let us consider a flat surface with a sharp leading edge attacked by a uniform fluid flow (Fig. 2.3).

Denote the uniform free stream speed as u_∞ and set the coordinate origin at the leading edge with $x = 0$ and $y = 0$ on the solid surface. The fluid is slowed down with a layer that is close to the solid surface, which is called boundary layer. The
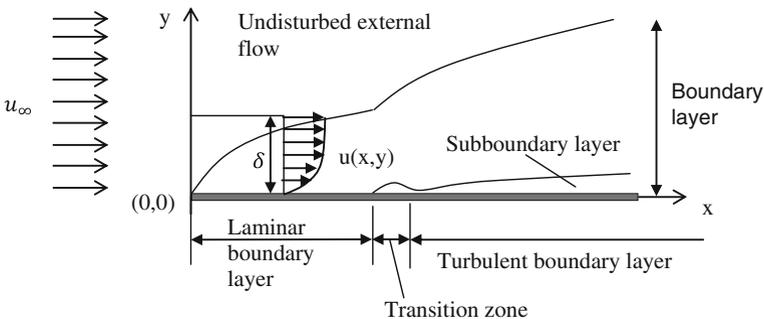

Fig. 2.3 Boundary layer concept

thickness of the boundary layer $\delta(x)$ is taken as the distance above the solid surface where the velocity reaches 0.99 u_∞. The boundary layer grows with the distance from the leading edge until it reaches a constant thickness. Then, we call it fully developed boundary layer.

The flow within a boundary layer also changes gradually from laminar to turbulent. And it is characterized with boundary layer Reynolds number Re_x based on u_∞ and x

$$\mathrm{Re}_x = \frac{\rho u_\infty x}{\mu} \tag{2.75}$$

The velocity profile within the laminar boundary layer is simplified as

$$\frac{u}{u_\infty} = \frac{2y}{\delta} - \frac{y^2}{\delta^2} \tag{2.76}$$

The skin drag is resulted from the shear stress on the solid surface (wetted area). For the real bluff bodies, flow separation occurs and it results in another drag effect called form drag or pressure drag. Overall, the drag is

$$F_D = C_D \left(\frac{1}{2} \rho u_\infty^2 \right) A \tag{2.77}$$

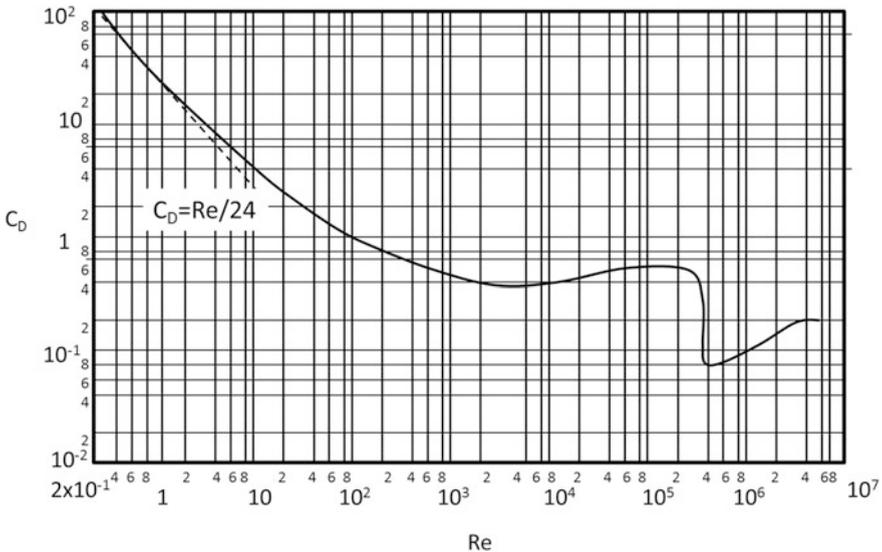where C_D is the drag coefficient based on the reference area, A.

Fig. 2.4 Drag coefficient versus Reynolds number for a sphere (*Data source* [11])

The drag coefficients are geometry dependent and mostly determined experimentally. The drag coefficients of spheres at different Reynolds number are shown Fig. 2.4. More complicated cases can be found in most fluid dynamics books.

2.3 Gas–Liquid Interfacial Behavior

2.3.1 Solubility and Henry's Law

According to International Union of Pure and Applied Chemistry (IUPAC), solubility is the analytical composition of a saturated solution expressed as a proportion of a designated solute in a designated solvent. The most widely used solvent is liquid, which can be a pure substance or a mixture. The extent of the solubility of a substance in a specific solvent is measured as the saturation concentration, where adding more solute does not increase the concentration of the solution and begin to precipitate the excess amount of solute. Solubility may be stated in units of concentration (C_i, kg/m^3), mol fraction (x_i, mol/mol) and other units. The solubility of a substance depends on many physical and chemical properties of the solute and the solvent such as temperature, pressure, and the pH.

Consider a process shown in Fig. 2.5, where gas i is mixed with another insoluble gas, and gas i is soluble. The gas molecules will enter the liquid phase and become part of the liquid mixture. Given enough time, the system reaches equilibrium state.

The Henry's law governs the equilibrium state,

$$P_i = Hx_i \tag{2.78}$$

where P_i = partial pressure of gas i in the gas phase above the liquid, x_i = the equilibrium concentration of gas i in the liquid phase, and H = Henry's law constant with a unit that is determined by that of P_i/x_i. When the partial pressure is in

Fig. 2.5 Absorption of gas i into liquid and Henry's Law
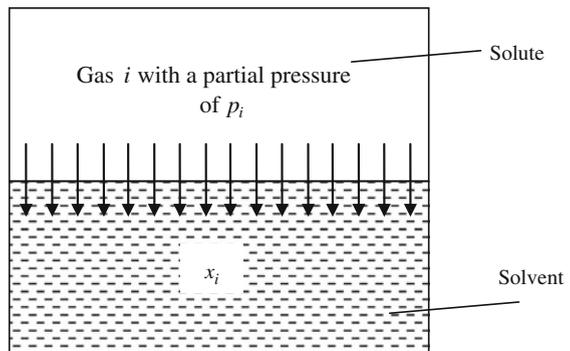
Pa and x_i in mol/mol, for example, the corresponding unit of H is [Pa/(mol in liquid/ mol of liquid)]. Common units of pressure are Pascal (Pa), atm, bar, and mmHg; those of solute concentration can be g/g, mol/mol, mol/m^3, mol/L, and so on. Users have to excuse unit conversion as needed.

In many engineering design practices, mole fraction of the air pollutant in the gas phase (y_i) is used to quantify the concentration of a gas in a gas mixture; it is a direct description of mass transfer between the two phases. In this case, the partial pressure of the target gas is calculated using Eq. (2.41), $P_i = y_i P$ and the Henry's law equation becomes

$$Py_i = Hx_i \tag{2.79}$$

A comprehensive compilation of Henry' law constants was made by Sander [15]. Based on the data therein, Henry's law constants for some typical gases in water at 25 °C or 298.15 K are summarized in Table 2.3.

Example 2.7: Gas solubility
Estimate the solubility of CO_2 in water in gram of CO_2 per kilogram of water under standard condition (25 °C, 1 atm).

Solution
The Henry's law constant for CO_2 in water at 20 °C and 1 atm is 29.41 atm/(mol of gas per kg of water) (Table 2.3). 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:

$$P_{CO_2} = 0.0314\,\% \times 1\,\text{atm} = 0.000314\,\text{atm}$$

Substituting H and P_{CO_2} values into Eq. (2.78) gives

$$x_{CO_2} = \frac{P_{CO_2}}{H} = \frac{0.000314\,\text{atm}}{29.41 \left(\frac{\text{atm}}{\text{mol of } CO_2 \text{ per kg of water}} \right)}$$

$$= 1.068 \times 10^{-5}\,\text{mol of } CO_2/\text{kg of water}$$

The next step is to convert the unit into gram of CO_2 per g of water with the molar weight of CO_2 being 44 g/mole.

$$x_{CO_2} = \frac{1.068 \times 10^{-5}\,\text{mol } CO_2 \times \frac{44\,\text{g}}{\text{mol}}}{\text{kg of water}} = 4.698 \times 10^{-4}\,\frac{\text{g of } CO_2}{\text{kg of water}}$$

Liquid temperature affects the solubility of a gas and the consequent value of Henry's law constant. Usually, the higher temperature, the lower solubility, and the greater Henry's law constant. The Henry's law constants of some typical air pollutants at different temperatures are listed in Table 2.4. More solubility data can be found in Perry's Chemical Engineers' Handbooks or similar publications.

Table 2.3 Henry's Law constants for air emission related gases in water at T = 298 K

Gas		H at 298 K with the unit of			
		$\dfrac{atm}{\left(\dfrac{\text{mole of gas}}{\text{liter of water}}\right)}$	$\dfrac{atm}{\left(\dfrac{\text{mole of gas}}{\text{kg of water}}\right)}$	$\dfrac{atm}{\left(\dfrac{\text{mole of gas}}{\text{mole of water}}\right)}$	$\dfrac{Pa}{\left(\dfrac{\text{mole of gas}}{\text{mole of water}}\right)}$
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_2S	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

Table 2.4 Henry's law constants for gases in water at different temperatures ($H = p_i/x_i$, atm/(mol gas/mol water))

Gas	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C
He	129,000	126,000	125,000	124,000	121,000	115,000
H_2	57,900	63,600	68,300	72,900	75,100	76,500
N_2	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
O_2	25,500	32,700	40,100	47,500	53,500	58,800
CH_4	22,400	29,700	37,600	44,900	52,000	57,700
C_2H_6	12,600	18,900	26,300	34,200	42,300	50,000
C_2H_4	5,520	7,680	10,200	12,700	–	–
CO_2	728	1,040	1,420	1,860	2,330	2,830
H_2S	268	367	483	609	745	884

The Henry's law indicates that the equilibrium mole fraction of a gas in liquid is proportional to the partial pressure of the gas above the liquid regardless of the total pressure. Generally, this linear relationship (Henry's law) is sufficiently accurate for pollutant gases at low partial pressures (see Fig. 2.6). This equilibrium state will be broken by change of the amount of the target gas in either gas or liquid phase. An increase in the gas phase concentration results in further absorption into the liquid; too much dissolved gas in the liquid phase results in desorption and a mass transfer from liquid to gas phase.

However, the Henry's law may not be valid when the partial pressure of a gas is too high. Fortunately, in most air emission control engineering problems, the partial pressures of gaseous pollutants of concern are low. Therefore, the Henry's law can be used to estimate the absorption rate with a reasonable accuracy.

2.3.2 Raoult's Law for Ideal Solution

For the gas–liquid system depicted in Fig. 2.5, molecules of the liquid phase also becomes part of the gas phase and form a vapor by evaporation. When the vapor

Fig. 2.6 Henry's law line
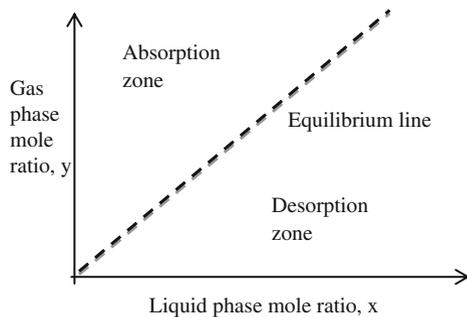
formed above the liquid-gas interface reaches its dynamic equilibrium, the rate at which liquid evaporates is equal to the rate that the gas is condensing back to liquid phase. This is called the vapor pressure. All liquids have vapor pressure, and the vapor pressure is constant regardless of absolute amount of the liquid substance.

The vapor pressure of the solution will generally decrease as solute dissolves in the liquid phase. As additional solute molecules fill the gaps between the solvent molecules and take up space, less of the liquid molecules will be on the surface and less will be able to break free to join the vapor.

Rather than explaining the Raoult's law based on sophisticated concept of entropy [8], let us explain it in a simple visual way. Consider a sealed container with only one species originally in liquid form (e.g., water). Eventually, we can get the saturated vapor at equilibrium which is sustained as the number of molecules leaving the liquid surface is equal to the number of molecules condensing back to the surface. Later on, we have added so much solute (e.g., salt into water) that there are less water molecules on the surface, because some spaces are taken by the solute salt molecules (Fig. 2.7). Since vapor is formed by the number of solvent (water) molecules that have enough energy to escape from the surface, with less solvent molecules on the surface, the vapor pressure will drop. However, reduced solvent molecules does not affect the ability of vaporized molecules to condense (or stick to the surface) because the vaporized molecules can be attached to both solvent and solute molecules. They are deemed to be able to attract each other, otherwise there would have been no solution in the first place. When the system reaches new equilibrium again, the vapor pressure is lowered.

The Raoult's law is mathematically described as

$$P_v = x_i P_v^0 \tag{2.80}$$

where x_i is the solute mole fraction in the solution, the unit of x_i is mol/mol and P_v^0 is the original vapor pressure. A solution that is governed by the Raoult's law is called an ideal solution. The Raoult's law only applies under ideal conditions in an ideal solution. It works fairly well for the solvent in dilute solutions, which we often
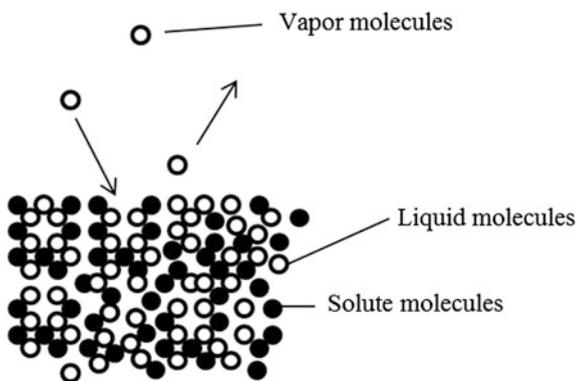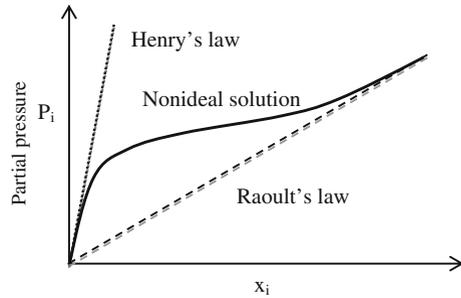

Fig. 2.7 Visualization of Rauolt's law

Fig. 2.8 Vapor pressure of a nonideal solution

encounter in air emission studies. In practice, there is no such thing as an ideal solution, it is unlikely for two different types of molecules behave as if they were the same: the forces of attraction between solvent and solute are exactly the same as between the original solvent molecules. However, very dilute solutions obey the Raoult's law to a reasonable approximation.

2.3.3 A Real Gas–Liquid System

For a real gas–liquid system, however, the vapor pressure decreases much faster than that calculated using Eq. (2.80) for extremely dilute solutions. As depicted in Fig. 2.8, the vapor pressure versus mole fraction of solvent in solution curve of a nonideal solution should follow Henry's law at low concentrations and Raoult's law at high concentrations.

2.3.4 Interfacial Mass Transfer

Lewis and Whitman (1924) two-film theory may be used to visualize the gas–liquid interfacial mass transfer. It is assumed that the gas and liquid phases are in turbulent contact with each other, and there is an interface area that separates these two phases. As shown in Fig. 2.9, near the interface, there is a small portion called film exists including a small portion (film) of the gas and another portion of liquid on either side of the interface. Beyond the films, fluids are assumed to be perfectly mixed with uniform concentrations. Mass transfer takes place in these two films. Fluids in these films are assumed to flow in a laminar or streamline motion. Therefore, molecular motion occurs by diffusion, which can be mathematically described. Concentration differences are negligible except in the films in the vicinity of the interface. Both films offer resistance to overall mass transfer. And the interface is at equilibrium described by Henry's law and it offers no resistance to mass transfer.
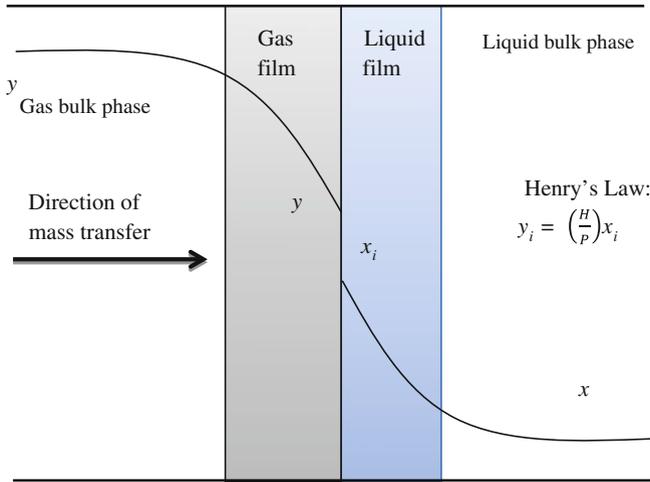
Fig. 2.9 Gas–liquid interfacial mass transfer two-film theory

In summary, according to the two-film theory, 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.

Since it is assumed in this theory that both gas and liquid bulk phases are completely mixed, the interface is at equilibrium with respect to gas molecules transferring through the interface. And, it implies that all mass transfer resistance is resulted from molecular diffusion through the gas and liquid films. With this background introduction, we can derive the mathematical expressions that follow.

The mass transfer per unit interface area is quantified by

$$n' = k_y(y - y_i) \quad \text{gas film} \tag{2.81}$$

$$n' = k_x(x_i - x) \quad \text{liquid film} \tag{2.82}$$

In this equation, n' = mole transfer rate of gas (mol/m^2 s), k_y = gas phase mass transfer coefficient (mol/m^2 s), k_x = liquid phase mass transfer coefficient (mol/m^2 s) and x, y = mole fractions in the bulk liquid and gas phases respectively.

The mass transfer coefficients, k_x and k_y, are determined experimentally. However, it is impractical to determine x_i and y_i at the gas–liquid interface. The mass transfer equation can be described with the bulk phase parameters.

Fig. 2.10 Interfacial mass transfer diving force
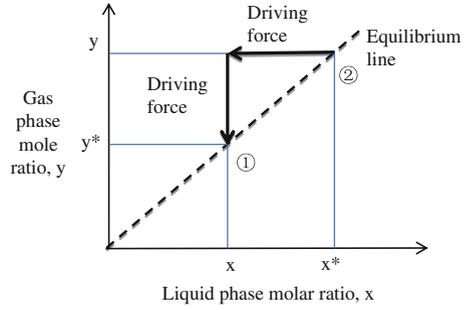
$$n' = K_y(y - y^*) \quad \text{gas phase} \tag{2.83}$$

$$n' = K_x(x^* - x) \quad \text{liquid phase} \tag{2.84}$$

where K_x, K_y = Overall mass transfer coefficients for the liquid and gas phases respectively (mol/m^2 s). x^*, y^* = Hypothetical mole fraction corresponding to y, x in the bulk fluids, and they are determined by the Henry's law as

$$y = Hx^* \tag{2.85}$$

$$y^* = Hx \tag{2.86}$$

The difference between the hypothetical mole fraction and the corresponding actual mole fraction results in the driving force illustrated in Fig. 2.10.

If we consider gas phase only in Eq. (2.83) above, the total mass transfer rate (mole/m^2 s) is described as

$$n' = K_y(y - y^*) = K_y[(y - y_i) + (y_i - y^*)] \tag{2.87}$$

Dividing both sides by K_y gives,

$$\frac{n'}{K_y} = (y - y_i) + H(x_i - x) \tag{2.88}$$

The single-phase mass transfer Eqs. (2.81) and (2.84) above also give

$$\frac{n'}{k_y} = y - y_i \quad \text{and} \quad \frac{n'}{k_x} = x_i - x \tag{2.89}$$

Substitute Eq. (2.89) into (2.88) and dividing both sides with n', one can get

$$\frac{1}{K_y} = \frac{1}{k_y} + \frac{H}{k_x} \tag{2.90}$$

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.

To understand Eq. (2.90), the mass transfer can be expressed in terms of driving potential (see Fig. 5.4) and the corresponding resistance

$$\frac{y - y^*}{R} = \frac{y - y^*}{R_x + R_y} \tag{2.91}$$

where R, R_x and R_y are overall resistance, liquid phase resistance, and gas phase resistance to mass transfer, respectively,

$$R = \frac{1}{K_y}, \quad R_y = \frac{1}{k_y}, \quad \text{and} \quad R_x = \frac{H}{k_x} \tag{2.92}$$

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 mas 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.

2.4 Practice Problems

1. Estimate the mass of a single molecule of hydrogen, CO_2 and ethane (C_2H_6).
2. Calculate the root-mean-square speed and kinetic energy of 1 mol of the following gases: He, N_2, O_2, Cl_2, and CH_4 at 300 K.
3. Which gas has the highest root-mean-square speed: Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), and Xenon (Xe)?
4. Name the two gases of the following: N_2, O_2, CO, CO_2, CH_4, and SO_2 that have the same kinetic energy and root-mean-square speed at 293 K.
5. Which gas has a lowest root-mean-square speed: Fluorine (F_2), Chlorine (Cl_2), SO_2, Krypton (Kr), and Nitrogen dioxide (NO_2)?
6. Explain why nitrogen (N_2) and carbon monoxide (CO) have the same molar kinetic energy at 293 K.
7. Compute the kinetic energy of one cubic meter of air, and CO_2 under standard condition.
8. At what temperature will the root-mean-square speed of CO_2 be the same as that of CH_4 at 300 K?
9. Which has the greater root-mean-square speed at 25 °C, NH_3 (g) or HCl (g)?

10. Which molecule has the highest root-mean-square speed (a) nitrogen molecule (N_2) at 100 °C, (b) Oxygen molecule (O_2) at 200 °C, (c) Chlorine molecule under STP conditions?

11. Assuming spherical oxygen molecules with a radius of 1.65×10^{-10} m, find the mean free path of oxygen molecules at sea level at 293 K.

12. If a gas after fuel combustion at 1000 K contains, by volume, 79 % N_2, 6 % O_2, 7 % CO_2, and 8 % H_2O, what is its molar weight? Can you approximate the molar weight of this flue gas with that of standard dry air?

13. What should be the pressure of N_2 (g) above the solution to increase the solubility of the N_2 (g) to a value of 100.0 mL N_2 per L?

14. What is the mole concentration of O_2 in a saturated solution when the O_2 pressure is 0.21 atm at 25 °C?

15. 15 mL of CO_2 (g) dissolves in 1.0L of water at 25 °C temperature and 1.0 atm pressure. What will be the mole concentration of CO_2 (g) in the saturated solution at 25 °C When the CO_2 pressure is 0.25 atm?

16. A truck tire at the gage pressure of 220 kPa and the temperature of 27 °C contains 12 L of air. Assume that the temperature drops to -40 °C. Determine the gage pressure in the tire.

17. At 27 °C and 1 atm the viscosity and density of air are 1.81×10^{-5} Pa.s and 1.2 kg/m^3, respectively. Determine the diameter and mean free path of an air molecule.

18. At 27 °C and 1 atm the viscosity and density of helium (He) are 1.9×10^{-5} Pa and 0.18 kg/m^3, respectively. Determine the diameter of helium molecule and diffusion coefficient of this gas.

19. At 20 °C and 1 atm the viscosity and density of methane are 2.01×10^{-5} Pa.s and 0.717 kg/m^3, respectively. Determine the diameter of methane molecule, mean free path, and diffusion coefficient.

20. Estimate the following maximum solubility of the air compounds CO_2, O_2 and CH_4 in water under standard conditions. Assume the gas phase is pure dry air.

21. The Henry's law constant of SO_2 at 20 °C in a SO_2-water system is 0.014×10^5 atm/mol fraction in water.
    What is the Henry's law constant with a unit of (Pa/mol fraction in water)? At 30 °C, H = 0.016×10^5 atm/mol fraction in water, does it imply a higher or lower SO_2 solubility in water?

22. Under certain condition, air density is 1.1 kg/m^3. Under the same condition, estimate the density of a gas mixture containing, by volume, 95 % CH_4 and 5 % CO? How many moles of CH_4 in a volume of 0.2 m^3 of this mixture gas?

23. Determine the volume occupied by 1 mol of ideal gas at 15 °C and 1 atm.

24. Find density of dry air at STP conditions (T = 25 °C and P = 1 atm). Assume that dry air has 79 % N_2, and 21.0 % O_2. Given molar weights of N_2 and O_2 are 28 and 32 g/mole, respectively.

References and Further Readings

1. Allen MD, Raabe OG (1985) Slip correction measurements of spherical solid aerosol particles in an improved millikan apparatus. Aerosol Sci Technol 4(3):269–286
2. Bird RB, Stewart WE, Lightfoot EN (1960) Transport phenomena. John Wiley and Sons Inc, New York
3. Cooper CD, Alley FC (2002) Air pollution control—a design approach, 3rd edn. Waveland Press, Inc., Long Grove, IL, USA
4. Crane Company (1988) Flow of fluids through valves, fittings, and pipe. Technical Paper No. 410 (TP 410). P A-5
5. CRC (2013) CRC handbook of chemistry and physics. In: Lide DR (ed), (94th edn), CRC Press, Inc., Boca Raton, Florida, USA
6. Einstein A (1905) On the kinetic molecular theory of thermal movements of particles suspended in a quiescent fluid An. Physik 17:549–560. (English translation: Investigation on the Theory of Brownian Movement, Furth R (ed), Dover, New York, 1956)
7. Flagan R, Seinfeld John H (2012) Fundamentals of air pollution engineering. Dover Publications Inc., New York, USA
8. Guggenheim EA (1937) The theoretical basis of Raoult's law. Trans Faraday Soc 33:151–156
9. Hibbeler RC (2010) Engineering mechanics: dynamics (12th Edn), Prentice Hall, Pearson Publishing Company, NJ, London
10. John HS, Richard CF, Auzmann W (1966) Kinetic theory of gases, W. A. Benjamin Inc., New York
11. Lapple CE, Shepherd CB (1940) Calculation of particle trajectories. Ind Eng Chem 32 (5):605–617
12. Montgomery RB (1947) Viscosity and thermal conductivity of air and diffusivity of water vapor in air. J Meteorol 4:193–196
13. National Research Council (1929) International critical tables, vol III. McGraw-Hill, New York, NY, USA
14. Otto E, Fissan H, Park SH, Lee KW (1999) The log-normal size distribution theory of Brownian aerosol coagulation for the entire particle size range: Part II. J Aerosol Sci 30 (1):16–34
15. Sander R (1999) Compilation of henry's law constants for inorganic and organic species of potential importance in environmental chemistry. http://www.mpch-mainz.mpg.de/∼sander/res/henry.html
16. Starzak ME (2010) Energy and enthropy. Chapter 13 Maxwell and boltzmann distribution. Springer, Berlin p 199