This is the general form of the diffusion coefficient. $\hat{V}_i$ is the mean speed of the diffusing particles and $\lambda_{c,i}$ is their mean free path considering all collision processes. For example, in a binary mixture in which only molecule-molecule collisions are important

$$D_{12} = \frac{\hat{V}_1 \lambda_{c,1}}{3} \quad \text{where} \quad \frac{1}{\lambda_{c,1}} = \frac{1}{\lambda_{c,1-1}} + \frac{1}{\lambda_{c,1-2}} \qquad \text{(IIIE-A2b,A3)}$$

where D_{12} connoted diffusion of species 1 through species 2. In that sense the diffusion coefficient, indeed the whole idea of diffusion, is dependent not only on the diffusing species but also on the species it is diffusing through. From the definitions of eqns. IIIE-A2b and A3, it is recognized that a hypothetical self-diffusion coefficient can be defined as

$$D_{11} = \frac{\hat{V}_1 \lambda_{c,1-1}}{3} \qquad \text{(IIIE-A2c)}$$

This is a property of the pure substance and it provides a useful guide to the diffusability of the species. ($D_{12} \Rightarrow D_{11}$, if species 1 and 2 are very similar.)

For a perfect gas and a perfect gax mixture, the self- and binary diffusion coefficients are obtained by substituting eqns. IIIE-5a, 13b, and A3 into eqn. IIIE-A2a

$$\rho D^*_{11} = \frac{2}{3\sigma^+_{11}}\left(\frac{M_1 kT}{\pi N_A}\right)^{\frac{1}{2}} \qquad \rho D^*_{12} = \frac{2\left(1 + \frac{y_2}{y_1}\right)}{3\left[\sigma^+_{11} + \left(\frac{y_2 M_1}{y_1 M_2}\right)\sigma^+_{12}\right]}\left(\frac{M_1 kT}{\pi N_A}\right)^{\frac{1}{2}} \qquad \text{(IIIE-A4a,A4b)}$$

A comparison between eqn. IIIE-A4a and eqn. IIIE-19b reveals that they are identical. The ratio, $(\mu_1/\rho_1 D_{11})$, is known as the Schmidt number, S_c.[26] Our theory predicts that it is unity for perfect gases. Data is closer to 0.75. Thus the simple hard sphere theory predicts the correct parametric form for the diffusion coefficients; but like the prediction of thermal conductivity, it is numerically imprecise.

Exercise A1. Use eqns. IIIE-A4 to predict the self-diffusion coefficients of nitrogen and oxygen at STP. Compre these results to the binary diffusion coefficients of the nitrogen and oxygen components in air at STP ($y_{O_2} = 0.23$, $y_{N_2} = 0.77$).