Calculation of the Diffusion Coefficient of Dilute Gases and of the Self-diffusion Coefficient of Dense Gases

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A corresponding-states correlation of low-density binary- and self-diffusion coefficients is presented. The equations are simple to use, are sufficiently accurate for most calculations, and correlate those data used in their derivation somewhat better than calculations based on the Lennard-Jones potential if potential parameters have to be estimated from the critical properties. The Enskog kinetic theory of dense gases is used in modified form to obtain an expression for the high-density diffusion coefficient for isotopic mixtures in terms of the viscosity and compressibility of the gas. Generalized viscosity and compressibility charts are then used to construct a graph for predicting a reduced self-diffusion coefficient as a function of reduced temperature $T_r = T/T_c$ and reduced pressure $p_r = p/p_c$. The effect of the pressure on the Schmidt number, Sc = $\mu/\rho\mathfrak{D}$, is also discussed. Finally the extension of this chart to nonisotopic mixtures is considered.

In the design and operation of gas-phase processes, one must have methods available for estimating various physical properties when experimental data are unavailable. The equation of state and thermodynamic properties of dilute and moderately dense gases can be calculated satisfactorily from intermolecular forces by means of statistical mechanics (*24, 3*). At higher densities the generalized charts of Hougen and Watson (*25*) and the revised tables of Lyderson, Greenkorn, and Hougen (*35, 18*) are more useful. The viscosity, thermal conductivity, and diffusion coefficients for dilute gases can be estimated from intermolecular forces by kinetic theory calculations (*24, 3*). Several charts have been prepared from experimental data for the prediction of the viscosity coefficient of dense gases (*8, 12, 13, 48, 25*), the most recent being that of Carr, Parent, and Peck (*9*). The thermal conductivity coefficient of dense gases can be estimated from the chart of Lenoir, Junk, and Comings (*33, 13*), which is a generalized representation of experimental data for several gases. The earlier charts of Comings and Nathan (*11*) and of Gamson (*16*) for the prediction of the thermal conductivity coefficient of dense gases were constructed from experimental viscosity and equation-of-state data by means of the Enskog dense-gas kinetic theory (*15*), inasmuch as there were not enough high-density thermal conductivity data available for the preparation of a dimensionless graphical representation. This paper presents an empirical method for the calculation of the diffusion coefficients of dilute gases; it also describes the construction of a chart for the prediction of the self-diffusion coefficient of dense gases analogous to those prepared for thermal conductivity by Comings and Nathan (*11*) and by Gamson (*16*).

In a system composed of two substances, *A* and *B*, the binary diffusion coefficient, $\mathfrak{D}_{AB}$, is defined by either of two equivalent relations (in the absence of thermal diffusion, pressure diffusion, and forced diffusion effects (*4*):

$$\mathbf{j}_A = -(c^2/\rho)M_A M_B \mathfrak{D}_{AB} (\partial \ln a_A/\partial \ln x_A)_{p,T}\nabla x_A \qquad (1)$$

$$\mathbf{\Phi}_A = -c\mathfrak{D}_{AB}(\partial \ln a_A/\partial \ln x_A)_{p,T}\nabla x_A \qquad (2)$$

in which ρ is the mass density (g. cm.^{-3}), c is the molar density (moles cm.^{-3}), a_A is the activity of substance *A*, x_A is the mole fraction of *A*, and M_A and M_B are the molecular weights of *A* and *B*. The quantity $\mathbf{j}_A$ is the mass flux of *A* (g. $\text{cm.}^{-2}/\text{sec.}^{-1}$) with respect to the local mass average velocity of the fluid system; $\mathbf{\Phi}_A$ is the molar flux of *A* (moles cm.^{-2} sec.^{-1}) with respect to the molar average velocity of the system. These definitions of $\mathfrak{D}_{AB}$ are exactly the same as those used in standard references on the kinetic theory of dilute gases (*24, 10*). However, due to the difficulty of obtaining reliable values of a_A, experimentalists generally use a diffusion coefficient $\mathfrak{D}_{AB}'$ defined by

$$\mathfrak{D}_{AB}' = \mathfrak{D}_{AB}(\partial \ln a_A/\partial \ln x_A)_{p,T} \qquad (3)$$

For dilute gas mixtures and for ideal solutions D_{AB}' is equal to $\mathfrak{D}_{AB}$.

The self-diffusion coefficient $\mathfrak{D}$ is defined as the limiting form of the binary diffusion coefficient $\mathfrak{D}_{AB}$, when the two interdiffusing species *A* and *B* have the same mass ($M_A = M_B$) and when the intermolecular potential energy function $\varphi(r)$ is the same for the interaction of two molecules of *A* and for two molecules of *B* ($\varphi_{AA}(r) = \varphi_{BB}(r)$). In practice there are three types of binary diffusion systems in which the above conditions are nearly fulfilled: (a) interdiffusion of *ortho* and *para* forms of molecules, (b) interdiffusion of heavy isotopes, and (c) interdiffusion of some pairs of molecules, such as CO_2 and N_2O, which have nearly the same molecular weights and almost the same Lennard-Jones (6–12) potential parameters (*24, 3*). Experimentally the coefficient of self-diffusion is usually determined by means of the interdiffusion of isotopes, one of which is radioactive. Self-diffusion coefficients have been measured at 1 atm. for eleven gases: Ne (*54, 20*), A (*54, 27, 26*), Kr (*19*), Xe (*19, 49*), H_2 (*21, 22, 50, 51*), N_2 (*54, 55*), O_2 (*54, 55*), CH_4 (*54*), CO_2 (*54, 55, 1*), HCl (*7*), and HBr (*7*). For dense gases, however, only two systems have been studied, $CH_4 - CH_3T$ (*28*) ($1.4 < T_r < 1.7$, $0.4 < p_r < 6.5$) and $CO_2 - C^{14}O_2$ (*40, 45, 46, 39*) ($1.0 < T_r < 1.3$, $0.1 < p_r < 8.0$).

EMPIRICAL EXPRESSIONS FOR THE BINARY- AND SELF-DIFFUSION COEFFICIENTS OF DILUTE GASES

The calculation of diffusion coefficients at low densities by means of the Chapman-Enskog theory has been described in the monograph of Chapman and Cowling (*10*). The result is written in terms of "collision integrals," which have been evaluated for the Lennard-Jones (6–12) potential (*23, 29*) and for the Buckingham (6-exp) potential (*36*). The method of calculating the diffusion coefficient from the Lennard-Jones (6–12) potential parameters has been discussed elsewhere (*24, 3*); a comparison with experimental data is given in Table 1. The calculated values (based on potential parameters determined from experimental viscosity data) are generally lower than the measured values; this discrepancy is probably due to the inadequacy of the Lennard-Jones (6–12) potential. The Buckingham (6-exp) potential seems to offer only a slight improvement over the Lennard-Jones (6–12) potential (*37*).

Since the number of gases for which the Lennard-Jones parameters are known is relatively small and since the Lennard-Jones potential is inadequate for polar molecules and many of the large, complex molecules, one must rely on semiempirical and empirical methods for calculation of diffusion coefficients in many instances. Hirschfelder, Curtiss, and Bird (*24, 3*) have suggested empirical relationships to estimate the Lennard-Jones parameters in terms of the properties of the substance at its critical point, at its melting point, at its boiling point, at its Boyle point, or at absolute zero. Wilke and Lee (*53*)

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have made an extensive comparison of these relations with experimental data; they have suggested a relation in terms of molal volumes estimated from Kopp's law and the rules of Le Bas. Wilke and Lee also show by a comparison with experimental data that better results may be obtained from Chapman-Enskog calculations in which the Lennard-Jones potential is employed, if the numerical constant is considered an empirical function of the molecular weights of the interdiffusing substances.

In addition to these empirical extensions of the Lennard-Jones potential calculations, numerous semiempirical relations have been suggested for the calculation of diffusion coefficients in dilute gases. Wilke and Lee (*53*) discuss the relations proposed by Gilliland (*17*, *42*) and by Arnold (*2*) and give comparisons with experimental data; they found the Arnold relation to be superior to that of Gilliland and to give results only slightly worse than the Lennard-Jones potential calculations with parameters determined from experimental viscosity data.

In an attempt to find a simple correlation which would be easier to use than the Gilliland and Arnold formulas, the principle of corresponding states (*3*, *25*) was applied to all available data for self-diffusion and binary-diffusion of dilute gases (excluding mixtures containing air[a]) (*43*). When plotted on log-log paper, mixtures containing hydrogen, helium, and water do not follow the general trend established by the majority of substances[a]; therefore these substances are not included in the correlation. The method of least squares was used to obtain the following equation for low-density binary-diffusion coefficients in nonpolar systems.[b]

$$(p\mathfrak{D}_{AB})_R = (3.882 \times 10^{-4})(T/T_{c,AB})^{1.823} \qquad (4)$$

where

$$(p\mathfrak{D}_{AB})_R = p\mathfrak{D}_{AB}(M_{AB})^{1/2}(p_{c,AB})^{-2/3}(T_{c,AB})^{-5/6} \qquad (5)$$

$$M_{AB} = 2M_AM_B/(M_A + M_B) \qquad (6)$$

$$T_{c,AB} = (T_{c,A}T_{c,B})^{1/2} \qquad (7)$$

$$p_{c,AB} = (p_{c,A}p_{c,B})^{1/2} \qquad (8)$$

The quantity $(p\mathfrak{D}_{AB})_R$ is not dimensionless; it would be so if $T_{c,AB}$ were replaced

TABLE 1

RESULTS OF A COMPARISON WITH EXPERIMENTAL DATA OF METHODS USED FOR THE CALCULATION OF DIFFUSION COEFFICIENTS IN DILUTE GASES

Gas or gas pair	Percent deviation[a] Equation (4)	Percent deviation[a] Lennard-Jones potential calculations with parameters determined from viscosity	Literature Cited
Ne	+ 9.3%	− 3.1%	*54*
A	+ 6.9	+ 4.1	*27, 54*
Xe	+ 6.2	− 0.5	*49*
Kr	+ 1.9	+ 0.3	*19*
O_2	− 9.9	− 7.0	*54*
N_2	− 5.1	− 7.6	*5, 54*
HCl	+ 0.8	+ 1.8	*7*
CO_2	+ 3.0	− 6.2	*5, 1, 54*
CH_4	− 9.4	−19.2	*54*
O_2–N_2	± 4.2	± 4.2	*31*
O_2–Benzene	±23.2	±22.3	*31*
N_2–CO	− 9.9	− 9.5	*5*
N_2–Ethane	− 0.4	− 3.0	*6*
N_2–Ethylene	− 3.0	− 4.3	*6*
N_2–*n*-butane	+ 5.1	+ 2.6	*6*
N_2–isobutane	+11.7	+ 5.6	*6*
CO–Ethylene	+30.5	+30.4	*31*
CO_2–O_2	−26.7	−28.9	*31*
CO_2–N_2	− 6.3	− 8.8	*5, 6*
CO_2–CO	− 3.6	− 5.5	*31*
CO_2–N_2O	− 5.8	−12.0	*31, 5, 1, 52*
CO_2–CS_2	+ 4.5	− 7.2	*31*
CO_2–CH_4	− 4.7	− 9.5	*31*
CO_2–Propane	+ 1.0	− 8.0	*52*
CO_2–Benzene	+ 4.8	− 5.9	*31*
CO_2–Methyl alcohol	− 5.0	+ 0.5	*31*
CO_2–Ethyl alcohol	+ 2.6	± 1.5	*31*
N_2O–Propane	− 0.1	− 8.3	*52*
Avg. deviation for 28 pairs[b]	7.3%	8.1%	
		Lennard-Jones potential calculations with parameters determined empirically from critical data (*24*, *3*)	
CO_2–Acetic Acid	−17.6	−29.4	*31*
CO_2–Propionic Acid	− 7.4	−21.3	*31*
CO_2–Butyric Acid	+23.9	±12.9	*31*
CO_2–*i*-Butyric Acid	− 2.7	− 7.4	*31*
CO_2–*n*-propyl alcohol	+ 2.9	−11.0	*31*
CO_2–*n*-butyl alcohol	+18.6	± 1.9	*31*
CO_2–Ethyl formate	+ 3.2	−11.8	*31*
CO_2–*n*-propyl formate	+ 5.1	−10.8	*31*
CO_2–Methyl acetate	+ 3.2	−12.4	*31*
CO_2–Ethyl acetate	+ 5.9	−10.7	*31*
CO_2–Isobutyl acetate	+ 8.2	− 2.2	*31*
CO_2–Methyl propionate	− 2.5	−17.2	*31*
CO_2–Ethyl propionate	+ 3.2	−13.2	*31*
CO_2–Methyl butyrate	+ 5.6	−12.1	*31*
CO_2–Ethyl butyrate	+ 6.6	−11.6	*31*
CO_2–Methyl isobutyrate	+ 5.2	−11.7	*31*
CO_2–Ethyl isobutyrate	+ 6.5	−11.2	*31*
CO_2–Ethyl ether	+ 0.6	−15.1	*31*
CO_2–Ethylene oxide	+ 0.6	− 9.6	*52*
N_2O–Ethylene oxide	− 0.4	− 9.6	*52*
Freon-12–benzene	− 4.4	−17.1	*32*
Freon-12–ethyl alcohol	+ 5.1	− 2.9	*32*
Avg. deviation for 22 pairs[b]	6.3%	12.0%	
Avg. deviation for 50 pairs[b]	6.9%		

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[a] The notation ± indicates that, in a determining of the average deviation for this gas pair over a range in temperature, approximately half of the calculated values were found to be greater (+) than the experimental values and half of the calculated values were less (−) than the experimental values.

[b] This average deviation is the arithmetic average of the absolute values of the average deviations for individual gas pairs.

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[a] Mixtures containing air were excluded from the correlation since it was not considered desirable to base a general correlation on the use of pseudocritical temperatures and pressures. That hydrogen, helium, and water mixtures did not follow the general trend when plotted as described above indicates the need for additional parameters to account for quantum effects (hydrogen and helium) and the effects of polar molecules (water) (*5*).

[b] Complete summaries of values of the critical constants have been compiled by Lydersen (*34*) and by Kobe and Lynn (*30*).

by $RT_{c,AB}$ in Equation (5). The results of comparison of Equation (4) with experimental data are given in Table 1. This table also contains a comparison of the Lennard-Jones potential calculations with experimental data using a) parameters determined from experimental viscosity data for those substances for which they are available, and b) parameters determined from the critical properties according to the relations suggested by Hirschfelder, Curtiss, and Bird (*3*; *24*, p. 245). The results of the comparison show that Equation (4) gives better results than the Lennard-Jones potential calculations when the potential parameters must be estimated from the critical properties. However it should be noted that this correlation is heavily weighted in favor of CO_2 mixtures and that this may not be generally true. Perhaps more important, the power-law temperature dependence expressed by Equation (4) is simple to use, and it is sufficiently accurate for most engineering calculations.

Although the data for water vapor mixtures did not follow Equation (4), they did exhibit a definite trend; they were analyzed by the same procedure. For *low-density binary systems containing water* as one component the equation obtained is

$$(p\mathfrak{D}_{AB})_R = (5.148 \times 10^{-4})(T/T_{c,AB})^{2.334} \qquad (9)$$

The results of a comparison of Equation (9) with experimental data are presented in Table 2.

EXPRESSIONS FOR THE TRANSPORT COEFFICIENTS OF DENSE GASES OF RIGID SPHERES

The theory which forms the basis for discussions of the transport phenomena in dense gases is Enskog's kinetic theory for a pure gas made up of rigid spheres (*24*, *15*, also chap. 16 of *10*). To date this theory in one of several modifications is the best theory available for calculating the temperature and density dependence of the transport coefficients. Enskog's kinetic theory for dense gases differs from his theory for dilute gases in that it takes into account the fact that the diameter of the molecules is not small with respect to the mean free path. His theory was developed for rigid spheres only; since more than two rigid spheres can not collide simultaneously, his theory does not take into account the effects of multiple collisions. Although the theoretical development is quite lengthy, the results may be expressed in a simple form by giving the ratio of the transport coefficients to that dilute gas values (indicated by a superscript ^{0})

$$\frac{\mu}{\mu^0} = (\tfrac{2}{3})\pi n\sigma^3(y^{-1} + 0.8 + 0.761y) \qquad (10)$$

$$\frac{k}{k^0} = (\tfrac{2}{3})\pi n\sigma^3(y^{-1} + 1.2 + 0.755y) \qquad (11)$$

$$\frac{n\mathfrak{D}}{(n\mathfrak{D})^0} = (\tfrac{2}{3})\pi n\sigma^3(y^{-1}) \qquad (12)$$

The quantity y is related to the equation of state for rigid spheres:

$$\begin{aligned} y &= pV/RT - 1 \\ &= (\tfrac{2}{3}\pi n\sigma^3) + 0.6250(\tfrac{2}{3}\pi n\sigma^3)^2 \\ &\quad + 0.2869(\tfrac{2}{3}\pi n\sigma^3)^3 \\ &\quad + 0.115(\tfrac{2}{3}\pi n\sigma^3)^4 + \cdots \qquad (13) \end{aligned}$$

Equation (13) is obtained from the virial expansion of the equation of state for rigid spheres. When Equation (13) is substituted in Equations (10), (11), (12), one then obtains the rigorous expressions for the coefficients of viscosity, thermal conductivity, and self-diffusion of a dense gas composed of rigid spheres.

PROPOSED EMPIRICAL MODIFICATIONS OF RIGID SPHERE THEORIES

Several suggestions have been made for extending Enskog's theory for applications to real gases:

(1) Enskog himself suggested a modification in the interpretation of the quantities y and σ. Enskog recommended that y be obtained from experimental p-V-T data according to the relation:

$$y = (V/R)(\partial p/\partial T)_V - 1 \qquad (14)$$

and that σ then be fixed by making the experimental and calculated values of the viscosity agree at the minimum in the curve of (μ/ρ) vs. ρ. In this way Equation (10) has been used successfully to predict the viscosity of the following substances:

CO_2 $T = 40.3°C$
$p = 45 - 155$ atm.
max. dev. = 6% (*15*)

N_2 $T = 50°C$
$p = 15 - 960$ atm.
max. dev. = 6% (*10*)

A $T = 0 - 50°C$
$p = 1 - 2000$ atm.
max. dev. = 10% (*38*)

TABLE 2

RESULTS OF A COMPARISON OF EQUATION (9) WITH EXPERIMENTAL DATA

Gas pair	Percent Deviation[g] Equation (9)	Literature Cited
H_2O–N_2	+ 8.8%	*41*
H_2O–O_2	± 3.4	*41*
H_2O–CO_2	± 5.4	*31*, *41*
H_2O–Methane	− 6.4	*41*
H_2O–Ethylene	− 9.2	*41*
H_2O–Methyl formate	− 2.8	*31*
H_2O–Methyl acetate	+ 9.6	*31*
H_2O–Methyl propionate	+10.6	*31*
H_2O–Freon-12	− 4.5	*32*
Avg. deviation[h]	6.7% for 9 gas pairs	

[g,h]See footnotes to Table 1, page 138.

(2) Drickamer and his collaborators have calculated y according to the rigid sphere expression, Equation (13), using the σ from the Lennard-Jones (6–12) potential. Jeffries and Drickamer (*28*) have reported[c] satisfactory agreement between the self-diffusion coefficients calculated according to this method and their own self-diffusion data for CH_4; on the other hand Robb and Drickamer (*40*) and Timmerhaus and Drickamer (*45*, *46*) have reported considerable discrepancy between their self-diffusion data for CO_2 and this method of calculation, the disagreements being worse at higher densities. O'Hern and Martin (*39*) also found wide deviations between results calculated in this manner and their own data for self-diffusion of CO_2. In addition, it has been found by the authors that this method, when applied to the calculation of the viscosity coefficient, gives poor agreement with experimental data.

PREPARATION OF HIGH DENSITY SELF-DIFFUSION COEFFICIENT CHART

Comings and Nathan (*11*) used Enskog's own modification to prepare a generalized chart for thermal conductivity. They divided Equation (11) by Equation (10); thereby they eliminated σ and obtained an expression for k in terms of k^0, μ/μ^0, and y; the quantity y was determined from Equation (14). Recently a few high-density measurements of thermal conductivity have been made for several simple gases (*47*); these data were found to be in agreement with the chart of Comings and Nathan by about 15%. However, the utility of this chart for the prediction of the thermal conductivity of polyatomic molecules is open to question; the Enskog theory is derived for monatomic molecules, whereas

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[c] In the paper of Jeffries and Drickamer the formula for $\mathfrak{D}$ is incorrect: $(\kappa T/\pi\mu)^{1/2}$ should be replaced by $(\kappa T/2\pi\mu)^{1/2}$. However the calculated values of $\mathfrak{D}$ given in their Table 1 are too low by about a factor of $\sqrt{2}$ (i.e., an error in the opposite direction from the error in the formula). Correspondence with one of the authors (*14*) has indicated that they got their measured coefficients (i.e., the numerical values listed under $\mathfrak{D}_{expt.}$) by forcing agreement between their (incorrect) theoretical values and the measured values at low pressures; it is their feeling that the agreement with the dense gas theory is as indicated in their original publication.

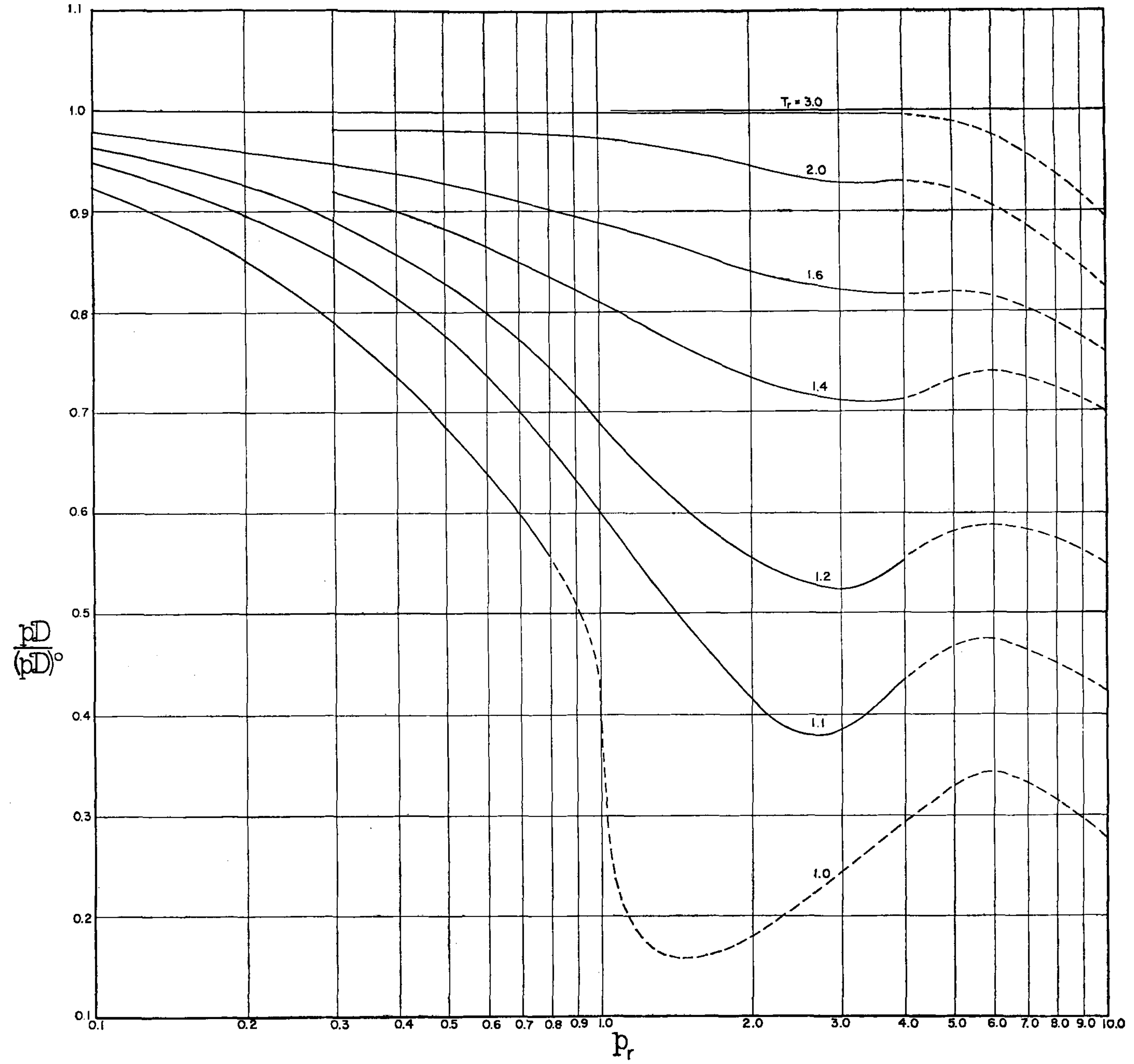

Fig. 1. Generalized chart for the coefficient of self-diffusion of gases at high densities.

it is known that the vibrational and rotational motions of molecules have to be taken into account in calculations involving energy transfer.

A chart for the prediction of self-diffusion coefficients in dense gases may be prepared in a similar way. Equation (12) may be written in a more convenient form[d]:

$$p\mathfrak{D}/(p\mathfrak{D})^0 = (\tfrac{2}{3})\pi n\sigma^3(Z/y) \qquad (15)$$

Division of Equation (15) by Equation (10) then gives:

$$p\mathfrak{D}/(p\mathfrak{D})^0 = (\mu/\mu^0)Z(1 + 0.8y + 0.761y^2)^{-1} \qquad (16)$$

Equation (14) may be expressed in terms of the reduced equation of state $Z = Z(p_r, T_r)$ thus:

$$y = Z\,\frac{1 + (\partial \ln Z/\partial \ln T_r)_{p_r}}{1 - (\partial \ln Z/\partial \ln p_r)_{T_r}} - 1 \qquad (17)$$

Hence to prepare a chart of $p\mathfrak{D}/(p\mathfrak{D})^0$ as a function of reduced temperature ($T_r = T/T_c$) and reduced pressure ($p_r = p/p_c$), one needs Z, the temperature and pressure derivatives of Z, and the ratio μ/μ^0. Figure 1 was prepared in this manner. The compressibility factor Z was taken from the tables of Lyderson, Greenkorn, and Hougen (*35*, *18*) for $Z_c = 0.27$. For most substances Z_c lies in the range from 0.25 to 0.29.) Large-scale plots of these Z data were made, and the temperature and pressure derivatives of Z were determined graphically. The ratios of μ/μ^0 were determined from the charts of Carr, Parent, and Peck (*9*) and from the chart of Comings, Mayland, and Egly (*12*).

In the use of Figure 1 for the estimation of the diffusion coefficients of dense gases, $(p\mathfrak{D})^0$ may be found from the Lennard-Jones (6-12) calculations (*24*, *3*). For larger molecules and for polar molecules Equations (4) and (9) can be used.

The experimental data of O'Hern and Martin (*39*) for the system $CO_2 - C^{14}O_2$ ($1.0 < T_r < 1.3$, $0.1 < p_r < 3.0$) were compared with values calculated from Figure 1 and Equation (4); the average error in the calculated values was 11%. For the data of Robb and Drickamer (*40*) and of Timmerhaus and Drickamer (*46*) for the system $CO_2 - C^{14}O_2$ (1.003 <

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[d] $\frac{n\mathfrak{D}}{(n\mathfrak{D})^0} = \frac{pN_\mathfrak{D}/ZRT}{(pN_\mathfrak{D}/RT)^0} = \frac{p\mathfrak{D}/Z}{(p\mathfrak{D})^0}$

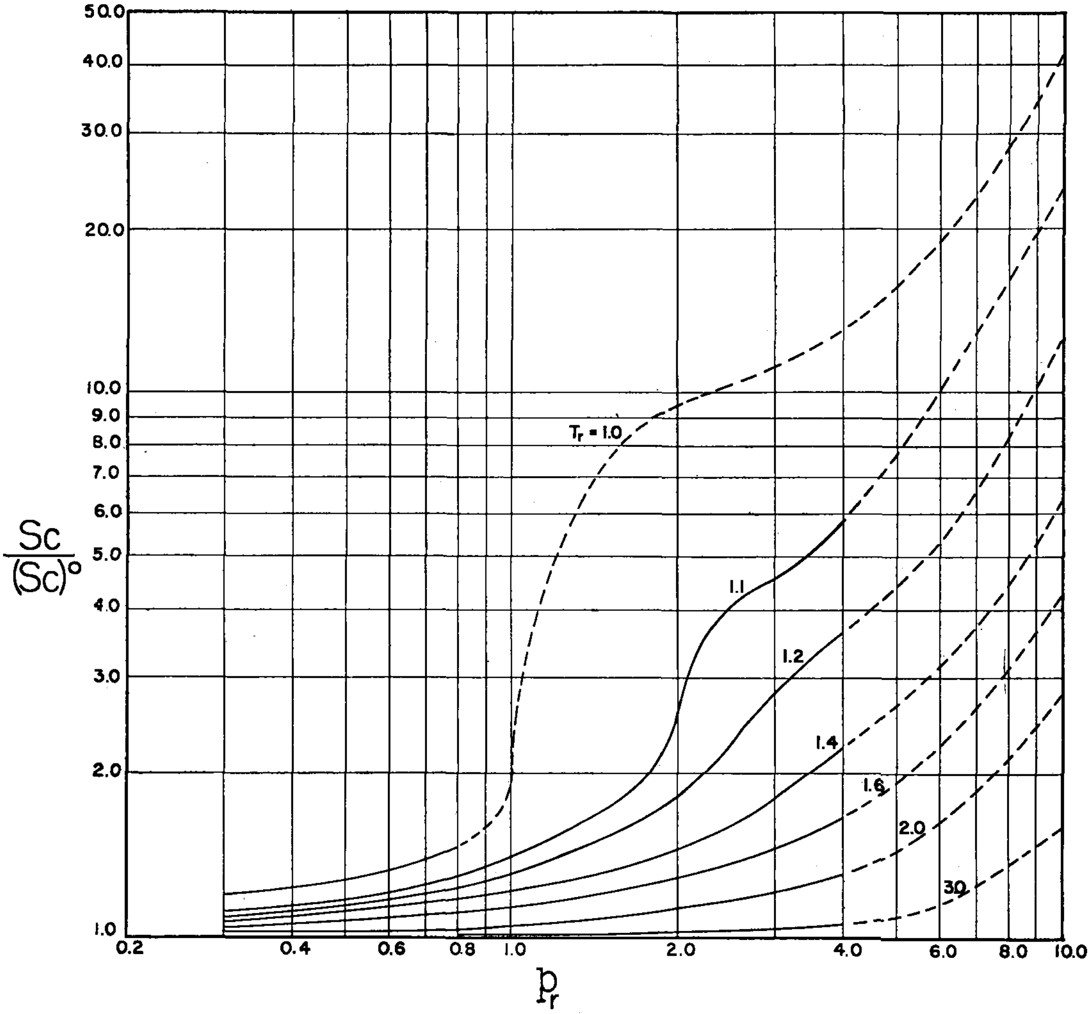

Fig. 2. Generalized chart for the Schmidt number of isotopic mixtures of gases at high densities.

$T_r < 1.05$, $0.1 < p_r < 8$) the average error was 44%. For the data of Jeffries and Drickamer (*28*) for the system $CH_4 - CH_3T$ ($1.4 < T_r < 1.7$, $0.4 < p_r < 6.5$) the average error was 99%. Possible errors in the work of Drickamer and his co-workers are discussed by O'Hern and Martin (*39*).[e]

O'Hern and Martin (*39*) also compared their data with Enskog's theory, using Equation (14) to calculate y as suggested by Enskog. They used experimental *p-V-T* data rather than generalized tables as were used above; however, they concluded that the calculated results were in error by about 33%, rather than the 11% as found here.

A chart of reduced Schmidt number, Sc/(Sc)°, can be prepared from Figure 1, since

$$\mathrm{Sc}/(\mathrm{Sc})^0 = \frac{(\mu/\mu^0)Z}{p\mathcal{D}/(p\mathcal{D})^0} \qquad (18)$$

Figure 2 was prepared in this manner.

It is possible to prepare a chart similar to Figure 1 with experimental viscosity and equation-of-state data in Equations (14) and (16). Such a chart was prepared by one of the authors (*43*); the same viscosity and equation of state data were used as were employed by Comings and Nathan (*11*) in preparing their chart of thermal conductivity. However, the authors do not feel the chart which resulted is as accurate as Figure 1.

Self-diffusion is a limiting case of binary-diffusion; binary-diffusion is more interesting from a practical standpoint. There are three possibilities which should be investigated with regards to the prediction of binary-diffusion coefficients in dense gases.

1) When more binary-diffusion data in dense gases become available, the possibility of using "pseudocritical" constants (*25*) should be investigated. Pseudocritical constants have been applied with reasonable success to the prediction of the viscosity of dense-gas mixtures (*9*). Comings (*13*) warns however, that this method leads "to serious inaccuracies for mixtures which are dissimilar chemically or when there is a large difference in the critical temperatures of the components." Further, Comings states that the pseudocritical rule can not be applied to the prediction of thermal conductivity in dense gases.

2) Thorne (*44*)[f] has extended Enskog's kinetic theory of dense gases to cover the case of binary-diffusion; to the authors' knowledge this work has never been verified experimentally. It may be possible to use Thorne's work as the basis for a generalized scheme for the prediction of binary-diffusion coefficients, similar to Figure 1.

3) In future high density experimental work, the relative merits in using diffusion coefficients defined for a) concentration "driving-forces" ($\mathcal{D}_{AB}'$) and b) activity "driving-forces" ($\mathcal{D}_{AB}$) should be explored. It is possible that diffusion coefficients defined for activity "driving-forces" may be better correlated.

CONCLUSIONS

1. Equations (4) and (9) are easy to use; the power-law temperature dependence is sufficiently accurate for many engineering calculations.
2. Figure 1 is at the present time the best available means to predict the temperature and pressure dependence of the self-diffusion coefficient of dense gases.

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[e] The average errors are the averages of the absolute errors in each case.

Table 3, giving a detailed comparison of calculated and experimental self-diffusion coefficients in dense gases has been deposited as document 5570 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or $1.25 for 35-mm. microfilm.

[f] Thorne's (*44*) definition of the binary diffusion coefficient does *not* agree with that defined in Equations (1) and (2), although *for the limiting case* of self-diffusion in dense gases both Thorne's expression and Equation (1) simplify to:

$$j_A = -\rho\mathcal{D}\,\nabla x_A \qquad (19)$$

3. There is a question concerning the dotted region above $p_r = 4$ in Figure 1; it is impossible to say whether the bumps in these curves are real or whether they are the result of errors in the viscosity chart, in the compressibility chart, or in the derivatives of the compressibility obtained graphically. Experimental data are needed to define the true shape of these curves. This chart may be useful to experimentalists in defining the most interesting ranges of temperature and pressure to study. Existing data cover only a small portion of this chart.
4. There are not at present enough high density binary-diffusion coefficient data to test the use of pseudocritical constants with Figure 1.

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NOTATION

a_A = activity of substance A
c = molar density, moles cm.$^{-3}$
$\mathfrak{D}$ = self-diffusion coefficient, cm.^{2} sec.$^{-1}$
$\mathfrak{D}_{AB}$ = binary-diffusion coefficient, cm.^{2} sec.$^{-1}$
j_A = mass flux of A, g. cm.$^{-2}$ sec.$^{-1}$, with respect to the local mass average velocity of the fluid system
k = thermal conductivity, cal. cm.$^{-1}$ sec.$^{-1}$°K^{-1}
m = mass of a molecule
M = molecular weight
n = number of molecules per unit volume
N = Avogadro number
p = pressure, atm.
R = gas law constant
T = temperature, °K
V = molar volume, cm^3 mole^{-1}
x_A = mole fraction of A
Z = compressibility factor = pV/RT
Sc = Schmidt number = $\mu/\rho\mathfrak{D}$
κ = Boltzmann constant = R/N
μ = viscosity, dyne sec. cm.$^{-2}$
ρ = density, g. cm.$^{-3}$
σ = diameter of rigid sphere molecule
Φ_A = mass flux of A, moles cm.$^{-2}$ sec.$^{-1}$, with respect to the molar average velocity of the system
$\varphi_{AA}(r)$ = intermolecular potential energy function

Subscripts

c = critical value of property
R = reduced quantity (not dimensionless)
r = property divided by its critical value (dimensionless)

Superscript

0 = low pressure value of property

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