3M
Organic Vapor Monitor

Sampling Rate

Validation Protocol

70-0701-3308-0(30.1)R2

Litho in U.S.A

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Sampling Rate Validation

The sampling rates for the (*) contaminants were determined by sampling a known air concentration in a laboratory generator-dilution system. This system consisted of a calibrated dry air gas meter, a syringe drive mechanism to deliver the liquid contaminant to a heat manifold, and an exposure device to hold six (6) monitors. The air concentrations of the contaminant were generated by delivering the contaminant at a known rate to an air flow through the heated manifold.

For the exposure period, the air concentration can be determined by measuring the total air volume and the initial and final weight of the syringe containing the contaminant. Five concentrations at one-tenth, one-half, one, two and four times the permissible exposure limit (PEL) were generated to measure the sampling rates. For the sampling rate validations, six samples at each of the five concentrations were collected. The recovery coefficients were determined by spiking the monitors with known amounts of the contaminant at the level corresponding to amounts collected when sampling air concentrations ranging from one-tenth to four times the permissible exposure level (PEL). Results from the 18 spiked samples (3 sets of 6 samples) and the 30 exposure samples results were used to form the basic statistical set of data.

In the sampling rate validation exposure, the monitors sampled known air concentration containing three to five contaminants. The length of the exposures were:

2 Hrs. — .1 PEL
2 Hrs. — .5 PEL
2 Hrs. — 1 PEL
1 Hr. — 2 PEL
.5 Hr. — 4 PEL

The validation results were treated according to the statistical protocol outline in the Documentation of the NIOSH Validation Tests DHEW No. 77-185. The validated sampling rates are tabulated for each contaminant as the mean of 30 samples with the variation reported as the precision of the sampling rate. These results along with the diffusion coefficients as calculated by the Hirschfelder equation are tabulated in Tables I, II and III. The technique for calculating the diffusion coefficient according to the Hirschfelder equation is outlined in Appendix A.

In Figure 1, the validated sampling rates are plotted as a function of the calculated diffusion coefficients for alcohols, aliphatics, cellosolves, esters and ketones. From a least squares fit of the data, the variation of sampling rate is ± 5%. In Figure 2, the validated sampling rates are plotted as a function of the calculated diffusion coefficient for aromatics and other cyclic compounds. In Figure 3, the validated sampling rates are plotted as a function of the calculated diffusion coefficient for the halogenated compounds.

For the compounds in the Sampling Guide and Analysis Guide other than those tabulated in Tables I, II and III, the sampling rates were determined from the diffusion coefficients calculated according to the Hirschfelder equation as outlined in Appendix A and the empirical relationships defined in Figures 1, 2 and 3. By this technique, it is possible to determine the sampling rates with an accuracy of at least ± 5%.

Table I

Compound	Hirschfelder Diffusion Coefficient (cm^2/sec)	Measured Sampling Rate (cc/min ± s.d.)
Ketones		
Acetone	.1096	40.1 ± .9
Diisobutyl Ketone	.0606	24.6 ± .8
Methyl Butyl Ketone	.0756	29.7 ± .7
Methyl Isobutyl Ketone	.0761	30.0 ± .4
Methyl Ethyl Ketone	.0943	36.3 ± .9
Methyl Propyl Ketone	.0838	33.0 ± .5
Alcohols		
n-Amyl Alcohol	.0787	31.2 ± .4
i-Amyl Alcohol	.0790	32.3 ± .4
Butyl Alcohol	.0879	34.3 ± .7
Diacetone Alcohol	.0707	28.2 ± .4
i-butyl Alcohol	.0908	35.9 ± .7
Propyl Alcohol	.1004	39.7 ± .7
Aliphatics		
Heptane	.0721	28.9 ± .7
Hexane	.0796	32.0 ± .7
Nonane	.0617	24.6 ± .6
Octane	.0664	26.6 ± .6
Pentane	.0864	34.5 ± .8
Cellosolve		
Butyl Cellosolve	.0681	28.2 ± .6
Cellosolve	.0820	32.4 ± .9
Cellosolve Acetate	.0682	26.6 ± .4
Methyl Cellosolve	.0911	36.3 ± .4
Methyl Cellosolve Acetate	.0740	29.0 ± .5
Esters		
n-Amyl Acetate	.0668	26.0 ± .5
s-Butyl Acetate	.0728	28.6 ± .4
Ethyl Acetate	.0883	34.5 ± .6
i-Butyl Acetate	.0793	31.0 ± .3
Methyl Acetate	.1009	37.0 ± .6
Propyl Acetate	.0793	30.1 ± .5

Table II

	Hirschfedler Diffusion Coefficient (cm^2/sec)	Measured Sampling Rate (cc/min ± s.d.)
Aromatics & Other Cyclic Compounds		
Benzene	.0947	35.5 ± .6
p.tert-Butyl Toluene	.0599	20.7 ± .4
Cumene	.0690	24.5 ± .9
Mesitylene	.0660	26.3 ± .7
Alpha Methyl Styrene	.0700	25.0 ± .5
Styrene	.0764	26.8 ± .8
Toluene	.0827	31.4 ± .6
Xylene	.0748	27.3 ± .5
Cyclohexanone	.0802	28.9 ± .3
Isophorone	.0635	21.7 ± .7
Cyclohexane	.0851	32.4 ± .7
Cyclohexene	.0876	32.3 ± .4
Methyl Cyclohexane	.0769	28.9 ± .4
Cyclohexanol	.0760	29.5 ± .3

Table III

Compound	Hirschfelder Diffusion Coefficient (cm^2/sec)	Measured Sampling Rate (cc/min ± s.d.)
Halogenated		
Carbon Tetrachlordie	.0857	30.2 ± .4
Chlorobenzene	.0812	29.3 ± .6
Chlorobromomethane	.1005	34.4 ± .9
o-Dichlorobenzene	.0732	27.8 ± .6
1,2 Dichloroethylene	.0992	35.2 ± .5
Ethyl Bromide	.1013	36.4 ± .3
Ethylene Dibromide	.0824	29.6 ± .4
Ethylene Dichloride	.0973	33.2 ± .7
Methylene Chloroform	.0855	30.9 ± .3
Methylene Chloride	.1102	37.9 ± .3
Perchloroethylene	.0786	28.3 ± .5
Propylene Dichloride	.0833	30.6 ± .4
1,1,2 Trichloroethane	.0836	29.7 ± .6
Trichloroethylene	.0874	31.1 ± .2

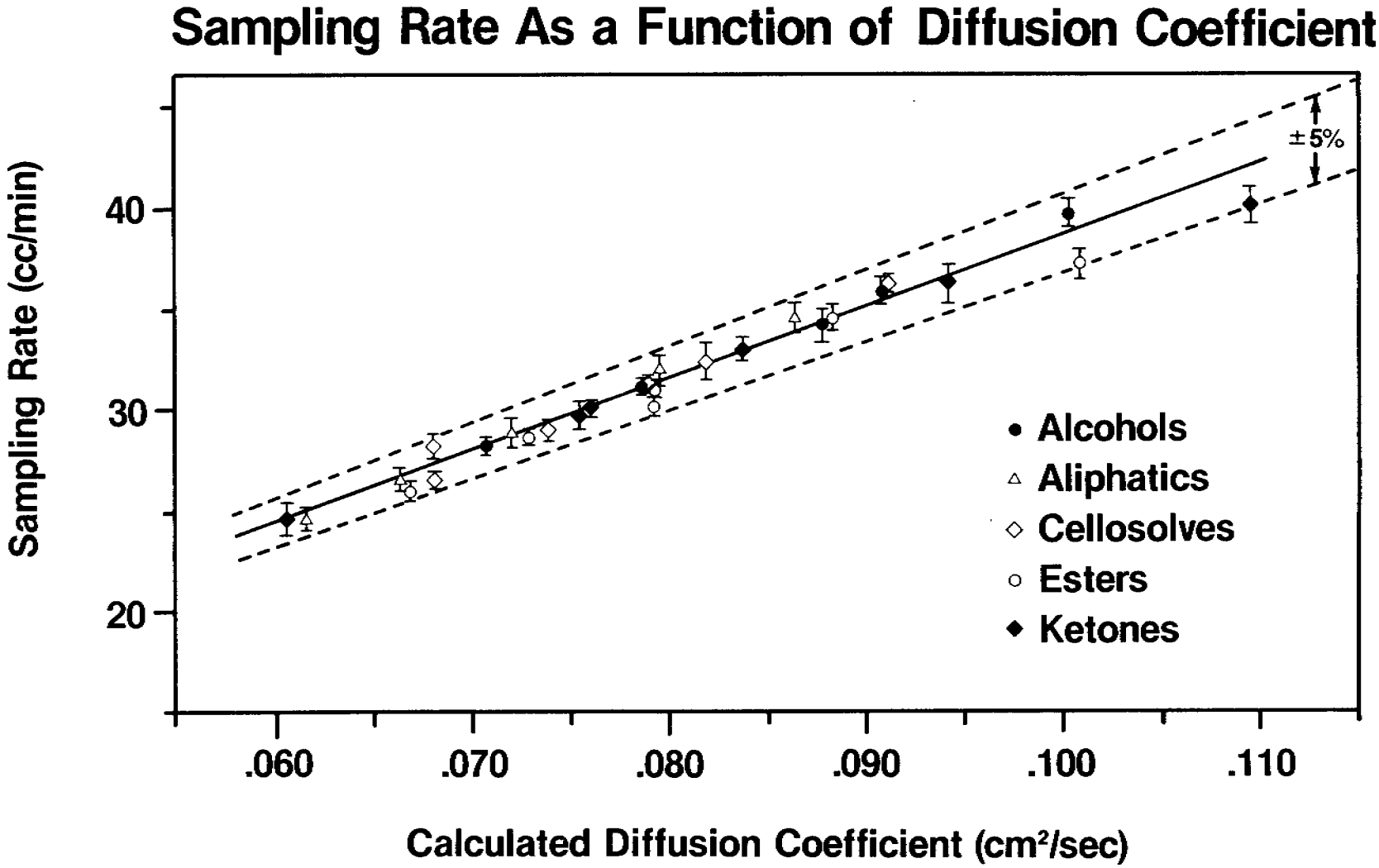


Figure 1

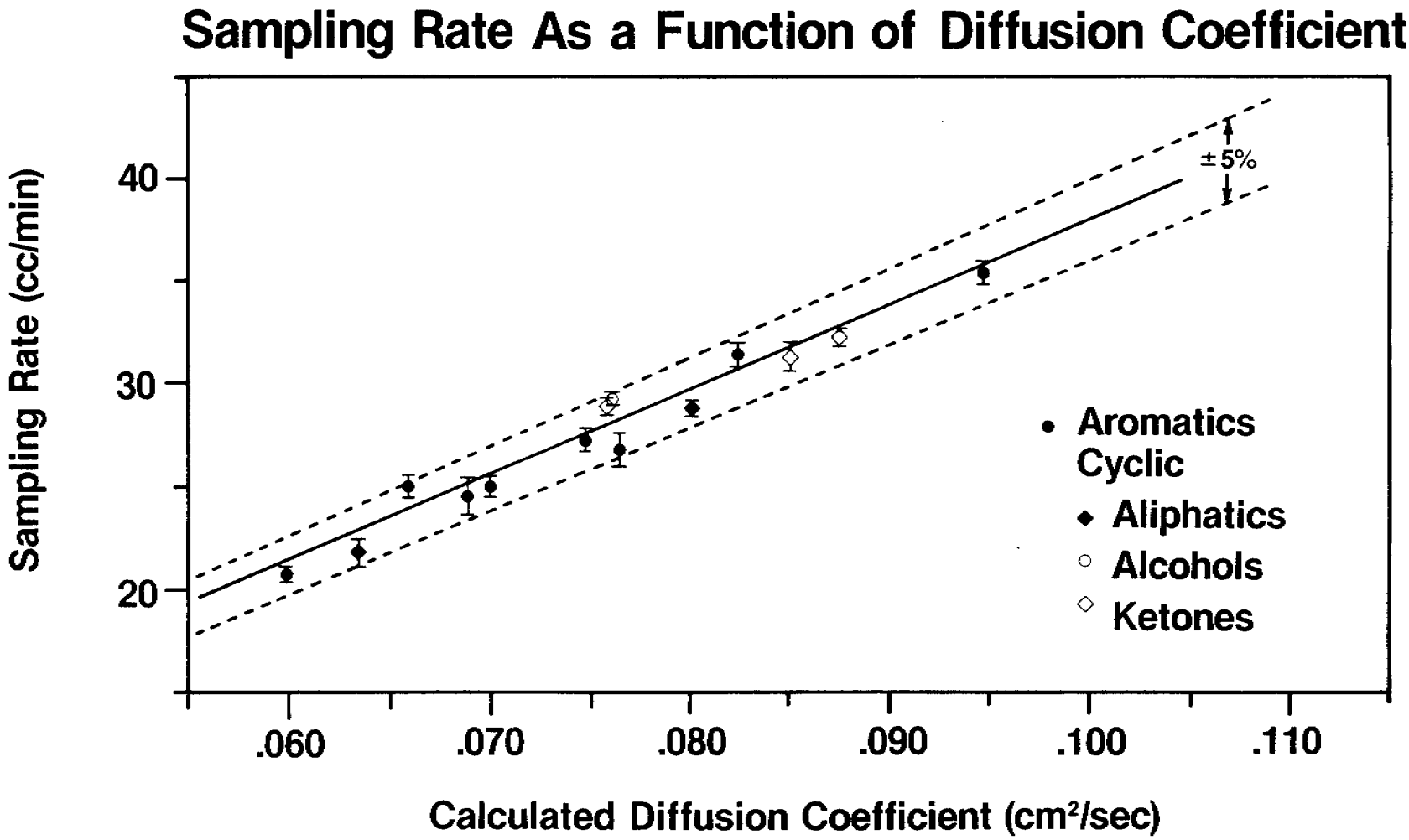
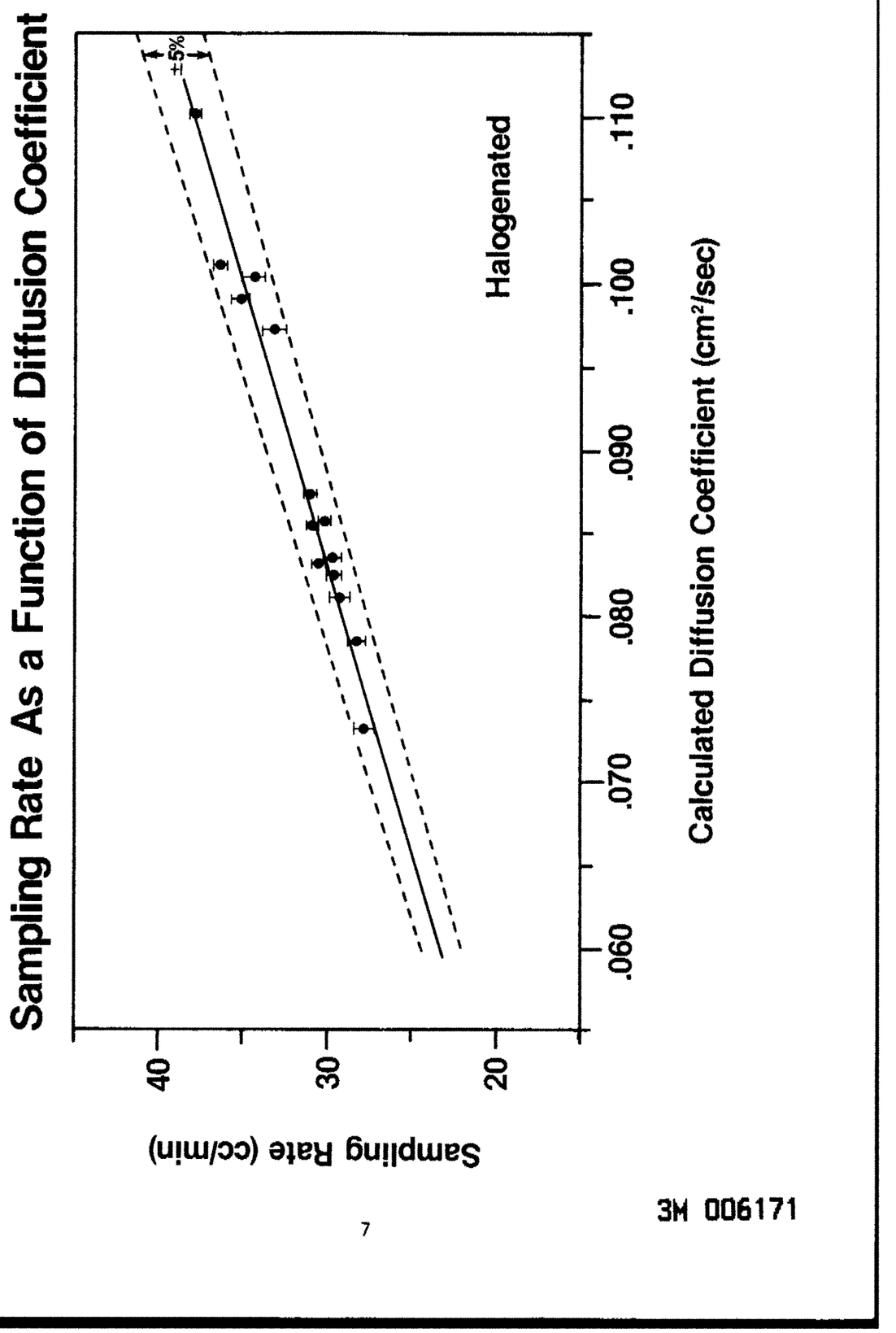


Figure 2

Figure 3



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Appendix A

Calculation of Diffusion Coefficient

Because diffusion coefficients are not available for all contaminants from the same experimental determination, it is therefore desirable to use accurate estimations as determined from the Wilks and Lee modification (Ind. Eng. Chem. 47,1253 [1955] of the equation by Hirschfelder, Bird and Spots (Trans. Am. Soc. Mech. Engrs., 71,921 [1949] as outlined in J. H. Perry, Ed. [Chem. Engrs. Handbook]).

It has been shown that excellent empirical correlation can be achieved between measured sampling rates and the calculated diffusion coefficients. Therefore, the sampling rates which were not measured can be determined with an accuracy of $\pm 5\%$ from the calculated diffusion coefficients using the emplirical relationship. The following outlines the Hirschfelder equation and defines the neccesary parameters needed for calculating the diffusion coefficient according to this technique.

Hirschfelder Equation

$$D_g = \frac{BT^{3/2}\sqrt{1/M_1 + 1/M_2}}{P\, r_{12}^2\, I_D}$$

Where

D_g = gas diffusivity (cm^2/sec)

$B = \left[10.7 - 2.46\sqrt{1/M_1 + 1/M_2}\right] \times 10^{-4}$

T = absolute temperature (°K)

M_1, M_2 = molecule weights of components 1 and 2

P = absolute pressure (atm)

r_{12} = collision diameter $\mathring{A}$

$= (r_1 + r_2)/2$

I_d = collision integral for diffusion, function of kT/ε_{12} (see Table I-Appendix A)

$\frac{\varepsilon_{12}}{k} = \sqrt{\left(\frac{\varepsilon_1}{k}\right)\left(\frac{\varepsilon_2}{k}\right)}$

k = Boltzmann constant
$= 1.38 \times 10^{-6}$ erg/°K

ε_{12} = energy of molecular interaction (ergs)

$\frac{\varepsilon}{k} = 1.15\, T_b$

$= 1.92\, T_m$

T_b = temperature of component boiling point (°K)

T_m = temperature of component melting point (°K)

Combining and simplifying the above expressions:

$$\frac{\varepsilon^1}{k} = \text{air value (97 °K)}$$

$$\frac{\varepsilon^{12}}{k} = \sqrt{(97\,°K)\,(1.15\,T_b)}$$

$$= \sqrt{(97\,°K)\,(1.92\,T_m)}$$

$$\frac{kT}{\varepsilon_{12}} = \frac{298.15}{\sqrt{(97\,°K)\,(1.15\,T_b)}}$$

$$= \frac{28.2}{\sqrt{T_b}}$$

From this value, the collision integral, I_d, can be found from the interpolated values tabulated in Table I of Appendix A.

The radius (r) can be determined from the summation of the atomic volumes tabulated in Table II of Appendix A.

$$r = 1.18\,(V)^{1/3}$$

$$V_2 = \Sigma v_{atomic} \text{ (see Table II Appendix A)}$$

$$r_1 = 3.62$$

$$r_{12}^2 = \left[(3.62 + 1.18\,V_2^{1/3})/2\right]^2$$

By combining all of the above expressions and values, the first equation can be expressed as the following:

$$D_g = \frac{\left[22.03 - 5.07\sqrt{.0345 + 1/M_2}\right]\left[\sqrt{.0345 + 1/M_2}\right]}{I_d\,(3.62 + 1.18\,V_2^{1/3})^2}$$

Example Calculations:

Methyl acetate $CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_3$

Molecular weight · 74

Boiling point (T_b) · 331 °K (58 °C)

$$\frac{kT}{\varepsilon_{12}} = \frac{28.2}{\sqrt{331}}$$

$$= 1.55$$

$$I_d = .5914$$

$$V_2 = 3(14.8) + 6(3.7) + 7.4 + 7.4$$

$$= 81.4$$

$$\sqrt[3]{V_2} = 4.33$$

$$D_g = \frac{(22.03 \cdot 5.07\sqrt{.0345 + 1/74})\ (\sqrt{.0345 + 1/74})}{(.5914)\ \left[3.62 + 1.18(4.33)\right]^2}$$

D_g = .1016 cm²/sec

Appendix A

Table 1

Interpolated Values of Collision Integral

kT/ε_{12}	I_D	kT/ε_{12}	I_D
1.00	0.7197	1.40	0.6166
.01	.7165	.41	.6148
.02	.7132	.42	.6131
.03	.7100	.43	.6114
.04	.7067	.44	.6096
.05	.7035	.45	.6078
.06	.7003	.46	.6061
.07	.6070	.47	.6044
.08	.6938	.48	.6026
.09	.6905	.49	.6008
1.10	0.6873	1.50	0.5991
.11	.6846	.51	.5976
.12	.6819	.52	.5960
.13	.6791	.53	.5945
.14	.6764	.54	.5929
.15	.6737	.55	.5914
.16	.6710	.56	.5899
.17	.6683	.57	.5883
.18	.6655	.58	.5868
.19	.6628	.59	.5852
1.20	0.6601	1.60	0.5837
.21	.6578	.61	.5823
.22	.6554	.62	.5810
.23	.6531	.63	.5796
.24	.6507	.64	.5783
.25	.6484	.65	.5769
.26	.6461	.66	.5755
.27	.6437	.67	.5742
.28	.6414	.68	.5728
.29	.6390	.69	.5715
1.30	0.6367	1.70	0.5701
.31	.6347	.71	.5689
.32	.6327	.72	.5677
.33	.6307	.73	.5665
.34	.6287	.74	.5653
.35	.6266	.75	.5640
.36	.6246	.76	.5628
.37	.6226	.77	.5616
.38	.6206	.78	.5604
.39	.6186	.79	.5592
1.40	0.6166	1.80	0.5580

Appendix A

Table II

LeBas Additivity Values & Rules - $V_2 = \sum V_{atomic}$

Element	Atomic Volue (V)
Carbon	14.8
Chlorine	
Terminal as in R-Cl	21.6
Medial as in R-CHCl-R	24.6
Fluorine	8.7
Hydrogen	3.7
Iodine	37.0
Nitrogen	15.6
In primary amines	10.5
In secondary amines	12.0
Oxygen	12.8
Doubly bound -C(=O)-	7.4
In aldehydes & ketones R-C(=O)-H, R-C(=O)-R	7.4
In methyl esters CH_3-O-C(=O)-R	9.1
In methyl ethers CH_3-O-R	9.9
In higher ethers & esters R-O-C(=O)-R, R-O-R	11.0
In acids R-C(=O)-OH	12.0
In union with S,P,N	8.3
Sulfur	25.6

Special Rules:

(1) Deduct 6 for three membered ring
(2) Deduct 8.5 for four membered ring
(3) Deduct 11.5 for five membered ring
(4) Deduct 15.0 for six membered ring
(5) Deduct 30.0 for naphthalene ring