Example 1.18.1

Determine the molar mass of a gas if its pressure is to fall to one-half of its value in a vertical distance of one kilometer at 298 K.

Solution

From the given data, we write

$$p = p_0/2, \quad h = 10^3\ \text{m} \quad \text{and} \quad g = 9.807\ \text{m s}^{-2}$$

Substituting these values in the expression

$$p = p_0 \exp(-Mgh/RT)$$

i.e.
$$M = -\frac{RT}{gh} \ln \frac{p}{p_0}$$

we get
$$M = -\frac{(8.314\ \text{J K}^{-1}\text{mol}^{-1})(298\ \text{K})}{(9.807\ \text{m s}^{-2})(10^3\ \text{m})} \ln\left(\frac{1}{2}\right) = 175.1\ \text{g mol}^{-1}$$

Example 1.18.2

Calculate the pressure of a barometer on an aeroplane which is at an altitude of 10 km. Assume the pressure to be 101.325 kPa at sea level and the mean temperature 243 K. Use the average molar mass of air (80% N_2 and 20% O_2).

Solution

From the given data, we have

$$p_0 = 101.325\ \text{kPa}, \quad h = 10\ \text{km} = 10^4\ \text{m}, \quad T = 243\ \text{K}$$

$$M = 0.8\,(0.028\ \text{kg mol}^{-1}) + 0.2\,(0.032\ \text{kg mol}^{-1}) = 0.028\,8\ \text{kg mol}^{-1}$$

Substituting these values in the expression

$$p = p_0 \exp(-Mgh/RT)$$

we get
$$p = (101.325\ \text{kPa}) \exp\left\{-\frac{(0.028\,8\ \text{kg mol}^{-1})(9.807\ \text{m s}^{-2})(10^4\ \text{m})}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(243\ \text{K})}\right\}$$
$$= (101.325\ \text{kPa})\,(0.247) = 25.036\ \text{kPa}$$

Problem 1.18.1

If the compression factor of a gas is $Z(p, T)$, we write equation of state as $pV/nRT = Z$ Show how this will affect the equation for the distribution of the gas in a gravitational field. From the differential equation for the distribution, show that if $Z > 1$, the distribution is broader for a real gas than for an ideal gas and converse is true if $Z < 1$. If $Z = 1 + bp$ where b is a function of temperature, integrate the equation and evaluate the constant of integration to obtain the explicit form of the distribution function.

Solution

We have $\mathrm{d}p = -g\rho\,\mathrm{d}h$

Since
$$pV = ZnRT = Z\frac{m}{M}RT, \quad \text{we obtain} \quad \frac{pM}{ZRT} = \frac{m}{V} = \rho$$

Therefore $$-\frac{\mathrm{d}p}{p}=\frac{Mg}{ZRT}\,\mathrm{d}h$$

For $Z > 1$ the term Mg/ZRT for a real gas will be less than the corresponding term for an ideal gas, hence the distribution will be broader for the real gas. If $Z < 1$, this term is greater for a real gas than for an ideal gas and hence the distribution of a real gas is not as broad as that of an ideal gas.

If $Z = 1 + bp$, we have

$$\mathrm{d}p=-\frac{p}{(1+bp)}\frac{Mg}{RT}\,\mathrm{d}h \quad \text{or} \quad \mathrm{d}p\left(\frac{1+bp}{p}\right)=-\frac{Mg}{RT}\,\mathrm{d}h$$

or $$\frac{\mathrm{d}p}{p}+b\,\mathrm{d}p=-\frac{Mg}{RT}\,\mathrm{d}h \quad \text{or} \quad \frac{\mathrm{d}(p/p^\circ)}{(p/p^\circ)}+b\,\mathrm{d}p=-\frac{Mg}{RT}\,\mathrm{d}h$$

where p° is standard unit pressure. Integrating this, we have

$$\ln(p/p^\circ)+bp=-\frac{Mgh}{RT}+C$$

The value of constant C is obtained by substituting $p = p_0$ at $h = 0$. Thus

$$C=\ln(p_0/p^\circ)+bp_0$$

The resultant expression becomes

$$\ln\frac{p}{p_0}+b(p-p_0)=-\frac{Mgh}{RT}$$

Problem 1.18.2 The temperature of air decreases linearly with altitude in accordance with the equation $T = T_0 - ah$, where a is a constant, h is altitude, T_0 is temperature at ground level and T is temperature at altitude h. Derive a modified form of the barometric equation taking into account this temperature dependence on altitude.

Solution We have $$\mathrm{d}p=-\rho g\,\mathrm{d}h$$

that is $$\mathrm{d}p=-\frac{pM}{RT}g\,\mathrm{d}h$$

or $$\int\frac{\mathrm{d}p}{p}=\frac{Mg}{R}\int\frac{\mathrm{d}h}{T}$$

Now, since $T=T_0-ah$, we can write

$$\mathrm{d}T=-a\,\mathrm{d}h \quad \text{or} \quad \mathrm{d}h=\mathrm{d}T/(-a)$$

Replacing $\mathrm{d}h$ in terms of $\mathrm{d}T$ in the above equation, we get

$$\int_{p_0}^{p} \frac{dp}{p} = -\frac{Mg}{R} \int_{T_0}^{T} \frac{1}{(-a)} \frac{dT}{T} = \frac{Mg}{aR} \int_{T_0}^{T} \frac{dT}{T}$$

or $$\ln \frac{p}{p_0} = \frac{Mg}{aR} \ln \frac{T}{T_0}$$

In terms of height, we have

$$\int_{p_0}^{p} \frac{dp}{p} = -\frac{Mg}{R} \int_{0}^{h} \frac{dh}{(T_0 - ah)}$$

i.e. $$\ln \frac{p}{p_0} = \frac{Mg}{Ra} \ln \left(\frac{T_0 - ah}{T_0} \right)$$

1.19 MOLECULAR COLLISIONS IN A GAS

While considering collisions of the molecules among themselves we assume the molecules to be rigid, non-interacting, and spherical with diameter σ. It is also assumed that all the molecules move with the same average speed $\overline{u}$.

Collision Cross-Section of Molecules

Two identical molecules of diameter σ will just touch each other when the distance separating their centres is σ. Thus, a moving molecule will collide with other molecules whose centres come within a distance of σ from its centre. The quantity $(\pi\sigma^2)$ is called the *collision cross-section* for the rigid spherical molecule. From Fig. 1.19.1 it is obvious that this collision cross-section is an area of an imaginary sphere of radius σ around the molecule within which the centre of another molecule cannot penetrate.

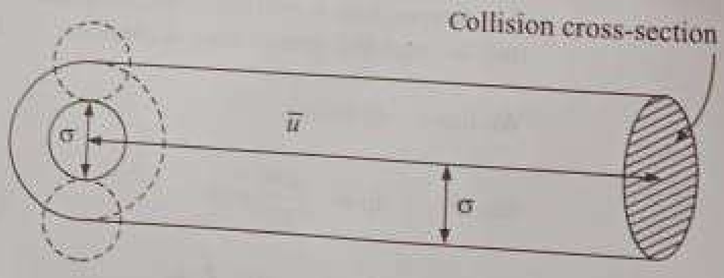


Fig. 1.19.1 Collision cross-section of a molecule

Expression of Number of Collisions

The volume swept by a single molecule in unit time is

$$V = (\pi\sigma^2)\,\overline{u}$$

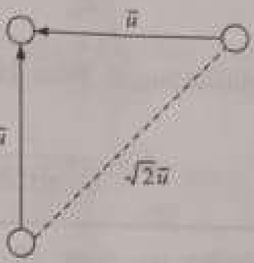
If N^* is the number of molecules per unit volume, then the number of molecules within the volume V is

$$N = VN^* = (\pi\sigma^2\overline{u})\,N^*$$

Hence, the number of collisions made by a single molecule in unit time will be

$$Z_1 = N = (\pi\sigma^2\bar{u})\,N^*$$

So far, it is assumed that only one molecule is moving and all the others are stationary. In practice, however, this is not true. In order to account for the movements of all molecules, one must consider the average velocity along the line of centres of two colliding molecules instead of the average velocity of a single molecule. If it is assumed that, on an average, molecules collide while approaching each other perpendicularly, then the average velocity along their centres is $\sqrt{2}\bar{u}$ as shown below.



Number of collisions made by a single molecule with other molecules per unit time is given by

$$Z_1 = \pi\sigma^2(\bar{u}_{\text{rel}})N^* = \sqrt{2}\pi\sigma^2\bar{u}\,N^* \tag{1.19.1}$$

The total number of bimolecular collisions Z_{11} per unit volume per unit time is given by

$$Z_{11} = \frac{1}{2}(Z_1\,N^*)$$

or $$Z_{11} = \frac{1}{2}(\sqrt{2}\pi\sigma^2\bar{u}\,N^*)N^* = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}\,N^{*2} \tag{1.19.2}$$

(Note that the division by two is essential since the simple multiplication of Z_1 by N^* would count every collision twice.)

If the collisions involve two unlike molecules, then the number of collisions Z_{12} per unit volume per unit time is given as

$$Z_{12} = \pi\sigma_{12}^2\left(\sqrt{\frac{8kT}{\pi\mu}}\right)N_1N_2 \tag{1.19.3}$$

where N_1 and N_2 are the number of molecules per unit volume of the two types of molecules, σ_{12} is the average diameter of the two molecules (i.e. σ $= (\sigma_1+\sigma_2)/2$) and μ is the reduced mass such that

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

The Mean Free Path The mean free path is *the average distance travelled by a molecule between two successive collisions*. We can express it as follows:

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No. of collisions made by a single molecule per unit time}}$$

$$= \frac{\bar{u}}{Z_1}$$

Substituting Z_1 from Eq. (1.19.1), we get

$$\lambda = \frac{\bar{u}}{\sqrt{2}\pi\sigma^2\bar{u}N^*} = \frac{1}{\sqrt{2}\pi\sigma^2 N^*} \qquad (1.19.4$$

Example 1.19.1 Calculate the values of σ, λ, Z_1 and Z_{11} for oxygen at 298.15 K at the pressure of 101.325 kPa, given van der Waals constant $b = 3.183 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}$.

Solution Number of molecules per unit volume,

$$N^* = \frac{p}{kT} = \frac{(101.325 \times 10^3\ \text{Pa})}{(1.3806 \times 10^{-23}\ \text{J K}^{-1})(298.15\ \text{K})} = 246.157 \times 10^{23}\ \text{m}^{-3}$$

The van der Waals constant b is

$$b = 4N_\text{A}\left(\frac{4}{3}\pi r^3\right)$$

Thus $$r = \left(\frac{3b}{16\pi N_\text{A}}\right)^{1/3} = \left(\frac{3 \times 3.183 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}}{16 \times 3.14 \times 6.022 \times 10^{23}\ \text{mol}^{-1}}\right)^{1/3}$$

$$= 1.467 \times 10^{-9}\ \text{dm}$$

Therefore

$$\sigma = 2r = 2.934 \times 10^{-9}\ \text{dm} = 2.934 \times 10^{-10}\ \text{m}$$

Average speed,

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \left\{\frac{8(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}{(3.14)(0.032\ \text{kg mol}^{-1})}\right\}^{1/2} = 444.25\ \text{m s}^{-1}$$

Mean free path,

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

$$= \frac{1}{(1.414)(3.14)(2.934 \times 10^{-10}\ \text{m})^2(246.157 \times 10^{23}\ \text{m}^{-3})} = 1.06 \times 10^{-7}\ \text{m}$$

$$\begin{aligned}Z_1 &= \sqrt{2}\pi\sigma^2\bar{u}\,N^*\\ &= (1.414)\,(3.14)\,(2.934\times10^{-10}\ \text{m})^2\,(444.25\ \text{m s}^{-1})\,(246.157\times10^{23}\ \text{m}^{-3})\\ &= 4.18\times10^{9}\ \text{s}^{-1}\end{aligned}$$

$$\begin{aligned}Z_{11} &= \frac{1}{2}Z_1N^* = \frac{1}{2}(4.18\times10^{9}\ \text{s}^{-1})(246.157\times10^{23}\ \text{m}^{-3})\\ &= 5.144\times10^{34}\ \text{m}^{-3}\ \text{s}^{-1}\end{aligned}$$

Example 1.19.2 Calculate λ, Z_1 and Z_{11} for oxygen at 298 K and 10^{-3} mmHg. Given: $\sigma = 3.61 \times 10^{-8}$ cm.

Solution From the given data, we have

$$N^* = \frac{p}{kT} = \frac{(10^{-3}\ \text{mmHg})(133.322\ \text{Pa/1 mmHg})}{(1.380\,6\times10^{-23}\ \text{J K}^{-1})(298\ \text{K})} = 3.24\times10^{19}\ \text{m}^{-3}$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \left(\frac{8(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{(3.14)(0.032\ \text{kg mol}^{-1})}\right)^{1/2} = 444.1\ \text{m s}^{-1}$$

Thus

$$\begin{aligned}Z_1 &= \sqrt{2}\pi\sigma^2\bar{u}\,N^*\\ &= (1.414)\,(3.14)\,(3.61\times10^{-10}\ \text{m})^2\,(444.1\ \text{m s}^{-1})(3.24\times10^{19}\ \text{m}^{-3})\\ &= 8.326\times10^{3}\ \text{s}^{-1}\end{aligned}$$

$$\begin{aligned}Z_{11} &= \frac{1}{2}Z_1N^* = \frac{1}{2}(8.326\times10^{3}\ \text{s}^{-1})\,(3.24\times10^{19}\ \text{m}^{-3})\\ &= 13.488\times10^{22}\ \text{m}^{-3}\ \text{s}^{-1}\end{aligned}$$

$$\begin{aligned}\lambda &= \frac{1}{\sqrt{2}\pi\sigma^2N^*} = \frac{1}{(1.414)(3.14)(3.61\times10^{-10}\text{m})^2(3.24\times10^{19}\text{m}^{-3})}\\ &= 5.334\times10^{-2}\ \text{m} = 5.334\ \text{cm}\end{aligned}$$

Example 1.19.3 The mean free path of the molecule of a certain gas at 300 K is 2.6×10^{-5} m. The collision diameter of the molecule is 0.26 nm. Calculate (a) pressure of the gas, and (b) number of molecules per unit volume of the gas.

Solution Here $\lambda = 2.6\times10^{-5}$m, $\sigma = 0.26\times10^{-9}$m, $T = 300$ K

Since

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2N^*}$$

we get

$$\begin{aligned}N^* &= \frac{1}{\sqrt{2}\pi\sigma^2\lambda} = \frac{1}{(1.414)(3.14)(0.26\times10^{-9}\text{m})^2(2.6\times10^{-5}\text{m})}\\ &= 1.281\times10^{23}\ \text{m}^{-3}\end{aligned}$$

Now,

$$\begin{aligned}p &= N^*kT = (1.281\times10^{23}\ \text{m}^{-3})\ (1.380\,6\times10^{-23}\ \text{J K}^{-1})\ (300\ \text{K})\\ &= 5.306\times10^{2}\ \text{J m}^{-3} \equiv 5.306\times10^{2}\ \text{Pa}\end{aligned}$$

Effect of Temperature and Pressure on Mean Free Path and Molecular Collisions

In order to discuss the effect of temperature and pressure on λ, Z_1 and Z_{11}, first we express the pressure and temperature dependence of N^* and $\bar{u}$. This can be done as follows.

Dependence of N^* on p and T

According to the ideal gas equation, we have

$$pV = nRT = \frac{N'}{N_\mathrm{A}}RT \quad \text{or} \quad p = \left(\frac{N'}{V}\right)\left(\frac{R}{N_\mathrm{A}}\right)T = \left(\frac{N'}{V}\right)kT$$

Thus, the number of molecules per unit volume is given by

$$N^* = \frac{N'}{V} = \frac{p}{kT} \tag{1.19.5}$$

Thus, $N^* \propto \dfrac{p}{T}$ (1.19.6)

Dependence of $\bar{u}$ on T

The average speed $\bar{u}$ is given as

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

Thus, $\bar{u} \propto \sqrt{T}$ (1.19.7)

Effects on Mean Free Path

Now from Eq. (1.19.4), we get

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

Thus, $\lambda \propto \dfrac{1}{N^*}$

Employing Eq. (1.19.6), we get

$$\lambda \propto \frac{T}{p} \tag{1.19.8}$$

Thus, $\lambda \propto T$ provided p is held constant

and $\lambda \propto \dfrac{1}{p}$ provided T is held constant.

Since, according to Gay Lussac's law, $p \propto T$ at constant volume, therefore Eq. (1.19.8) under these conditions modifies to

$$\lambda \propto \text{(constant)}$$

that is, there will be no effect of changing T or p on λ if the volume of the gas is kept constant.

Effects of p and T on Molecular Collisions

From Eq. (1.19.1), we have

$$Z_1 = \sqrt{2}\pi\sigma^2\, \bar{u}\, N^*$$

or

$$Z_1 \propto \bar{u}\, N^*$$

Employing Eq. (1.19.6) and Eq. (1.19.7), this modifies to

$$Z_1 \propto (\sqrt{T})\left(\frac{p}{T}\right) \quad \text{or} \quad Z_1 \propto \frac{p}{\sqrt{T}} \tag{1.19.9}$$

Thus, $Z_1 \propto p$ when temperature is held constant and $Z_1 \propto 1/\sqrt{T}$ when pressure is held constant.

The effect of changing p or T at constant volume can be described by making use of Gay-Lussac's law in Eq. (1.19.9). Thus, we have

$$Z_1 \propto \frac{T}{\sqrt{T}} \propto \sqrt{T} \qquad \text{(volume constant)}$$

and

$$Z_1 \propto \frac{p}{\sqrt{p}} \propto \sqrt{p} \qquad \text{(volume constant)}$$

From Eq. (1.19.2), we have

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}\, N^{*2} \quad \text{or} \quad Z_{11} \propto \bar{u}\, N^{*2}$$

Employing Eq. (1.19.6) and Eq. (1.19.7), this modifies to

$$Z_{11} \propto (\sqrt{T})\left(\frac{p}{T}\right)^2 \quad \text{or} \quad Z_{11} \propto \frac{p^2}{T^{3/2}}$$

Thus, $Z_{11} \propto p^2$ provided temperature is held constant and $Z_{11} \propto T^{-3/2}$ provided pressure is held constant.

The effect of changing p or T at constant volume can again be described by making use of Gay-Lussac's law. Thus

$$Z_{11} \propto \frac{p^2}{T^{3/2}} \propto \frac{T^2}{T^{3/2}} \propto T^{1/2} \qquad \text{(volume constant)}$$

and

$$Z_{11} \propto \frac{p^2}{T^{3/2}} \propto \frac{p^2}{p^{3/2}} \propto p^{1/2} \qquad \text{(volume constant)}$$

1.20 VISCOSITY

Introduction

The internal friction which opposes the relative motion of adjacent layers of a fluid is known as viscosity.

Viscosity of Gases

In a laminar flow of a fluid in a cylindrical tube, layers just touching the sides of the tube are stationary, and velocities of the adjacent layers increase towards the centre of the tube, the layer in the centre of the tube has a maximum velocity. There thus exists a velocity gradient amongst different layers of a liquid.

In case of gases, because of their continuous movement, there occurs an interchange of molecules between two layers, with the result that a fraction of momentum of one layer is passed over to the other layer. The net effect is to decrease the relative rate of movement of one layer with respect to the other. In order to maintain a uniform velocity gradient, one has to apply a force along the direction of movement of the layers. This applied force is a measure of internal friction or viscosity of the fluid.

Viscosity of Liquids

In case of liquids, this internal friction arises because of intermolecular attractions. Molecules in a slower moving layer try to decrease the velocity of the molecules in a faster moving layer and vice versa, with the result that some tangential force is required to maintain a uniform flow.

Definition of Coefficient of Viscosity

The tangential force F required to maintain uniform velocity of layers will depend upon two factors, viz.,

(i) Area A of contact between the two adjacent layers
(ii) Velocity gradient $\mathrm{d}u/\mathrm{d}z$

Thus,
$$F \propto A\frac{\mathrm{d}u}{\mathrm{d}z} \quad \text{that is} \quad F = \eta A\frac{\mathrm{d}u}{\mathrm{d}z} \tag{1.20.1}$$

where η is known as the *coefficient of viscosity* (or simply viscosity). It is the tangential force that must be applied in order to maintain a velocity difference of unity between two parallel layers unit distance apart and having unit area of contact. SI unit of the coefficient of viscosity is N m^{-2}s. In CGS units, it has the unit of dyn cm^{-2} s and is known as the poise unit.

Expression of Viscosity of Gases

Viscosity in case of a gas arises because of transfer of momentum across the layers of the gas. Consider a layer P–P′ at a height z, (Fig. 1.20.1), moving with a velocity u_z. Let the velocity gradient be $\mathrm{d}u/\mathrm{d}z$. Let us consider the molecules entering and leaving this layer. We assume:

(i) That the flow velocity u_z is very small as compared with the mean gas velocity $\bar{u}$.

(ii) That the only molecules reaching P–P′ are those which, on an average, have just made their last collision at a distance λ from the height z.

(iii) The number of molecules passing downwards or upwards through a unit area per unit time = $N^*\bar{u}/4$, where N^* is the number of molecules per unit volume and $\bar{u}$ is the average speed of gaseous molecules.[†]

[†] Assuming statistical motion of molecules, the number of molecules will come out to be $N^*\bar{u}/6$ as one sixth of the molecules will be moving along each of the positive and negative directions of x-, y-, and z-axes. However, the explicit expression of $N^*\bar{u}/4$ can be derived statistically by using velocity-component distribution function (Eq. 4.14.12 of Volume 5 of this series of book).

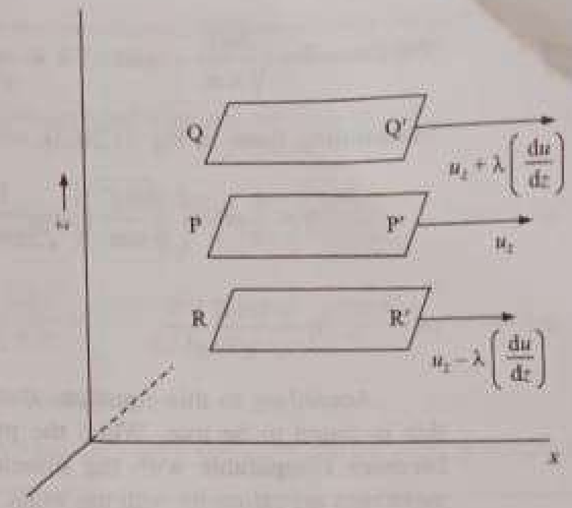


Fig. 1.20.1 Display of velocity gradient with the height of layer

In the plane P–P′, the amount of horizontal momentum coming up through a unit area per unit time is

$$(mu)\uparrow = m\left(\frac{1}{4}N^*\bar{u}\right)\left(u_z - \lambda\frac{du}{dz}\right)$$

and the amount of horizontal momentum coming down

$$(mu)\downarrow = m\left(\frac{1}{4}N^*\bar{u}\right)\left(u_z + \lambda\frac{du}{dz}\right)$$

The net downward flow of x momentum in unit time

$$(mu)\downarrow - (mu)\uparrow = \frac{1}{2}N^*\bar{u}\,m\lambda\frac{du}{dz}$$

Since momentum transfer in unit time is numerically equal to the force, therefore, the force acting in the x-direction on a unit area of the layer is

$$F = \frac{1}{2}mN^*\bar{u}\lambda\frac{du}{dz}$$

Comparing this with Eq. (1.20.1) with A = unit area, we get

$$\eta = \frac{1}{2}mN^*\bar{u}\lambda = \frac{1}{2}\rho\bar{u}\lambda \qquad (1.20.2)^{\dagger}$$

where ρ is the density of the medium.

[†] The more rigorous calculations based on the hard sphere model gives the expression of viscosity as $\eta = (5\pi/32)\,mN^*\bar{u}\,\lambda$.

Effect of p and T on Viscosity of Gases

We have $\bar{u} = \sqrt{\dfrac{8kT}{\pi m}}$ and $\lambda = \dfrac{1}{\sqrt{2}\pi\sigma^2 N^*}$

Substituting these in Eq. (1.20.2), we have

$$\eta = \frac{1}{2} m N^* \left(\sqrt{\frac{8kT}{\pi m}}\right)\left(\frac{1}{\sqrt{2}\pi\sigma^2 N^*}\right)$$

or
$$\eta = \frac{(mkT)^{1/2}}{\pi^{3/2}\sigma^2} \tag{1.20.3}$$

According to this equation, η is independent of pressure. Experimentally this is found to be true. When the pressure is so low that the mean free path becomes comparable with the dimensions of the apparatus, the collisions of molecules are primarily with the walls, and under such circumstances, Eq. (1.20.2) is not applicable.

Equation (1.20.3) shows that η should also be independent of density of gas and this is in agreement with the experimental observations. This equation also suggests that $\eta \propto T^{1/2}$, but a somewhat larger exponent more like $T^{0.7}$ is observed for real gases, partly due to the fact that the cross-sectional diameter becomes smaller at higher temperatures due to increased penetration of the potential energy barrier by gas molecules of higher velocities. In contrast with the viscosity of ideal gases, the viscosity of liquids decreases with the rise in temperature.

Example 1.20.1

The van der Waals constant b for n-heptane is 0.265 4 dm^3 mol^{-1}. Estimate the coefficient of viscosity of this gas at 298 K. Calculate σ from b assuming molecules to be spherical.

Solution

We are given that $b = 0.265\,4\ \mathrm{dm^3\ mol^{-1}}$

Since
$$b = 4N_A\left(\frac{4}{3}\pi r^3\right)$$

we get
$$r = \left(\frac{3b}{16N_A\pi}\right)^{1/3} = \left\{\frac{3(0.265\,4\ \mathrm{dm^3\ mol^{-1}})}{16(6.022\times10^{23}\ \mathrm{mol^{-1}})(3.14)}\right\}^{1/3}$$
$$= 0.297\,4\times10^{-8}\ \mathrm{dm}$$

Therefore $\sigma = 2r = 0.594\,8\times10^{-8}\ \mathrm{dm}$

Molar mass of n-heptane $= 100\ \mathrm{g\ mol^{-1}} = 0.1\ \mathrm{kg\ mol^{-1}}$

Thus
$$\eta = \frac{\sqrt{mkT}}{\pi^{3/2}\sigma^2} = \frac{\{(0.1\ \mathrm{kg}/6.022\times10^{23})(1.380\,6\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})\}^{1/2}}{(3.14)^{3/2}(0.594\,8\times10^{-9}\ \mathrm{m})^2}$$

$$= \frac{(2.613\,8\times10^{-23}\ \mathrm{J^{1/2}\ kg^{1/2}})}{(1.968\,5\times10^{-18}\ \mathrm{m^2})} = 1.328\times10^{-5}\ \mathrm{J^{1/2}\ kg^{1/2}\ m^{-2}}$$

$$= 1.328\times10^{-5}\ \mathrm{N\ m^{-2}\ s} = 1.328\times10^{-4}\ \mathrm{dyn\ cm^{-2}\ s} = 1.328\times10^{-4}\ \mathrm{poise}$$

Example 1.20.2 Calculate the number of collisions per square metre per second of O_2 molecules with a wall at a pressure of 101.325 kPa and temperature 298 K.

Solution Number of collisions per unit area per unit time $= \frac{1}{4} N^* u_{av}$

Now $$N^* = \frac{p}{kT} = \frac{101.325 \times 10^3 \text{ N m}^{-2}}{(1.380\,6 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} = 2.463 \times 10^{25} \text{ m}^{-3}$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} = \left\{\frac{8(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{3.14(0.032 \text{ kg mol}^{-1})}\right\}^{1/2} = 444.1 \text{ m s}^{-1}$$

Hence, Number of collisions

$$= \frac{1}{4} N^* \bar{u} = \frac{1}{4}(2.463 \times 10^{25} \text{ m}^{-3})(444.1 \text{ m s}^{-1}) = 2.734 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}$$

1.21 SELF DIFFUSION AND EFFUSION PROCESSES

Introduction to Self Diffusion Movement of molecules from high-density region to low-density region constitutes the phenomenon of self diffusion. Experimentally, the self diffusion is given by Fick's law:

$$J_z = -D \frac{\mathrm{d}c}{\mathrm{d}z} \tag{1.21.1}$$

where J_z is the net flow of matter per unit area per unit time and D is the coefficient of diffusion.

Expression of Coefficient of Diffusion Consider a unit area in the gaseous layer at height z (Fig. 1.21.1). The number of molecules per unit volume at height z relative to zero level is given by

$$N = N_0 + \left(\frac{\partial N}{\partial z}\right) z \tag{1.21.2}$$

where N_0 is the number of molecules per unit volume at $z = 0$.

Also consider two layers at the heights $z - \lambda$ and $z + \lambda$ respectively, where λ is the mean free path of gaseous molecules. Only those molecules will pass through the layer at the height z who have their last collision at a distance λ from this layer. Hence, the number of molecules passing downward through a unit area at the height z per unit time is given by

$$N\downarrow = \frac{1}{4} N^*_{z+\lambda}\, \bar{u} = \frac{1}{4}\left[N_0 + \left(\frac{\partial N}{\partial z}\right)(z+\lambda)\right]\bar{u}$$

Similarly, the number of molecules coming up from the lower layer is

$$N\uparrow = \frac{1}{4} N^*_{z-\lambda}\, \bar{u} = \frac{1}{4}\left[N_0 + \left(\frac{\partial N}{\partial z}\right)(z-\lambda)\right]\bar{u}$$

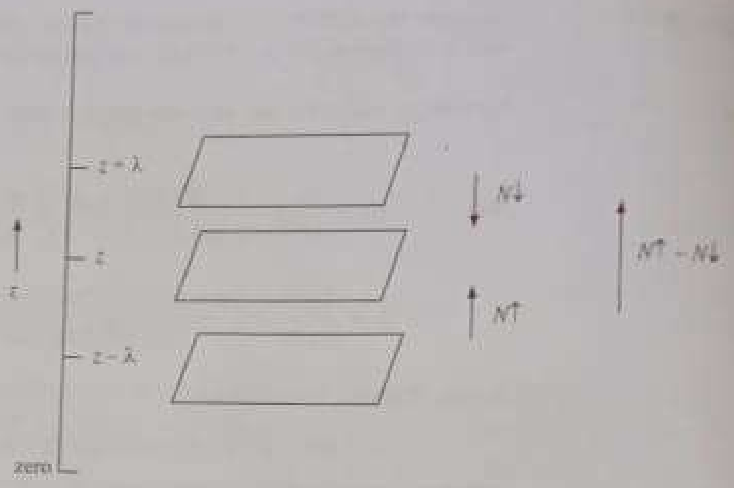


Fig. 1.21.1 Process of self diffusion

The net flow of the molecules in the upward direction is

$$N\uparrow - N\downarrow = \frac{1}{4}\bar{u}\left[\left\{N_0 + \left(\frac{\partial N}{\partial z}\right)(z-\lambda)\right\} - \left\{N_0 + \left(\frac{\partial N}{\partial z}\right)(z+\lambda)\right\}\right]$$

$$= -\frac{1}{2}\bar{u}\lambda\left(\frac{\partial N}{\partial z}\right) \qquad (1.21.3)$$

Comparing Eq. (1.21.3) with Eq. (1.21.1), we get

$$D = \frac{1}{2}\bar{u}\lambda \qquad (1.21.4$$

Effect of p and T on the Diffusion Coefficient

We have

$$\bar{u} = \sqrt{\frac{8kT}{\pi m}} \qquad (1.21.5$$

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*} = \frac{kT}{\sqrt{2}\pi\sigma^2 p} \qquad (1.21.6$$

Substituting Eqs (1.21.5) and (1.21.6) in Eq. (1.21.4), we get

$$D = \frac{1}{2}\left(\sqrt{\frac{8kT}{\pi m}}\right)\left(\frac{kT}{\sqrt{2}\pi\sigma^2 p}\right) \qquad (1.21.7$$

Hence, the coefficient of diffusion depends

(i) inversely on pressure at constant temperature, and
(ii) directly on $T^{3/2}$ at constant pressure.