

program of fundamental research sponsored both by industrial contributions and by the U. S. Army, Corps of Engineers Research and Development Laboratories. The authors gratefully acknowledge the financial and technical assistance given by the many sponsoring organizations, and the advice and criticism offered by members of the staff of the Soil Stabilization Laboratory.

NOMENCLATURE

a_H = activity of hydrogen ion, gram-mole per liter
 a_{Na} = activity of sodium ion, gram-mole per liter
 E = streaming potential, stat-volts
 e = void ratio, cc. of void per cc. of dry solid
 K = permeability coefficient in presence of counterelectro-osmosis, sq. cm.
 K^* = permeability coefficient in absence of counterelectro-osmosis, sq. cm.
 L = thickness of porous bed, cm.
 L' = actual length of flow path in porous bed, cm.
 U = superficial linear flow velocity in presence of counterelectro-osmosis, cm. per second
 U^* = superficial linear flow velocity in the absence of counterelectro-osmosis, cm. per second
 U_{osm} = linear electro-osmosis flow velocity in pores, cm. per second
 Δp = pressure drop across porous bed, gram/cm.(sec.)
 ϵ = dielectric constant

λ = specific conductance of liquid and surface of porous medium, stat-mhos per cm.
 η = viscosity of liquid, gram/(cm.)²(sec.)
 ζ = zeta potential, stat-volts

LITERATURE CITED

- (1) Booth, F., *Proc. Roy. Soc. (London)*, **203A**, 533 (1950).
- (2) Carman, P. C., *Trans. Inst. Chem. Engrs. (London)*, **15**, 150 (1937).
- (3) Cornell University, Final Report, Soil Solidification Research, Vol. II, 1951.
- (4) Elton, G. A. H., *Proc. Roy. Soc. (London)*, **194A**, 259, 275 (1948); **197A**, 568 (1949).
- (5) Fuerstenau, D. W., Sc. D. thesis, Massachusetts Institute of Technology, 1953.
- (6) Grace, H. P., *Chem. Eng. Progr.*, **49**, 303, 367 (1953).
- (7) Henniker, J. C., *Revs. Mod. Phys.*, **21**, 322 (1949).
- (8) Kruyt, H. R., "Colloid Science," Vol. I, Elsevier Publishing Co., New York, 1952.
- (9) Michaels, A. S., and Lin, C. S., *IND. ENG. CHEM.*, **46**, 1239 (1954).
- (10) Muskat, M., "Flow of Homogeneous Fluids through Porous Media," McGraw-Hill, New York, 1937.
- (11) Prutton, C. F., and Maron, S. H., "Fundamental Principles of Physical Chemistry," p. 469, Macmillan, New York, 1950.
- (12) Ruth, B. E., *IND. ENG. CHEM.*, **38**, 564 (1946).

RECEIVED for review June 26, 1954.

ACCEPTED December 23, 1954.

Estimation of Diffusion Coefficients for Gases and Vapors

C. R. WILKE AND C. Y. LEE

Division of Chemical Engineering, University of California, Berkeley, Calif.

AS THE theory and engineering applications of diffusional operations are advanced, increasing need arises for diffusion coefficients of gases and vapors. In view of the scarcity of reliable experimental data, methods of predicting such information assume a useful role. The general objective of this paper is to review critically the existing methods for estimation of diffusivities. An effort has been made to establish the relative accuracy of various procedures by comparison of calculated results with a body of selected experimental data.

REVIEW OF PREVIOUS CORRELATIONS

Gilliland (7) developed an empirical formula based on the hard sphere model of the classical kinetic theory (15). Collision diameters were assumed proportional to the cube roots of the molar volumes at the normal boiling point as in the earlier method of Arnold. Examination of available data led to the relation:

$$D_{12} = \frac{0.0043T^{3/2} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2}}{P(V_1^{1/3} + V_2^{1/3})^2} \quad (1)$$

As used in this paper, the diffusion coefficient is the proportionality constant in the rate equation for mass transfer in absence of convection or other modes of transfer, defined as follows for unidirectional diffusion:

$$N_1 = \frac{-D_{12}A}{RT} \times \frac{dp_1}{dz}$$

where N_1 = rate of diffusion of component 1 of a binary mixture, gram-moles per second
 D_{12} = diffusion coefficient, sq. cm. per second
 A = cross-sectional area perpendicular to direction of diffusion, sq. cm.
 p_1 = partial pressure of component 1, atm.

R = gas constant, cc.-atm./gram-mole-° K.
 T = temperature, ° K.
 z = distance in direction of diffusion

In using Equation 1, values of V should be obtained in the same way as were those used by Gilliland—namely, using Kopp's law of additive volumes, with the rules and values for each element given by LeBas (18). Values of atomic volumes have been summarized in several other sources (1, 23, 30).

Arnold Method. Arnold (1) adopted the general equation form proposed by Sutherland (25) containing an additional term involving the Sutherland constant, C_{12} , to account for deviations from the hard sphere model. Upon examination of available data to determine the best numerical constant, Arnold recommended the equation:

$$D_{12} = \frac{0.00837T^{3/2} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2}}{P(V_1^{1/3} + V_2^{1/3})^2 \left(1 + \frac{C_{12}}{T} \right)} \quad (2)$$

As outlined by Arnold, the Sutherland constant, C_{12} , may be calculated from the expression:

$$C_{12} = \left[\frac{2 \sqrt{V_1^{1/3} V_2^{1/3}}}{V_1^{1/3} + V_2^{1/3}} \right]^3 \sqrt{C_1 C_2} = F \sqrt{C_1 C_2} \quad (3)$$

The constants, C_1 and C_2 , are to be obtained from the absolute boiling temperature,

$$C_1 = 1.47T_{B_1} \quad (4)$$

From Equations 3 and 4 it can readily be seen that

$$C_{12} = 1.47F(T_{B_1} T_{B_2})^{1/2} \quad (5)$$

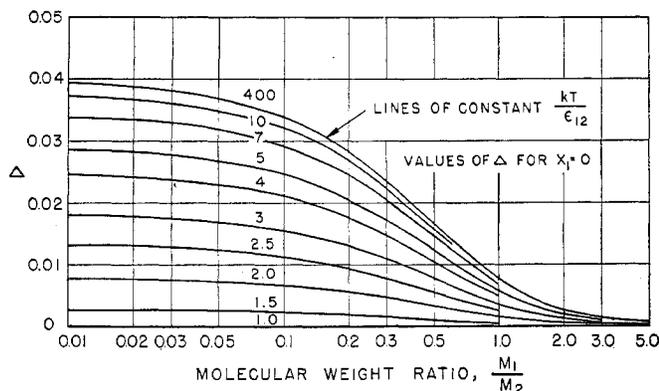


Figure 1. Values of Δ as mole fraction of one component approaches zero

In absence of experimental data V is obtained by using Kopp's law of additive volumes, or calculated from viscosity data.

Hirschfelder, Bird, and Spatz Method. If the proper function for potential energy of interaction between any two molecules is known, the more rigorous kinetic theory as developed by Chapman and Cowling (8) may be employed to give improved expressions for D and their temperature properties. Hirschfelder, Bird, and Spatz (8-11) have carried out such calculations for nonpolar gases which have an energy of attraction varying with the inverse sixth power of the distance between centers of adjacent molecules and a repulsive energy varying with the inverse twelfth power. For pairs of nonpolar gases the first approximation for the diffusion coefficient is expressed as follows

$$D_{12} = \frac{BT^{3/2} \left(\frac{M_1 + M_2}{M_1 M_2} \right)^{1/2}}{Pr_{12}^2 W^{(1)}(1) (1 - \Delta)} \quad (6)$$

The numerical constant, B , is equal to 9.2916×10^{-4} according to theory.

The collision integral, $W^{(1)}(1)$, has been calculated by Hirschfelder, Bird, and Spatz as a function of kT/ϵ . Representative values are listed in Table I.

Table I. Collision Integrals for Viscosity and Diffusion

kT/ϵ	$V/W^{(2)}(2; kT/\epsilon)$	$W^{(1)}(1; kT/\epsilon_{12})$
0.30	0.3596	1.331
0.50	0.4432	1.033
0.75	0.5432	0.8335
1.00	0.6301	0.7197
1.25	0.7023	0.6479
1.5	0.7613	0.5991
2.0	0.8523	0.5373
2.5	0.9172	0.4998
3.0	0.9657	0.4745
4.0	1.036	0.4418
5.0	1.085	0.4211
10.0	1.222	0.3712
50.0	1.550	0.2878
100.0	1.714	0.2585
400.0	2.095	0.2085

For mixtures of two nonpolar gases

$$r_{12} = \frac{r_1 + r_2}{2} \quad (7)$$

and

$$\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2} \quad (8)$$

For collisions between a polar and a nonpolar molecule, modified forms of equations are suggested (14). With these modifications Equation 6 applies to systems containing a polar and a nonpolar component. However, the energy of interaction among polar molecules, valence-unsaturated molecules, and cigar-shaped molecules is very different from that between nonpolar molecules. Before Equation 6 may be considered strictly applicable to systems containing such molecules, the collision integral

should be evaluated according to their respective potential functions. The labor involved is formidable and as yet this has not been accomplished.

The term Δ in Equation 6 is a correction factor, a small quantity usually less than 0.03, which varies with gas composition. Detailed equations for Δ have been given (8, 9). Δ is a complicated function of mole fraction, molecular weights, viscosities, the first approximation to the diffusion coefficient, and additional functions of kT/ϵ_{12} . However, these equations are so lengthy that their use may not be justified for many engineering calculations, particularly when the force constants have been estimated. As a first approximation to Δ for a given gas system it is suggested that Δ values for mole fractions of each component equal to zero be obtained and an average value calculated, assuming Δ to be linear in mole fraction. Values of Δ at zero mole fraction are presented in Figure 1. This procedure is not completely satisfactory, as Δ may deviate considerably from a linear function, but it should accomplish a major part of the correction. This procedure was adopted in subsequent applications of Equation 6.

ESTIMATION OF FORCE CONSTANTS FOR SIMILAR MOLECULES

Both ϵ/k and r_0 may be calculated from knowledge of gas viscosity at two temperatures by solving the equation for viscosity (9).

$$\eta \times 10^7 = \frac{266.93(MT)^{1/2}}{r_0^2} \left[\frac{V}{W^2(2)} \right] \quad (9)$$

where η = viscosity, grams per cm. second, and $V/W^2(2)$ = a function of kT/ϵ which has been evaluated by Hirschfelder, Bird, and Spatz. Representative values are given in Table I.

Equation 9 has been well substantiated by experimental evidence and provides the most satisfactory basis for obtaining the force constants.

In absence of viscosity data Hirschfelder, Curtiss, and Bird (12) recommend the following equations, which supersede those of the earlier work (8).

$$\epsilon/k = 0.77T_c \quad (10)$$

$$= 1.15T_b \quad (11)$$

$$= 1.92T_m \quad (12)$$

Prior to publication of the above equations, in the course of the present work examination of force constant data to check the earlier suggestions of Hirschfelder, Bird, and Spatz (8) indicated the following equations to be satisfactory:

$$\epsilon/k = 0.75T_c \quad (13)$$

$$\epsilon/k = 1.21T_b \quad (14)$$

Because the collision integrals are relatively insensitive to small errors in ϵ/k , Equations 10 and 11 are considered to be equivalent to 13 and 14 within the limits of precision of subsequent comparisons (Table IV). The relationships developed between T_c and T_b by Meissner (22) indicate that the value 1.21 in Equation 14 should be preferable to the value 1.39 (8), assuming that Equation 13 is valid. Unavailable critical and boiling data may be estimated with the equations of Meissner.

The collision diameter may be calculated from a single value of viscosity in Equation 6 using ϵ/k from Equations 13 and 14. Alternatively Hirschfelder, Bird, and Spatz recommend:

$$r_0 = 0.833V_c^{1/3} \quad (15)$$

where $r_0 = \text{\AA}$, and V_c = critical volume, cc. per gram-mole

Bromley and Wilke (4) have tested the general form of equation proposed by Licht and Stechert (20) and obtained a result which in terms of r_0 becomes

Table II. Selected Diffusion Data for Test of Methods

System	Reference	Temp., ° K.	Exptl. Diffusion Coefficient, Sq. Cm./Sec. (at 1 Atm.)
Air-benzene	(19)	298	0.0962
Air-ethyl alcohol	(19)	298	0.135
Air-ethyl ether	(27)	293	0.0896
Air-diphenyl	(7)	491	0.160
Air-I ₂	(27)	298	0.0834
Air-nitrobenzene	(19)	298	0.0868
Air-n-heptadecane	(3)	298	0.423
Air-n-hexadecane	(3)	298	0.0405
Air-n-octadecane	(3)	298	0.0397
Air-n-octane	(21)	298	0.0602
Air-water	(19)	298	0.260
CO ₂ -ethyl alcohol	(17)	273	0.0693
CO ₂ -ethyl ether	(27)	273	0.0541
CO ₂ -H ₂	(6)	273.2	0.550
CO ₂ -CH ₄	(6)	273.2	0.153
CO ₂ -N ₂	(2)	288	0.158
CO ₂ -N ₂ O	(29)	298	0.117
CO ₂ -C ₂ H ₆	(29)	298	0.0863
CO ₂ -H ₂ O	(27)	297.7	0.184
CO-C ₂ H ₄	(27)	273	0.151
CO-H ₂	(27)	273	0.622
CO-N ₂	(2)	288	0.211
CO-O ₂	(27)	273	0.185
Freon 12-benzene	(19)	298	0.0385
Freon 12-ethanol	(19)	298	0.0475
Freon 12-water	(19)	298	0.105
He-A	(6)	273.2	0.641
He-benzene	(19)	298	0.384
He-ethyl alcohol	(19)	298	0.494
He-Ne	(27)	293	1.23
He-nitrobenzene	(19)	298	0.372
He-H ₂	(27)	293	1.64
He-H ₂ O	(19)	298	0.908
H ₂ -NH ₃	(27)	293	0.849
H ₂ -A	(25)	293.2	0.770
H ₂ -benzene	(27)	273	0.317
H ₂ -CCl ₄	(27)	296	0.345
H ₂ -C ₂ H ₆	(27)	273	0.439
H ₂ -ethyl alcohol	(27)	340	0.578
H ₂ -C ₂ H ₄	(17)	293	0.483
H ₂ -ethyl ether	(27)	293	0.354
H ₂ -HCl	(27)	294	0.795
H ₂ -CH ₄	(6)	273.2	0.625
H ₂ -N ₂	(27)	293	1.205
H ₂ -N ₂ O	(6)	273.2	0.535
H ₂ -O ₂	(6)	273.2	0.697
H ₂ -C ₂ H ₂	(27)	300	0.450
H ₂ -SO ₂	(17)	273	0.483
H ₂ -H ₂ O	(27)	293	0.850
N ₂ -NH ₃	(27)	293	0.241
N ₂ -C ₂ H ₄	(27)	300	0.187
N ₂ -H ₂	(2)	288	0.743
N ₂ -I ₂	(27)	273	0.070
N ₂ -NO	(27)	293	0.232
N ₂ -O ₂	(6)	273	0.181
N ₂ O-C ₂ H ₆	(29)	298	0.086
O ₂ -NH ₃	(27)	293	0.253
O ₂ -benzene	(27)	296	0.0939
O ₂ -CCl ₄	(27)	298	0.0731
O ₂ -C ₂ H ₄	(27)	293	0.182
NH ₃ -C ₂ H ₄	(27)	293	0.177
A-Ne	(27)	293	0.329
C ₂ H ₆ -C ₂ H ₆	(27)	293	0.085
C ₂ H ₆ -CH ₄	(27)	293	0.163

$$r_o = 2.34 \frac{T^{1/3}}{p_c} \quad (16)$$

Examination of data as in the case of ϵ/k suggested an alternative method of estimation of r_o based on molal volume at the normal boiling point, which may be expressed as:

$$r_o = 1.18V^{1/3} \quad (17)$$

Equation 17 appears to be somewhat more satisfactory than Equation 15 or 16. The $1/3$ power on V_c has been retained in Equation 15, as it has a theoretical basis in the Lennard-Jones and Devonshire theory of gases and liquids (8), although the data seem to correlate better *vs.* $V_c^{0.39}$. In application of Equation 17 molal volumes may be estimated from Kopp's law and the rules of LeBas as in the methods of Gilliland and Arnold.

COMPARISON OF EQUATIONS WITH EXPERIMENTAL DIFFUSION DATA

To serve as a basis for comparison in determining the relative accuracy of the foregoing methods, experimental diffusion data were selected from reliable sources for 64 systems at atmospheric pressure and near room temperature. (All methods of this paper pertain to moderate pressure systems where ideal gas behavior may be assumed—i.e., where the product DP is independent of

Table III. Force Constants and Collision Diameters for Components of Selected Systems

Gas	$\epsilon/k, ^\circ K.$ Viscosity	$r_o, \text{A.}$ from Viscosity
Air	97.0	3.617
Ammonia	315	2.624
Argon	124.0	3.418
Benzene	440	5.270
CO ₂	190	3.996
CO	110.3	3.590
CCl ₄	327	5.881
C ₂ H ₆	250	4.418
C ₂ H ₅ OH	391	4.455
Diphenyl	600	6.223 ^a
Ethyl ether	350 ^b	5.424 ^a
C ₂ H ₄	205	4.282
Freon 12	288 ^b	5.110 ^d
Helium	6.03	2.70
n-Heptadecane	800	7.923 ^a
H ₂	33.3	2.968
HCl	360	3.305
Iodine	550	4.982
CH ₄	136.5	3.882
Neon	35.7	2.80
Nitrobenzene	539 ^b	4.931 ^a
NO	119	3.47
N ₂	91.5	3.681
N ₂ O	220	3.879
n-Octadecane	820 ^c	7.963 ^a
n-Octane	320	7.451
O ₂	113.2	3.433
Propane	254	5.061
SO ₂	252	4.290
Water	363	2.655
	356 ^d	2.649 ^e

All values obtained from viscosity are taken from Hirschfelder, Bird, and Spatz (8), unless otherwise noted. A more complete table is presented by Hirschfelder, Curtiss, and Bird (13).

^a Values estimated from diffusion data.

^b Values estimated from T_c .

^c Values estimated from boiling temperature.

^d (5). ^e (24).

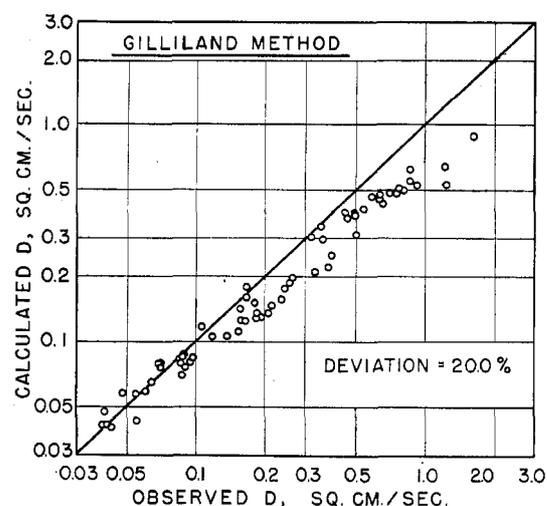


Figure 2. Comparison of experimental data with results calculated by Gilliland equation

pressure.) These data are summarized in Table II. In view of the uncertainty and lack of precision in many investigations reported in the literature, use of this limited number of data from selected sources covering a wide range of diffusion coefficients and related properties was considered preferable to use of a larger body of data selected at random. Also, for a large majority of the systems force constants based on viscosity (see Table III) were known for the individual components.

Diffusivities calculated by Equations 1 and 2 and by Equation 6 with force constants from viscosity are presented in Figures 2, 3, and 4. Comparison between calculated and observed results from Table II are illustrated for these three methods. The methods of Arnold and of Hirschfelder, Bird, and Spatz gave nearly comparable results, with the latter somewhat better. The method of Gilliland gives poor agreement for these systems. Various equations for estimating force constants were employed in connection with Equation 6 to obtain additional comparisons of

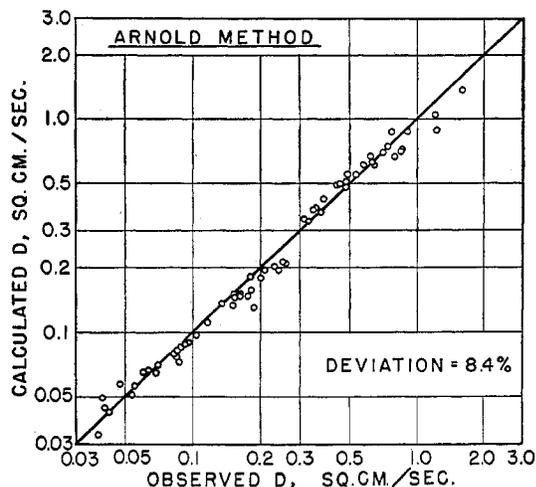


Figure 3. Comparison of experimental data with results calculated by Arnold equation

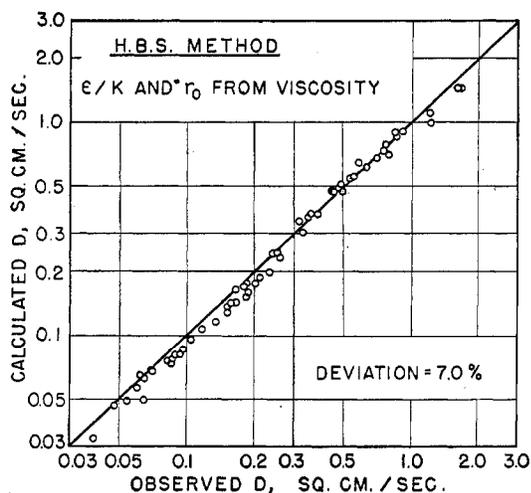


Figure 4. Comparison of experimental data with results calculated by Hirschfelder, Bird, and Spetz equation

ϵ/k and r_0 from viscosity

Table IV. Deviations Between Experimental Data and Calculated Values for 64 Systems

Item	Method	Equation	Average % Deviation	Maximum % Deviation
1	Gilliland	1	20.0	46.8
2	Arnold	2	8.4	20.5
3	Hirschfelder, Bird and Spetz, ϵ/k and r_0 from viscosity	6	7.0	21.4
4	r_0 from T_c/p_c (Eq. 16), ϵ/k from viscosity	6	10.1	31.3
5	r_0 from V (Eq. 17), ϵ/k from viscosity	6	10.3	24.9
6	r_0 from V_c (Eq. 15), ϵ/k from viscosity	6	11.8	32.7
7	r_0 from V (Eq. 17), $\epsilon/k = 1.21 T_b$ (Eq. 14)	6	12.0	31.0
8	Modified Hirschfelder, Bird, Spetz, Eq. 18, ϵ/k and r_0 from viscosity	18	3.9	16.0
9	r_0 from T_c/p_c (Eq. 16), ϵ/k from viscosity	18	9.4	32.7
10	r_0 from V (Eq. 17), ϵ/k from viscosity	18	7.0	21.9
11	r_0 from V_c (Eq. 15), ϵ/k from viscosity	18	10.2	37.6
12	r_0 from viscosity, $\epsilon/k = 0.75 T_c$ (Eq. 13)	18	5.4	26.0
13	r_0 from viscosity, $\epsilon/k = 1.39 T_b$ (Eq. 14)	18	7.2	24.9
14	r_0 from viscosity, $\epsilon/k = 1.21 T_b$ (Eq. 14)	18	5.1	20.5
15	r_0 from V (Eq. 17), $\epsilon/k = 1.21 T_b$ (Eq. 14)	18	7.7	24.5

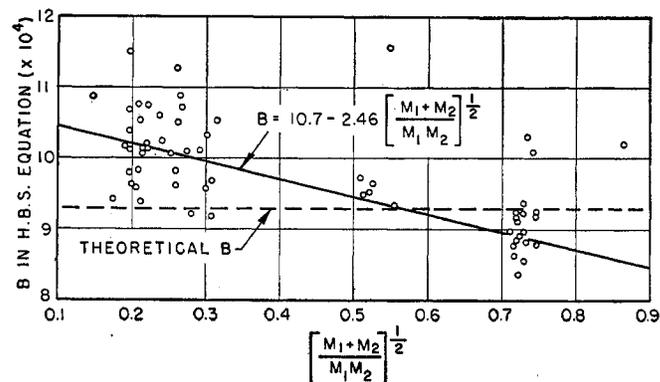


Figure 5. Variation of constant in Hirschfelder, Bird, and Spetz equation

calculations with observed data. Average and maximum deviations between calculation and experiment are summarized in Table IV for all methods.

It is of interest to compare the three methods with respect to the effect of temperature on the diffusion coefficient. The equation of Gilliland is theoretically at variance with the Arnold and the Hirschfelder, Bird, and Spetz equations. The two latter methods consider possible molecular interaction upon collision and therefore in principle should give more satisfactory results. This conclusion is borne out by the relatively meager experimental evidence available. Table V shows the temperature behavior of the carbon dioxide-air system over a range of 293° to 1500° K., as observed by Kilbanova, Pomerantsev, and Frank-Kamenetski (16). Results calculated by each method, assuming the value at 293° K. to be correct, are also given. The Arnold and the Hirschfelder, Bird, and Spetz methods agree closely, probably within the limits of experimental error, while the Gilliland equation gives low values at higher temperatures.

POSSIBLE MODIFICATION OF HIRSCHFELDER, BIRD, AND SPETZ EQUATION

As a means of studying deviations of Equation 6 from experimental results, values of the constant B were computed for each system given in Table III which would make the equation agree with experiment. Force constants were based on viscosity. Various attempts were made to relate these values of B to properties of the systems. As shown in Figure 5, there appears to be some correlation of the constant with the molecular weight group $\left[\frac{M_1 + M_2}{M_1 M_2}\right]^{1/2}$. Assuming a linear relationship, the data of Figure 5 may be approximated by the equation:

$$B = 10.7 - 2.46 \left[\frac{M_1 + M_2}{M_1 M_2}\right]^{1/2} \quad (18)$$

Results obtained employing Equation 18 in connection with Equation 6 for the systems are shown in Figure 5 and Table IV. The average and maximum deviations between calculated and experimental values are significantly less than those obtained with Equation 6, using the theoretical value of 9.2916×10^{-4} for B .

Table V. Variation of D with Temperature for Carbon Dioxide-Air System

T, ° K.	Diffusion Coefficient, Sq. Cm./Sec.			
	Exptl. data (smoothed)	Arnold method	H.B.S. method	Gilliland method
293	0.151			
400	0.273	0.267	0.266	0.242
600	0.555	0.543	0.523	0.448
800	0.915	0.905	0.883	0.690
1000	1.32	1.28	1.28	0.970
1300	1.97	1.97	1.97	1.42
1500	2.45	2.49	2.52	1.77

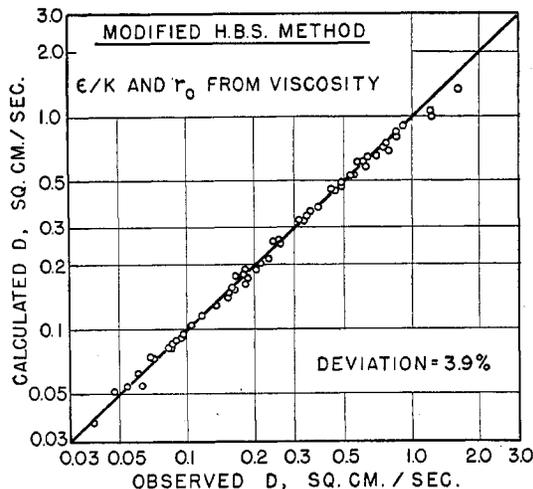


Figure 6. Comparison of experimental data with results calculated by modified Hirschfelder, Bird, and Spatz equation

Further results using estimated force constants are summarized in Table IV, items 9 to 15. Figure 7 shows results obtained with Equation 18 using force constants estimated from boiling point and molar volume. This procedure seems comparable in accuracy to the Arnold method for these systems.

DISCUSSION

One of the reasons for using Equation 18 was to obtain a "best possible" correlation of the data using force constants based on viscosity, and then to use this relation as a basis for comparing the various procedures for estimating the force constants. Methods of obtaining r_0 are compared in Table IV, items 8 to 11. Estimation of r_0 from molar volume (Equation 17) appears most satisfactory. Use of T_c/P_c yields slightly better results than use of critical volume. However, experimental uncertainty in measurement of critical properties may contribute to the apparent inaccuracy. Methods of estimating ϵ/k are compared in Table IV, items 12 to 14. Equation 13 ($\epsilon/k = 0.755 T_c$) and Equation 14 ($\epsilon/k = 1.21 T_f$) show essentially equivalent behavior. As noted previously, Equations 10 and 11 should be essentially equivalent to 13 and 14.

It is recognized that Equation 18 is highly empirical and that its use can be justified only on the basis of the improved correlation obtained for the present systems. It is believed that the deviations of B from the theoretical value as shown in Figure 5 represent some failure in the theory, which should ultimately be improved by a more fundamental approach. To seek modified relations for obtaining the force constants for dissimilar molecules from the values for the pure components would seem more promising ultimately than the more simple expedient of modifying the numerical constant in the diffusion equation.

NOMENCLATURE

- B = numerical constant equal to 9.2916×10^{-4} according to theory
 C = Sutherland's constant for diffusion, ° K.
 D = diffusion coefficient, sq. cm. per second
 k = gas constant/molecule, Boltzmann's constant
 M = molecular weight
 P = total pressure, atm.
 r = molecular diameter
 r_{12} or r_0 = collision diameter, Å.
 T = absolute temperature, ° K.
 T_b = normal boiling point, ° K.
 T_c = critical temperature, ° K.
 T_m = melting point, ° K.
 $\frac{V}{W^{(2)}} = \text{function of } kT/\epsilon$
 V = molar volume at normal boiling point, cc. per gram-mole (total molar volume of each component)
 V_c = critical volume, cc. per gram-mole

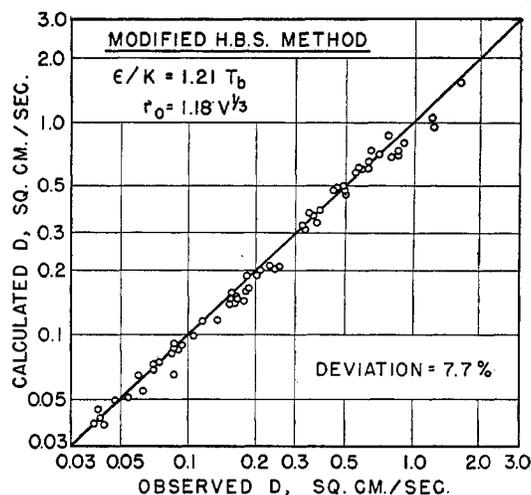


Figure 7. Results of modified Hirschfelder, Bird, and Spatz equation using estimated force constants

- $W^{(2)}$ = collision integral for diffusion, function of kT/ϵ
 Δ = small correction term seldom exceeding 0.03
 ϵ = maximum energy of attraction
 η = viscosity, gram/cm.-sec.

Subscripts 1 and 2 denote components 1 and 2, respectively.

REFERENCES

- (1) Arnold, J. H., *IND. ENG. CHEM.*, **22**, 1091 (1930).
- (2) Boardman, L. E., and Wild, N. E., *Proc. Roy. Soc. (London)*, **A162**, 511 (1937).
- (3) Bradley, R. S., and Shellard, A. D., *Ibid.*, **A198**, 239 (1949).
- (4) Bromley, L. A., and Wilke, C. R., *IND. ENG. CHEM.*, **43**, 1641 (1951).
- (5) Buddenberg, J. W., and Wilke, C. R., *Ibid.*, **41**, 1345 (1949).
- (6) Chapman, Sydney, and Cowling, T. G., "Mathematical Theory of Nonuniform Gases," Cambridge University Press, Teddington, 1939.
- (7) Gilliland, E. R., *IND. ENG. CHEM.*, **26**, 681 (1934).
- (8) Hirschfelder, J. O., Bird, R. B., and Spatz, E. L., *Chem. Rev.*, **44**, 205 (1949).
- (9) Hirschfelder, J. O., Bird, R. B., and Spatz, E. L., *J. Chem. Phys.*, **16**, 968 (1948).
- (10) Hirschfelder, J. O., Bird, R. B., and Spatz, E. L., *Trans. Am. Soc. Mech. Engrs.*, **71**, 921 (1949).
- (11) Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids," pp. 538-40, Wiley, New York, 1954.
- (12) Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., *Trans. Am. Soc. Mech. Engrs.*, **71**, 245, 8.6-4 (1949).
- (13) *Ibid.*, pp. 1110-12.
- (14) *Ibid.*, p. 6000, Eq. 8.6-3, 8.6-4.
- (15) Kennard, E. H., "Kinetic Theory of Gases," p. 195, McGraw-Hill Book Co., New York, 1938.
- (16) Kilbanova, Pomerantsev, and Frank-Kamenetskii, *J. Tech. Phys. (U.S.S.R.)*, **12**, 14-30 (1942).
- (17) Landolt-Börnstein, "Physikalisch-chemische Tabellen," J. Springer, Berlin, (1923-35).
- (18) LeBas, G., *Chem. News*, **99**, 206 (1909).
- (19) Lee, C. Y., and Wilke, C. R., *IND. ENG. CHEM.*, **46**, 2381 (1954).
- (20) Licht, W., Jr., and Stechert, D. G., *J. Phys. Chem.*, **48**, 23 (1944).
- (21) Mack, Edward, Jr., *J. Am. Chem. Soc.*, **47**, 2468 (1925).
- (22) Meissner, H. P., *Chem. Eng. Progr.*, **45**, 149 (1949).
- (23) Perry, J. H., "Chemical Engineer's Handbook," McGraw-Hill Book Co., New York.
- (24) Rowlinson, J. S., *Trans. Faraday Soc.*, **47**, 120 (1951).
- (25) Sutherland, *Phil. Mag.*, **36**, 507 (1893).
- (26) Titani, T., *Bull. Chem. Soc. (Japan)*, **5**, 41 (1930).
- (27) Trautz, M., and Müller, W., *Ann. Physik*, **414**, 333 (1935).
- (28) Waldmann, L., *Naturwissenschaften*, **32**, 223 (1944).
- (29) Wall, F. T., and Kidder, G. A., *J. Phys. Chem.*, **50**, 235 (1946).
- (30) Wilke, C. R., *Chem. Eng. Progr.*, **45**, 219 (1949).