

2.2 Diffusion Coefficients for Gases

The diffusion coefficient can be derived for an ideal gas by using the simplified discussion presented by Sherwood et al. (1975). From kinetic theory, the diffusion coefficient is assumed to be directly proportional to the mean molecular velocity and the mean free path, λ .

$$D \propto \bar{U}\lambda \quad (2-1)$$

For an ideal gas the motion of the molecule is assumed to be totally random, with the mean free path, λ , being inversely proportional to both the average cross-sectional area of the molecules, A , and the number density, n , of all molecules in a specified volume. Since the number density of an ideal gas varies directly with pressure and inversely with the temperature, this becomes

$$\lambda \propto \frac{1}{nA} \propto \frac{T}{PA} \quad (2-2)$$

But the mean molecular velocity is related to the temperature and molecular weight of the molecule by the expression

$$\bar{U} \propto \left(\frac{T}{M}\right)^{1/2} \quad (2-3)$$

where \bar{U} is the mean velocity and M is the molecular weight. Thus for a binary system the equations above can be combined and extended to yield

$$D_{AB} \propto \left(\frac{T}{M_A} + \frac{T}{M_B}\right)^{1/2} \frac{T}{PA} \quad (2-4)$$

or

$$D_{AB} = \frac{K'T^{3/2}}{PA_{avg}} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2} \quad (2-5)$$

where A_{avg} is the average cross-sectional area of both types of molecules and K' is a constant of proportionality.

Various semiempirical equations similar to the one above have been derived using kinetic theory as a basis. Gilliland (1934) proposed that the diffusivity be calculated from the equation

$$D_{AB} = 4.3 \times 10^{-9} \frac{T^{3/2}}{P(V_A^{1/3} + V_B^{1/3})^2} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2} \quad (2-6)$$

where D_{AB} = diffusivity, m²/s,

T = absolute temperature, K,

M = molecular weight, kg/kgmol,

V = molar volume at the normal boiling point, m³/kgmol,

P = total pressure, atm (101.3 kN/m²).

Atomic and molecular volumes are presented in Table 2-1.

TABLE 2-1. ATOMIC AND MOLECULAR VOLUMES AT THE NORMAL BOILING POINT
(TREYBAL, 1968)

	Atomic Volume $\times 10^3$ ($m^3/kgatom$)		Molecular Volume $\times 10^3$ ($m^3/kgmol$)
Bromine	27.0	Air	29.9
Carbon	14.8	Br ₂	53.2
Chlorine	24.6	Cl ₂	48.4
Hydrogen	3.7	CO	30.7
Iodine	37.0	CO ₂	34.0
Nitrogen	15.6	COS	51.5
Nitrogen in primary amines	10.5	H ₂	14.3
Nitrogen in secondary amines	12.0	H ₂ O	18.9
Oxygen	7.4	H ₂ S	32.9
Oxygen in methyl esters	9.1	I ₂	71.5
Oxygen in higher esters	11.0	N ₂	31.2
Oxygen in acids	12.0	NH ₃	25.8
Oxygen in methyl ethers	9.9	NO	23.6
Oxygen in higher ethers	11.0	N ₂ O	36.4
Sulfur	25.6	O ₂	25.6
Benzene ring	-15.0	SO ₂	44.8
Naphthalene ring	-30.0		

Although Gilliland's equation provides a reasonably accurate means for predicting diffusion coefficients and is satisfactory for engineering work, the semiempirical equation proposed by Fuller et al. (1966) is recommended. Their equation, which results from a curve fit to available experimental data, is

$$D_{AB} = \frac{1.0 \times 10^{-9} T^{1.75}}{P[(\sum v)_A^{1/3} + (\sum v)_B^{1/3}]^2} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \quad (2-7)$$

where D_{AB} has the units m^2/s ; T is the absolute temperature, K; and pressure is given in atmospheres. The diffusion volumes, $\sum v$, are the sum of the atomic volumes of all elements for each molecule. Atomic and diffusion volumes given in Table 2-2 should be used in Eq. (2-7). Fuller et al.'s equation is reported to predict diffusivities to within 7% of experimental values and can be used for both polar and nonpolar gases.

TABLE 2-2. ATOMIC AND MOLECULAR DIFFUSION VOLUMES
FOR THE EQUATION OF FULLER ET AL. (1966)^a

Atomic and Structural Diffusion Volume Increments, $v \times 10^3$ ($m^3/kgatom$)			
C	16.5	(Cl)	19.5
H	1.98	(S)	17.0
O	5.48	Aromatic ring	-20.2
(N)	5.69	Heterocyclic ring	-20.2

TABLE 2-2. (CONTINUED)
 Diffusion Volumes for Simple Molecules, $\Sigma v \times 10^3$ (m³/kgmol)

H ₂	7.07	CO	18.9
D ₂	6.70	CO ₂	26.9
He	2.88	N ₂ O	35.9
N ₂	17.9	NH ₃	14.9
O ₂	16.6	H ₂ O	12.7
Air	20.1	(CCl ₂ F ₂)	114.8
Ar	16.1	(SF ₆)	69.7
Kr	22.8	(Cl ₂)	37.7
(Xe)	37.9	(Br ₂)	67.2
Ne	5.59	(SO ₂)	41.1

*Parentheses indicate that the value listed is based on only a few data points.

Chapman and Enskog (Hirschfelder et al., 1954), working independently, related the properties of gases to the forces acting between the molecules. Using the Lennard-Jones 6-12 potential to relate the attractive and repulsive forces between atoms, Hirschfelder et al. (1949) developed the following equation to predict the diffusivity for nonpolar gas pairs:

$$D_{AB} = \frac{1.858 \times 10^{-27} T^{3/2}}{P \sigma_{AB}^2 \Omega_D} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \quad (2-8)$$

where D_{AB} = diffusivity, m²/s,

T = absolute temperature, K,

M = molecular weight, kg/kgmol,

P = absolute pressure, atm,

σ_{AB} = collision diameter, m,

Ω_D = collision integral.

The Lennard-Jones equation is

$$\phi_{AB}(r) = 4\epsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r} \right)^{12} - \left(\frac{\sigma_{AB}}{r} \right)^6 \right] \quad (2-9)$$

where $\phi_{AB}(r)$ = potential energy,

ϵ_{AB} = maximum energy of attraction,

σ_{AB} = collision diameter,

r = molecular separation distance.

Repulsive and attractive forces are accounted for in the equation above by the r^{-12} and r^{-6} terms, respectively. For a binary system the Lennard-Jones force constants, ϵ_{AB} and σ_{AB} , are evaluated from pure component data using the following relationships:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad (2-10)$$

and

$$\frac{\epsilon_{AB}}{k} = \left(\frac{\epsilon_A}{k} \times \frac{\epsilon_B}{k} \right)^{1/2} \quad (2-11)$$

where k is the Boltzmann constant.

Collision diameters and force constants for a number of pure substances are given in Table 2-3. When collision diameters and force constants are not available, they may be estimated from the following relationships:

$$\sigma = 8.33V_c^{1/3} \quad (2-12)$$

or
$$\sigma = 11.8V^{1/3} \quad (2-13)$$

and
$$\frac{\epsilon}{k} = 0.75T_c \quad (2-14)$$

or
$$\frac{\epsilon}{k} = 1.21T_b \quad (2-15)$$

where V_c = critical volume, m³/kgmol,

T_c = critical temperature, K,

V = molar volume at the normal boiling point, m³/kgmol,

T_b = normal boiling-point temperature, K,

σ = collision diameter, 10⁻¹⁰ m.

TABLE 2-3. COLLISION DIAMETERS AND ENERGY PARAMETERS FOR THE LENNARD-JONES EQUATION (SVEHLA, 1962)

Molecule	Compound	$\sigma \times 10^{10}$ (m)	ϵ/k (K)
Ar	Argon	3.542	93.3
He	Helium	2.551	10.22
Kr	Krypton	3.655	178.9
Ne	Neon	2.820	32.8
Xe	Xenon	4.047	1.0
Air	Air	3.711	78.6
AsH ₃	Arsine	4.145	259.8
BCl ₃	Boron chloride	5.127	337.7
BF ₃	Boron fluoride	4.198	186.3
B(OCH ₃) ₃	Methyl borate	5.503	396.7
Br ₂	Bromine	4.296	507.9
CCl ₄	Carbon tetrachloride	5.947	322.7
CF ₄	Carbon tetrafluoride	4.662	134.0
CHCl ₃	Chloroform	5.389	340.2
CH ₂ Cl ₂	Methylene chloride	4.898	356.3
CH ₃ Br	Methyl bromide	4.118	449.2
CH ₃ Cl	Methyl chloride	4.182	350
CH ₃ OH	Methanol	3.626	481.8
CH ₄	Methane	3.758	148.6
CO	Carbon monoxide	3.690	91.7
COS	Carbonyl sulfide	4.130	336.0
CO ₂	Carbon dioxide	3.941	195.2
CS ₂	Carbon disulfide	4.483	467
C ₂ H ₂	Acetylene	4.033	231.8
C ₂ H ₄	Ethylene	4.163	224.7
C ₂ H ₆	Ethane	4.443	215.7
C ₂ H ₅ Cl	Ethyl chloride	4.898	300

TABLE 2-3. (CONTINUED)

<i>Molecule</i>	<i>Compound</i>	$\sigma \times 10^{10}$ (m)	ϵ/k (K)
C ₂ H ₅ OH	Ethanol	4.530	362.6
C ₂ N ₂	Cyanogen	4.361	348.6
CH ₃ OCH ₃	Methyl ether	4.307	395.0
CH ₂ CHCH ₃	Propylene	4.678	298.9
CH ₃ CCH	Methylacetylene	4.761	251.8
C ₃ H ₆	Cyclopropane	4.807	248.9
C ₃ H ₈	Propane	5.118	237.1
<i>n</i> -C ₃ H ₇ OH	<i>n</i> -Propyl alcohol	4.549	576.7
CH ₃ COCH ₃	Acetone	4.600	560.2
CH ₃ COOCH ₃	Methyl acetate	4.936	469.8
<i>n</i> -C ₄ H ₁₀	<i>n</i> -Butane	4.687	531.4
<i>i</i> -C ₄ H ₁₀	Isobutane	5.278	330.1
C ₂ H ₅ OC ₂ H ₅	Ethyl ether	5.678	313.8
CH ₃ COOC ₂ H ₅	Ethyl acetate	5.205	521.3
<i>n</i> -C ₅ H ₁₂	<i>n</i> -Pentane	5.784	341.1
C(CH ₃) ₄	2,2-Dimethylpropane	6.464	193.4
C ₆ H ₆	Benzene	5.349	412.3
C ₆ H ₁₂	Cyclohexane	6.182	297.1
<i>n</i> -C ₆ H ₁₄	<i>n</i> -Hexane	5.949	399.3
Cl ₂	Chlorine	4.217	316.0
F ₂	Fluorine	3.357	112.6
HBr	Hydrogen bromide	3.353	449
HCN	Hydrogen cyanide	3.630	569.1
HCl	Hydrogen chloride	3.339	344.7
HF	Hydrogen fluoride	3.148	330
HI	Hydrogen iodide	4.211	288.7
H ₂	Hydrogen	2.827	59.7
H ₂ O	Water	2.641	809.1
H ₂ O ₂	Hydrogen peroxide	4.196	289.3
H ₂ S	Hydrogen sulfide	3.623	301.1
Hg	Mercury	2.969	750
HgBr ₂	Mercuric bromide	5.080	686.2
HgCl ₂	Mercuric chloride	4.550	750
HgI ₂	Mercuric iodide	5.625	695.6
I ₂	Iodine	5.160	474.2
NH ₃	Ammonia	2.900	558.3
NO	Nitric oxide	3.492	116.7
NOCl	Nitrosyl chloride	4.112	395.3
N ₂	Nitrogen	3.798	71.4
N ₂ O	Nitrous oxide	3.828	232.4
O ₂	Oxygen	3.467	106.7
PH ₃	Phosphine	3.981	251.5
SF ₆	Sulfur hexafluoride	5.128	222.1
SO ₂	Sulfur dioxide	4.112	335.4
SiF ₄	Silicon tetrafluoride	4.880	171.9
SiH ₄	Silicon hydride	4.084	207.6
SnBr ₄	Stannic bromide	6.388	563.7
UF ₆	Uranium hexafluoride	5.967	236.8

Values of the collision integral, Ω_D , have been evaluated for the Lennard-Jones 6-12 potential by Hirschfelder et al. (1954). These values are presented in Table 2-4. The collision integral can be calculated with good accuracy from the relationship proposed by Neufeld et al. (1972). The Lennard-Jones potential is shown in Figure 2-1.

TABLE 2-4. VALUES OF THE COLLISION INTEGRAL Ω_D BASED ON THE LENNARD-JONES POTENTIAL (HIRSCHFELDER ET AL., 1954*)

kT/ϵ	Ω_D	kT/ϵ	Ω_D	kT/ϵ	Ω_D
0.30	2.662	1.65	1.153	4.0	0.8836
0.35	2.476	1.70	1.140	4.1	0.8788
0.40	2.318	1.75	1.128	4.2	0.8740
0.45	2.184	1.80	1.116	4.3	0.8694
0.50	2.066	1.85	1.105	4.4	0.8652
0.55	1.966	1.90	1.094	4.5	0.8610
0.60	1.877	1.95	1.084	4.6	0.8568
0.65	1.798	2.00	1.075	4.7	0.8530
0.70	1.729	2.1	1.057	4.8	0.8492
0.75	1.667	2.2	1.041	4.9	0.8456
0.80	1.612	2.3	1.026	5.0	0.8422
0.85	1.562	2.4	1.012	6	0.8124
0.90	1.517	2.5	0.9996	7	0.7896
0.95	1.476	2.6	0.9878	8	0.7712
1.00	1.439	2.7	0.9770	9	0.7556
1.05	1.406	2.8	0.9672	10	0.7424
1.10	1.375	2.9	0.9576	20	0.6640
1.15	1.346	3.0	0.9490	30	0.6232
1.20	1.320	3.1	0.9406	40	0.5960
1.25	1.296	3.2	0.9328	50	0.5756
1.30	1.273	3.3	0.9256	60	0.5596
1.35	1.253	3.4	0.9186	70	0.5464
1.40	1.233	3.5	0.9120	80	0.5352
1.45	1.215	3.6	0.9058	90	0.5256
1.50	1.198	3.7	0.8998	100	0.5130
1.55	1.182	3.8	0.8942	200	0.4644
1.60	1.167	3.9	0.8888	400	0.4170

Hirschfelder et al. use the symbols T^ for kT/ϵ and $\Omega^{(1,1)*}$ for Ω_D .

From the various diffusion equations for gases, it is noted that the diffusivity increases with the 1.5 to 1.8 power of the absolute temperature but is inversely proportional to the system pressure. At low pressures, the diffusion coefficient is not affected by composition. The equation derived by Hirschfelder et al. is recommended for extrapolating experimental data for moderate pressure ranges. Upon simplifying Eq. (2-8), we have

$$D_{AB,T_1,P_1} = D_{AB,T_1,P_2} \frac{P_1}{P_2} \left(\frac{T_2}{T_1} \right)^{3/2} \frac{\Omega_{T_1}}{\Omega_{T_2}} \quad (2-16)$$

Sec. 2.3 Diffusion Coefficients for Liquids

Dilute electrolyte solutions

In an electrolyte solution the solute dissociates into cations and anions. Because the size of the ions are different than the original molecule, their mobility through the solvent will also be different. On the basis of previous discussions, the smaller ion might be expected to diffuse faster than the larger ion. However, so that a separation of electric charge does not occur, both ionic species must diffuse at the same rate.

Nernst (1888) developed the first equation for predicting diffusion coefficients in electrolyte solutions by relating the diffusivity to electrical conductivities. His equation, which is valid at infinite dilution, is

$$D_{AB}^{\circ} = \frac{RT}{F^2} \frac{\lambda_+^{\circ} \lambda_-^{\circ}}{\lambda_+^{\circ} + \lambda_-^{\circ}} \frac{|Z_-| + |Z_+|}{|Z_+ Z_-|} \quad (2-30)$$

$$= 8.931 \times 10^{-14} T \frac{\lambda_+ \lambda_-}{\lambda_+ + \lambda_-} \frac{|Z_-| + |Z_+|}{|Z_+ Z_-|} \quad (2-31)$$

where

- F = Faraday constant, A·s/g-equiv.,
 D_{AB}° = diffusion coefficients at infinite dilution, m²/s,
 λ_+° = cationic conductance at infinite dilution,
 (A/cm²)(cm/V)(cm³/g-equiv.),
 λ_-° = anionic conductance at infinite dilution,
 (A/cm²)(cm/V)(cm³/g-equiv.),
 $\lambda_+^{\circ} + \lambda_-^{\circ}$ = electrolyte conductance at infinite dilution,
 (A/cm²)(cm/V)(cm³/g-equiv.),
 Z_+ = cation valence,
 Z_- = anion valence,
 T = absolute temperature, K.

The equation of Nernst has been verified experimentally for dilute solutions. Selected ionic conductances at infinite dilution are given in Table 2-7 for use with Eq. (2-31). An extensive list of values is given by Robinson and Stokes (1959).

TABLE 2-7. IONIC CONDUCTANCES AT INFINITE DILUTION IN WATER AT 25°C (ROBINSON AND STOKES, 1959)

Cation	λ_+°	Anion	λ_-°
Ag ⁺	61.9	Br ⁻	78.4
H ⁺	349.8	Cl ⁻	76.35
Li ⁺	38.7	ClO ₃ ⁻	64.6
Na ⁺	50.1	ClO ₄ ⁻	67.4
K ⁺	73.5	F ⁻	55.4
NH ₄ ⁺	73.6	I ⁻	76.8
Ca ²⁺	59.5	NO ₃ ⁻	71.46
Cu ²⁺	56.6	OH ⁻	198.6
Mg ²⁺	53.0	CO ₃ ²⁻	69.3
Zn ²⁺	52.8	SO ₄ ²⁻	80.0