Table 5.1-1 *Experimental values of diffusion coefficients in gases at one atmosphere*

Gas pair	Temperature (K)	Diffusion coefficient (cm^2/sec)
Air–benzene	298.2	0.096
Air–CH_4	282.0	0.196
Air–C_2H_5OH	273.0	0.102
Air–CO_2	282.0	0.148
Air–H_2	282.0	0.710
Air–H_2O	289.1	0.282
	298.2	0.260
	312.6	0.277
	333.2	0.305
Air–He	282.0	0.658
Air–n-hexane	294.0	0.080
Air–toluene	299.1	0.086
Air–aniline	299.1	0.074
Air–2-propanol	299.1	0.099
CH_4–He	298.0	0.675
CH_4–H_2	298.0	0.726
CH_4–H_2O	307.7	0.292
CO–N_2	295.8	0.212
^{12}CO–^{14}CO	373.0	0.323
CO–H_2	295.6	0.743
CO–He	295.6	0.702
CO_2–H_2	298.2	0.646
CO_2–N_2	298.2	0.165
CO_2–O_2	296.0	0.156
CO_2–He	298.4	0.597
CO_2–CO	315.4	0.185
CO_2–H_2O	307.4	0.202
CO_2–SO_2	263.0	0.064
$^{12}CO_2$–$^{14}CO_2$	312.8	0.125
CO_2–propane	298.1	0.087
H_2–N_2	297.2	0.779
H_2–O_2	316.0	0.891
H_2–He	317.0	1.706
H_2–Ar	317.0	0.902
H_2–Xe	341.2	0.751
H_2–SO_2	285.5	0.525
H_2–H_2O	307.1	0.915
H_2–NH_3	298.0	0.783
H_2–ethane	298.0	0.537
H_2–n-hexane	288.7	0.290
H_2–cyclohexane	288.6	0.319
H_2–benzene	311.3	0.404
N_2–O_2	316.0	0.230
	293.2	0.220
N_2–He	317.0	0.794
N_2–Ar	316.0	0.216
N_2–NH_3	298.0	0.230
N_2–H_2O	298.2	0.293
N_2–SO_2	263.0	0.104
N_2–ethane	298.0	0.148

(*Continued*)

Table 5.1-1 (*Continued*)

Gas pair	Temperature (K)	Diffusion coefficient (cm^2/sec)
N$_2$–*n*-butane	298.0	0.096
N$_2$–isobutane	298.0	0.090
N$_2$–*n*-hexane	288.6	0.076
N$_2$–*n*-octane	303.1	0.073
N$_2$–2,2,4-trimethylpentane	303.3	0.071
N$_2$–benzene	311.3	0.102
O$_2$–He (He trace)	298.2	0.737
(O$_2$–trace)	298.2	0.718
O$_2$–He	317.0	0.822
O$_2$–H$_2$O	308.1	0.282
O$_2$–CCl$_4$	296.0	0.075
O$_2$–benzene	311.3	0.101
O$_2$–*n*-hexane	288.6	0.075
O$_2$–*n*-octane	303.1	0.071
O$_2$–2,2,4-trimethylpentane	303.0	0.071
He–Ar	298.0	0.742
He–H$_2$O	298.2	0.908
He–NH$_3$	297.1	0.842
Ar–Ne	303.0	0.327
Ar–Kr	303.0	0.140
Ar–Xe	329.9	0.137
Ne–Kr	273.0	0.223
Ethylene–H$_2$O	307.8	0.204

Source: Data from Hirschfelder *et al.* (1954), Marrero and Mason (1972), and Poling *et al.* (2001).

equals unity, the diffusion process has proceeded significantly. In other words, where z^2 equals $4Dt$, the diffusion has penetrated a distance z in the time t.

In gases, this penetration distance is much larger than in other phases. For example, the diffusion coefficient of water vapor diffusing in air is about 0.3 cm^2/sec. In 1 second, the diffusion will penetrate 0.5 cm; in 1 minute, 4 cm; and in 1 hour, 30 cm.

5.1.1 Gaseous Diffusion Coefficients From the Chapman–Enskog Theory

The most common method for theoretical estimation of gaseous diffusion is that developed independently by Chapman and by Enskog (Chapman and Cowling, 1970). This theory, accurate to an average of about eight percent, leads to the equation

$$D = \frac{1.86 \cdot 10^{-3} T^{3/2} (1/\tilde{M}_1 + 1/\tilde{M}_2)^{1/2}}{p\sigma_{12}^2 \Omega} \tag{5.1-1}$$

in which D is the diffusion coefficient measured in cm^2/sec, T is the absolute temperature in Kelvin, p is the pressure in atmospheres, and the $\tilde{M}_i$ are the molecular weights.

Table 5.1-2 *Lennard–Jones potential parameters found from viscosities*

Substance		$\sigma(\text{Å})$	$\varepsilon_{12}/k_B(\text{K})$
Ar	Argon	3.542	93.3
He	Helium	2.551	10.2
Kr	Krypton	3.655	178.9
Ne	Neon	2.820	32.8
Xe	Xenon	4.047	231.0
Air	Air	3.711	78.6
Br_2	Bromine	4.296	507.9
CCl_4	Carbon tetrachloride	5.947	322.7
$CHCl_3$	Chloroform	5.389	340.2
CH_2Cl_2	Methylene chloride	4.898	356.3
CH_3Cl	Methyl chloride	4.182	350.0
CH_3OH	Methanol	3.626	481.8
CH_4	Methane	3.758	148.6
CO	Carbon monoxide	3.690	91.7
CO_2	Carbon dioxide	3.941	195.2
CS_2	Carbon disulfide	4.483	467.0
C_2H_2	Acetylene	4.033	231.8
C_2H_4	Ethylene	4.163	224.7
C_2H_6	Ethane	4.443	215.7
C_2H_5Cl	Ethyl chloride	4.898	300.0
C_2H_5OH	Ethanol	4.530	362.6
CH_3OCH_3	Methyl ether	4.307	395.0
CH_2CHCH_3	Propylene	4.678	298.9
C_3H_8	Propane	5.118	237.1
n-C_3H_7OH	n-Propyl alcohol	4.549	576.7
CH_3COCH_3	Acetone	4.600	560.2
n-C_4H_{10}	n-Butane	4.687	531.4
iso-C_4H_{10}	Isobutane	5.278	330.1
n-C_5H_{12}	n-Pentane	5.784	341.1
C_6H_6	Benzene	5.349	412.3
C_6H_{12}	Cyclohexane	6.182	297.1
n-C_6H_{14}	n-Hexane	5.949	399.3
Cl_2	Chlorine	4.217	316.0
HBr	Hydrogen bromide	3.353	449.0
HCN	Hydrogen cyanide	3.630	569.1
HCl	Hydrogen chloride	3.339	344.7
HF	Hydrogen fluoride	3.148	330.0
HI	Hydrogen iodide	4.211	288.7
H_2	Hydrogen	2.827	59.7
H_2O	Water	2.641	809.1
H_2S	Hydrogen sulfide	3.623	301.1
Hg	Mercury	2.969	750.0
NH_3	Ammonia	2.900	558.3
NO	Nitric oxide	3.492	116.7
N_2	Nitrogen	3.798	71.4
N_2O	Nitrous oxide	3.828	232.4
O_2	Oxygen	3.467	106.7
SO_2	Sulfur dioxide	4.112	335.4

Note: Data from Hirschfelder *et al.* (1954).

Table 5.1-3. *The collision integral* Ω

k_BT/ε	Ω	k_BT/ε	Ω	k_BT/ε	Ω
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	300	0.4360

Source: Data from Hirschfelder et al. (1954).

TABLE 24.3 ATOMIC DIFFUSION VOLUMES FOR USE IN ESTIMATING D_{AB} BY METHOD OF FULLER, SCHETTLER, AND GIDDINGS

Atomic and Structure Diffusion-Volume Increments, v

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

Diffusion Volumes for Simple Molecules, v

H_2	7.07	Ar	16.1	H_2O	12.7
D_2	6.70	Kr	22.8	$CClF_2$	114.8
He	2.88	CO	18.9	SF_6	69.7
N_2	17.9	CO_2	26.9	Cl_2	37.7
O_2	16.6	N_2O	35.9	Br_2	67.2
Air	20.1	NH_3	14.9	SO_2	41.1

Table 5.2-1 *Diffusion coefficients at infinite dilution in water at 25 °C*

Solute	$D(\cdot 10^{-5}$ cm^2/sec)
Acetic acid	1.21
Acetone	1.16
Ammonia	1.64
Argon	2.00
Benzene	1.02
Benzoic acid	1.00
Bromine	1.18
Carbon dioxide	1.92
Carbon monoxide	2.03
Chlorine	1.25
Ethane	1.20
Ethanol	0.84
Ethylene	1.87
Glycine	1.06
Helium	6.28
Hemoglobin	0.069
Hydrogen	4.50
Hydrogen sulfide	1.41
Methane	1.49
Methanol	0.84
n-Butanol	0.77
Nitrogen	1.88
Oxygen	2.10
Ovalbumin	0.078
Propane	0.97
Sucrose	$(0.5228 - 0.265c_1)^a$
Urea	$(1.380 - 0.0782c_1 + 0.00464c_1^2)^a$
Urease	0.035
Valine	0.83

Note: [a]Known to very high accuracy, and so often used for calibration; c_1 is in moles per liter.
Source: Data from Cussler (1976) and Poling *et al.* (2001).

only about twenty percent (Poling *et al.*, 2001). Nonetheless, this equation remains the standard against which alternative correlations are judged.

The Stokes–Einstein equation is

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi\mu R_0} \tag{5.2-1}$$

where f is the friction coefficient of the solute, k_B is Boltzmann's constant, μ is the solvent viscosity, and R_0 is the solute radius. The temperature variation suggested by this equation is apparently correct, but it is much smaller than effects of solvent viscosity and solute radius. A discussion of these larger effects follows.

The diffusion coefficient varies inversely with viscosity when the ratio of solute to solvent radius exceeds five. This behavior is reassuring because the Stokes–Einstein equation is derived by assuming a rigid solute sphere diffusing in a continuum of solvent. Thus, for a large solute in a small solvent, Eq. 5.2-1 seems correct.

Table 5.2-2 *Diffusion coefficients at infinite dilution nonaqueous liquids*

Solvent	Solute[a]	$D(\cdot 10^{-5}\ cm^2/sec)$
Chloroform	Acetone	2.35
	Benzene	2.89
	Ethyl alcohol (15 °C)	2.20
	Ethyl ether	2.14
	Ethyl acetate	2.02
Benzene	Acetic acid	2.09
	Benzoic acid	1.38
	Cyclohexane	2.09
	Ethyl alcohol (15 °C)	2.25
	n-Heptane	2.10
	Oxygen (29.6 °C)	2.89
	Toluene	1.85
Acetone	Acetic acid	3.31
	Benzoic acid	2.62
	Nitrobenzene (20 °C)	2.94
	Water	4.56
n-Heptane	Carbon tetrachloride	3.70
	Dodecane	2.73
	n-Hexane	4.21
	Propane	4.87
	Toluene	4.21
Ethanol	Benzene	1.81
	Iodine	1.32
	Oxygen (29.6 °C)	2.64
	Water	1.24
	Carbon tetrachloride	1.50
n-Butanol	Benzene	0.99
	p-Dichlorobenzene	0.82
	Propane	1.57
	Water	0.56
n-Heptane	Benzene	3.40

Note: [a]Temperature 25 °C except as indicated.
Source: Data from Poling *et al.* (2001).

When the solute radius is less than five times that of the solvent, Eq. 5.2-1 breaks down (Chen *et al.*, 1981). This failure becomes worse as the solute size becomes smaller and smaller. Errors are especially large in high-viscosity solvents; the diffusion seems to vary with a smaller power of viscosity often around (–0.7). In extremely high-viscosity materials, diffusion becomes independent of viscosity: the diffusion of sugar in jello is very nearly equal to the diffusion of sugar in water.

The reason for this altered viscosity dependence is that viscosity often depends on much longer range interactions than diffusion. For example, in jello, the polymeric collagen forms hydrogen bonds that form a three-dimensional elastic network, which of course has very high viscosity. However, sugar and salts diffusing through this network are much smaller than the distances between these hydrogen bonds, so these solutes behave just as if they are diffusing through water. As evidence of this, the concentration dependence of the diffusion coefficient of potassium chloride diffusing in water–polyethylene glycol mixtures is exactly the same as that in water. Diffusion reflects short-range interactions.

Table 24.4 Molecular Volumes at Normal Boiling Point for Some Commonly Encountered Compounds

Compound	Molecular volume, cm^3/g mole	Compound	Molecular volume, in cm^3/g mole
Hydrogen, H_2	14.3	Nitric oxide, NO	23.6
Oxygen, O_2	25.6	Nitrous oxide, N_2O	36.4
Nitrogen, N_2	31.2	Ammonia, NH_3	25.8
Air	29.9	Water, H_2O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H_2S	32.9
Carbon dioxide, CO_2	34.0	Bromine, Br_2	53.2
Carbonyl sulfide, COS	51.5	Chlorine, Cl_2	48.4
Sulfur dioxide, SO_2	44.8	Iodine, I_2	71.5