2s. Molecular Diffusion of Gases

R. C. ROBERTS

University of Maryland—Baltimore County

Symbols

C	concentration of gas
D	diffusion coefficient
k	Boltzmann's constant
m	molecular mass
p	gas pressure
T	absolute temperature
t	time
$\bar{V}$	average velocity of molecules
x, y, z	rectangular position coordinates
λ	mean free path
σ_r	effective collision diameter

In the simple diffusion of one gas into another, the concentration of either component obeys the equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(D\frac{\partial C}{\partial z}\right) \tag{2s-1}$$

where C = concentration of gas component
t = time
x, y, z = position coordinates
D = diffusion coefficient

Although the diffusion coefficient is, in general, a function of temperature, pressure, and concentration, it can often be considered as constant provided the variations of temperature, pressure, etc., are small. The usual cgs units for the diffusion coefficient are cm^2/sec.

The elementary kinetic theory of gases shows that, for a two-component mixture,

$$D_{12} = \frac{1}{3}\frac{n_1\lambda_2\bar{V}_2 + n_2\lambda_1\bar{V}_1}{n_1 + n_2} \tag{2s-2}$$

where n = molecular density
λ = mean free path
$\bar{V}$ = average velocity of molecules
1, 2 = subscripts denoting different gas components

The more exact theories show a quite complicated behavior for D. For example, in a model consisting of rigid elastic spheres

$$D_{12} = \frac{3}{8(n_1 + n_2)\sigma_r^2}\left[\frac{kT(m_1 + m_2)}{2\pi m_1 m_2}\right]^{\frac{1}{2}} \tag{2s-3^1}$$

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[1] Continued on p. 2-252.

TABLE 2s-1. DIFFUSION COEFFICIENTS D_0 AT STANDARD TEMPERATURES AND PRESSURE

(p = 760 mm Hg; T = 273°K)

Gas pair	D_0, cm²/sec	α
H_2O-CO_2	0.202 (34.4°C)	2
H_2O-air	0.219	1.75
H_2O-H_2	1.02 (34.4°C)	1.75
Ethyl alcohol-CO_2	0.0686	2
Ethyl alcohol-air	0.099	2
Ethyl alcohol-H_2	0.377	2
Ethyl ether-CO_2	0.0541	2
Ethyl ether-air	0.0786	2
Ethyl ether-H_2	0.299	2
Benzene-O_2	0.0797	1.75
Benzene-H_2	0.318	1.75
CCl_4-O_2	0.0636	
CCl_4-H_2	0.293	
Acetone-H_2	0.361	
Mercury-N_2	0.1190	2
Iodine-N_2	0.070	2
Iodine-air	0.0692	2
He-Ar	0.641	1.75
H_2-D_2	1.20	
H_2-O_2	0.697	1.75
H_2-N_2	0.674	1.75
H_2-CO	0.651	1.75
H_2-CO_2	0.550	1.75
H_2-CH_4	0.625	1.75
H_2-SO_2	0.480	1.75
H_2-N_2O	0.535	1.75
H_2-C_2H_4	0.602 (25°C)	1.75
H_2-Ar	0.77 (20°C)	
O_2-N_2	0.181	1.75
O_2-CO	0.185	1.75
O_2-CO_2	0.139	2
CO-N_2	0.192	
CO-CO_2	0.137	1.75
CO-C_2H_4	0.116	1.75
CO_2-N_2	0.144	
CO_2-CH_4	0.153	1.75
CO_2-N_2O	0.096	
H_2-air	0.611	1.75
O_2-air	0.178	1.75
CO_2-air	0.138	2
CH_4-air	0.196	
Ar-N_2	0.20 (20°C)	
Ar-O_2	0.20 (20°C)	
Ar-CO_2	0.14 (20°C)	
H_2-SF_6	0.420 (25°C)	
H_2-C_2H_6	0.537 (25°C)	
N_2-C_2H_6	0.148 (25°C)	
N_2-C_2H_4	0.163 (25°C)	
N_2-n-C_4H_{10}	0.0960 (25°C)	
N_2-*iso*-C_4H_{10}	0.0908 (25°C)	
H_2-*cis*-butene-2	0.378 (25°C)	
N_2-*cis*-butene-2	0.095 (25°C)	
H_2O-He	0.90 (34.4°C)	
H_2O-N_2	0.256 (34.4°C)	

Note. The values for the last ten pairs are taken from refs. 9 and 12.

TABLE 2s-2. DEPENDENCE OF DIFFUSION COEFFICIENTS ON CONCENTRATION

Pair of gases	n_1/n_2	D_{12}
First gas H_2; second gas CO_2	3	0.594
	1	0.605
	$\frac{1}{3}$	0.633
First gas He; second gas A	2.65	0.678
	2.26	0.693
	1.66	0.696
	1	0.706
	0.477	0.712
	0.311	0.731

TABLE 2s-3. DEPENDENCE OF DIFFUSION COEFFICIENT ON PRESSURE

Gas pair	D, cm²/sec	t, °C	p, mm Hg	$\frac{Dp}{760}$
CO_2-air..........	0.1653	17.6	751	0.163
CO_2-air..........	0.3376	15.2	364	0.162
CO_2-air..........	0.4139	15.7	309	0.164
CO_2-H_2..........	0.6142	12.8	757	0.612
CO_2-H_2..........	0.9184	15.4	510	0.616
H_2-O_2............	0.8012	11.4	748	0.790
H_2-O_2............	1.1718	15.8	512	0.791

TABLE 2s-4. COEFFICIENTS OF SELF-DIFFUSION*

Gas	Temp, °K	D, cm²/sec, experimental
Hydrogen (para-hydrogen into ortho-hydrogen)	273	1.285 ± 0.0025
	85	0.172 ± 0.008
	20.4	0.00816 ± 0.0002
Deuterium into hydrogen	288	1.24
Neon	293	0.473 ± 0.002
Argon	326.7	0.212 ± 0.002
	295.2	0.180 ± 0.001
	273.2	0.158 ± 0.002
	194.7	0.0833 ± 0.0009
	90.2	0.028 ± 0.0010
Krypton	294.0	0.09 ± 0.004
Xenon	292.1	0.0443 ± 0.002
Nitrogen	293	0.200 ± 0.008
Methane (p = 60 mm Hg)	292	26.32 ± 0.73
Hydrogen chloride	295.0	0.1246
Hydrogen bromide	295.3	0.0792
Uranium hexafluoride (p = 10 mm Hg)	303	$D \times \rho = (234 \pm 9) \times 10^{-6}$ g/cm × sec

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* p = 760 mm Hg except where noted.

where m = mass of molecule
n = number of molecules per cm^3
T = absolute temperature
σ_r = effective molecular collision diameter
k = Boltzmann's constant
1, 2 = subscripts denoting different gas components

It should be noted that the diffusion coefficient is symmetric with respect to its component variables; i.e., $D_{12} = D_{21}$. In the special case when both gas components are identical, we have the condition of self-diffusion where the coefficient is denoted by D_{11}. The diffusion of two different isotopes of the same gas is an example of self-diffusion, e.g., deuterium into hydrogen.

For most gases a convenient reduction formula may be given to reduce the diffusion coefficient to standard temperature T and pressure p. It is

$$D = D_9 \left(\frac{T}{T_0}\right)^\alpha \frac{p_0}{p} \tag{2s-4}$$

where α varies between 1.75 and 2. This is reasonably valid over a range of normal temperature and pressure.

The preceding tables contain data on the diffusion coefficients for a number of gases and vapors. In Table 2s-1 values of α are given (if known) so that Eq. (2s-4) may be used to convert the coefficients to other than standard temperature and pressure. Tables 2s-2 and 2s-3 give certain data on the variation of D with pressure and concentration. Table 2s-4 gives some of the latest data on self-diffusion.

Chapman and Cowling (ref. 1) should be consulted for the advanced theory. A good bibliography may be found in Jost (ref. 2) and in ref. 10.

References

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