Collisions in a Multicomponent Hard-Sphere Gas

We now modify our model system to contain more than one substance. We first consider collisions between two molecules of the same substance. If other substances are present a molecule might collide with other types of molecules between two collisions with others of its own kind. The effect of such collisions will be to put bends in the collision cylinder. The results for a one-component gas can be applied to the collisions between molecules of the same substance in a multicomponent gas if we interpret the mean free path between collisions as the sum of the lengths of the portions of the collision cylinder between collisions with molecules of other substances.

We now consider the rate of collisions of unlike molecules. The radius of the collision cylinder (the collision diameter) for collisions between molecules of substance 1 and substance 2 is denoted by d_{12} and is equal to the sum of the radii of the molecules, or half the sum of their diameters:

$$d_{12} = \frac{1}{2}(d_1 + d_2) \tag{9.8-23}$$

Assume that molecule 1 is of substance 1 and is moving at $\langle v_1 \rangle$, the mean speed of molecules of substance 1, and that molecule 2 is of substance 2 and is moving at $\langle v_2 \rangle$, the mean speed of molecules of type 2. Assume again that the average collision takes place at right angles. Figure 9.20 must be modified, as shown in Figure 9.21. In order for the molecules to collide the distances from the location of the collision must be proportional to the speeds of the molecules:

$$x = t_c \langle v_1 \rangle, \quad y = t_c \langle v_2 \rangle \tag{9.8-24}$$

where $\langle v_1 \rangle$ is the mean speed of particles of type 1, $\langle v_2 \rangle$ is the mean speed of particles of type 2, and where t_c is the time yet to elapse before the collision occurs. The molecular separation is given by the theorem of Pythagoras:

$$r = t_c\left[\langle v_1\rangle^2 + \langle v_2\rangle^2\right]^{1/2} \tag{9.8-25}$$

We denote the *mean relative speed* by $\langle v_{12}\rangle$:

$$\langle v_{\text{rel}}\rangle = \langle v_{12}\rangle = \sqrt{\langle v_1\rangle^2 + \langle v_2\rangle^2} = \sqrt{\frac{8k_\text{B}T}{\pi m_1} + \frac{8k_\text{B}T}{\pi m_2}}$$

$$\boxed{\langle v_{12}\rangle = \sqrt{\frac{8k_\text{B}T}{\pi\mu_{12}}}} \tag{9.8-26}$$

where m_1 and m_2 are the two molecular masses and where μ_{12} is called the *reduced mass* of particles 1 and 2:

$$\boxed{\frac{1}{\mu_{12}} = \frac{1}{m_1} + \frac{1}{m_2}} \tag{9.8-27}$$

$$\boxed{\mu_{12} = \frac{m_1 m_2}{m_1 + m_2}} \tag{9.8-28}$$

Our derivation is crude, but Eq. (9.8-26) is the correct expression for the mean relative speed. For a pair of identical particles, μ is equal to $m/2$, so that Eq. (9.8-26) is valid for that case as well as for two different substances.

EXAMPLE 9.20

Calculate the mean relative speed of nitrogen and oxygen molecules at 298 K.

Solution

Let nitrogen be substance 1 and oxygen be substance 2.

$$\langle v_{12} \rangle = \sqrt{\frac{8k_B T}{\pi \mu_{12}}} = \sqrt{\frac{8RT}{\pi N_{Av}\mu_{12}}}$$

$$N_{Av}\mu_{12} = \frac{(0.0280\,\mathrm{kg\,mol^{-1}})(0.0320\,\mathrm{kg\,mol^{-1}})}{0.0280\,\mathrm{kg\,mol^{-1}} + 0.0320\,\mathrm{kg\,mol^{-1}}} = 0.0149\,\mathrm{kg\,mol^{-1}}$$

$$\langle v_{12} \rangle = \sqrt{\frac{8(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{\pi(0.0149\,\mathrm{kg\,mol^{-1}})}} = 650\,\mathrm{m\,s^{-1}}$$

When we take account of the fact that the molecules of substance 2 are moving, the mean free path between collisions of a single particle of substance 1 with particles of substance 2 is given by

$$\lambda_{1(2)} = \frac{\langle v_1 \rangle}{\langle v_{12} \rangle}\frac{1}{\pi d_{12}^2 \mathcal{N}_2} = \sqrt{\frac{m_2}{m_1 + m_2}}\frac{1}{\pi d_{12}^2 \mathcal{N}_2} \tag{9.8-29}$$

We interpret $\lambda_{1(2)}$ as the sum of the lengths of the straight portions of the collision cylinder between bends caused by collisions of other types than 1–2 collisions. The mean free path of a molecule of substance 2 between collisions with molecules of substance 1 is denoted by $\lambda_{2(1)}$ and is obtained by switching the indices 1 and 2 in Eq. (9.8-29). Note that $\lambda_{2(1)}$ is not necessarily equal to $\lambda_{1(2)}$.

The formula for the *mean rate of collisions* of one molecule of substance 1 with molecules of substance 2 is analogous to Eq. (9.8-21):

$$z_{1(2)} = \frac{1}{\tau_{1(2)}} = \frac{\langle v_1 \rangle}{\lambda_{1(2)}} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu_{12}}}\pi d_{12}^2 \mathcal{N}_2 \qquad (9.8\text{-}30)$$

The rate of collisions of a molecule of substance 2 with molecules of substance 1 is obtained by switching the indices 1 and 2 in Eq. (9.8-30). The rate $z_{2(1)}$ is not necessarily equal to $z_{1(2)}$.

The *total rate per unit volume of collisions* between molecules of substance 1 and molecules of substance 2 is equal to the collision rate of Eq. (9.8-30) times the number density of molecules of substance 1, and is also equal to the collision rate of Eq. (9.8-29) times the number density of molecules of type 2:

$$Z_{12} = z_{1(2)}\mathcal{N}_1 = z_{2(1)}\mathcal{N}_2 = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu_{12}}}\pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 = \langle v_{12}\rangle \pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 \qquad (9.8\text{-}31)$$

There is no need to divide by 2 as in Eq. (9.8-22). The two molecules in a given collision are of different substances so that there is no double counting. This equation should be easy to remember because all four factors are things to which the rate should be proportional. The most important physical fact shown in Eq. (9.8-31) is this: *The total rate of collisions between molecules of two substances is proportional to the number density of each substance*.

9.69 Assume that the mole fraction of carbon dioxide in the earth's atmosphere is 0.000306.

a. Estimate the mean free path between CO_2-CO_2 collisions in the atmosphere at sea level if the temperature is 298 K (collisions with molecules of other substances can intervene, so that the free path in question can have bends in it).

b. Estimate the number of collisions with other CO_2 molecules per second undergone by a CO_2 molecule under the conditions in part a.

Assume that a certain region of interstellar space contains

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At 70 K, $B_2 = -3.2 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}}$
At 140 K, $B_2 = -9.65 \times 10^{-5}\,\mathrm{m\,mol^{-1}}$
At 300 K, $B_2 = -1.55 \times 10^{-5}\,\mathrm{m\,mol^{-1}}$
$B_2 = 0$ at 403.5 K

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a. $z_{1(2)} = 5.87 \times 10^9\,\mathrm{s^{-1}}$
b. $z_{2(1)} = 2.94 \times 10^9\,\mathrm{s^{-1}}$
c. number of collisions per second $= 3.54 \times 10^{33}\,\mathrm{s^{-1}}$