The Self-Diffusivity of Substances in the Gaseous and Liquid States

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Relationships applicable for the prediction of self-diffusivities of gases and liquids have been developed from available experimental values and an application of dimensional analysis. Separate relationships were found to apply for gases at normal pressures and for gases at elevated pressures. *For the liquid state a different dependence on the conditions of temperature* and pressure was observed and was taken into account to develop the relationship for this state of aggregation.

Theoretical relationships for the transport properties of fluids have received considerable attention in the last 50 yr. For gases at moderate pressures, expressions derived from kinetic theory can be used to calculate the transport properties with sufficient accuracy. Generalized relationships for the calculation of these properties have recently been developed (*12, 27, 36, 37*), and they offer a sound alternative to the somewhat involved theoretical relationships of Chapman and Enskog (*7, 16*). Such relationships have been developed from existing data for the viscosity (*36, 37*) and the thermal conductivity (*27*) of gases at normal pressures.

The generalized dimensional approach can be extended to consider the transport properties of dense gases and liquids. So far, the application of kinetic theory principles to a gas at high pressures has not succeeded in producing expressions that adequately describe its behavior (*7, 16*). Along these lines, Enskog (*11*) in 1922 published what can be considered the best theoretical approach to date. The Enskog treatment, however, is limited by the assumption that the gas is composed of rigid spheres. Attempts to overcome this limitation have been advanced from statistical mechanical concepts by Rice, Kirkwood, Ross, and Zwanzig (*31*), and Snider and Curtiss (*35*). Unfortunately, these more recent treatments do not yield expressions that exhibit a definite improvement over that advanced by Enskog (*11*).

The application of a dimensional analysis approach to available high-pressure data offers a more direct means for establishing the dependence of a transport property on the conditions of the systems. Such an approach has been successfully applied for the prediction of viscosity (*19, 39*) and thermal conductivity (*38*) of gases at high pressures and also for the liquid state. Following this line of reasoning, it should be possible to develop a generalized method capable of defining the self-diffusivity of gases at normal and elevated pressures and of liquids as well. The difficulty of obtaining reliable self-diffusivity measurements has contributed largely to the present lack of a dependable method capable of predicting this transport property in the dense gaseous and liquid states. However, the recent experimental contributions of Durbin (*10*), Naghizahdeh and Rice (*28*), Becker, Vogell, and Zigan (*2*), and O'Hern and Martin (*30*) have produced sufficient reliable self-diffusivities to make possible the development of a generalized method for predicting this transport property.

SELF-DIFFUSIVITY AT NORMAL PRESSURES

Self-diffusivity is an idealized quantity that can be approximated experimentally by the interdiffusion of isotopic forms of a gas or a liquid and is of importance as one of the fundamental physical properties of substances. It is also conceivable that a procedure of establishing the self-diffusivity can be extended to a method capable of predicting the diffusivity of a substance in a multicomponent system.

Rigorous kinetic theory for monatomic gases yields expressions for the various transport coefficients in terms of a set of integrals. Thus, the self-diffusion coefficient can be expressed as

$$\mathcal{D}_{11} = 262.80 \times 10^{-5} \frac{\sqrt{T^3/M}}{\pi\sigma^2\Omega^{(1,1)*}(T^*)} \qquad (1)$$

where $\Omega^{(1,1)*}(T^*)$ is the collision integral which depends on the force law for the molecular interaction. From Equation (1), and the assumption that the self-diffusivity of a substance is a function of its critical constants, molecular weight, and temperature for pressures close to 1 atm., it follows that

$$(\pi\mathcal{D}_{11})^* = f(T_c,\ P_c, v_c, M, T, R) \qquad (2)$$

or that

$$(\pi\mathcal{D}_{11})^* = \alpha T_c^{\,a} P_c^{\,b} v_c^{\,c} M^d T^e R^f \qquad (3)$$

A dimensional analysis treatment of Equation (3) yields

$$(\pi\mathcal{D}_{11})^*\,\delta = \alpha' T_R^{\,m} z_c^{\,n} \qquad (4)$$

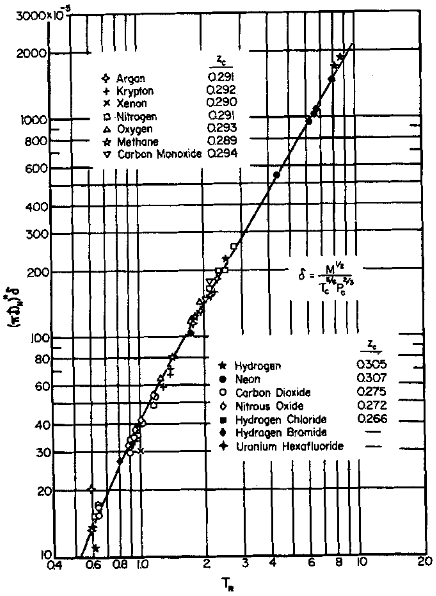

Fig. 1. Relationship between $(\pi D_{11})^*\delta$ and T_R for pure substances at normal pressures.

where $\delta = M^{1/2}/T_c^{5/6}P_c^{2/3}$. The modulus δ is similar to one used by Slattery and Bird (*34*) in their development of a relationship for diffusion coefficients. However, Slattery and Bird (*34*) treat self-diffusivity together with the diffusivity in binary systems and also do not differentiate between polar and nonpolar gases. In addition, their treatment does not include the effect of z_c, the critical compressibility factor.

The self-diffusivities available in the literature for fourteen substances have been used to establish α' and the exponents m and n of Equation (4). The substances examined include monatomic and diatomic gases (*3, 13, 14, 15, 17, 33, 43, 44, 46*), carbon dioxide (*1, 3, 42, 44, 45, 46*), nitrous oxide (*1, 3*), methane (*44*), hydrogen chloride (*4*), hydrogen bromide (*4*), and uranium hexafluoride (*29*), and present a spectrum of values that range from $z_c = 0.266$ for hydrogen chloride to $z_c = 0.307$ for neon. For these substances, the dependence of $(\pi\mathcal{D})^*\delta$ on T_R is presented in Figure 1. From this figure, it is apparent that the effect of z_c on $(\pi\mathcal{D})^*\delta$ is insignificant, and therefore exponent $n = 0$. The relationships of Figure 1 can be expressed analytically as follows:

$$(\pi\mathcal{D}_{11})^*\delta = 44.0 \times 10^{-5}\, T_R^{1.716} \quad \text{for } T_R > 1.5 \qquad (5)$$

$$(\pi\mathcal{D}_{11})^*\delta = 2.427 \times 10^{-5}\, [7.907\, T_R - 1.66]^{1.333} \quad \text{for } T_R < 1.5 \qquad (6)$$

SELF-DIFFUSIVITY OF DENSE GASES AND LIQUIDS

An approach different from that utilized previously for the viscosity (*19, 39*) and thermal conductivity (*38*) of dense gases and liquids is required for the correlation of self-diffusivity. The residual approach cannot be applied to self-diffusivity, because the isothermal relationships of $(\pi\mathcal{D}_{11})$ vs. ρ_R, the reduced density, are not parallel for the entire range of density (*24, 25*). Despite this fact, Kennedy and Thodos (*20*) used the residual self-diffusivities $(\pi\mathcal{D}_{11})^* - (\pi\mathcal{D}_{11})$ for carbon dioxide to develop a reduced state correlation between $\pi\mathcal{D}_{11}/P_c\mathcal{D}_c$ and reduced temperature for lines of constant reduced pressure. Kennedy and Thodos found that their method reproduced the experimental self-diffusivities for carbon dioxide in the dense gaseous state with reasonable accuracy. For the liquid region, for which no experimental values were available, they utilized the modified form of the Einstein-Stokes equation, as suggested by Li and Chang (*22*):

$$\frac{\mathcal{D}_{11}\mu}{\kappa T} = \frac{1}{2\pi}\left(\frac{N}{v}\right)^{1/3} \qquad (7)$$

Slattery and Bird (*34*) used the Enskog relationships for the viscosity and self-diffusivity to obtain an expression for the ratio $\pi\mathcal{D}_{11}/(\pi\mathcal{D}_{11})^*$ in terms of the viscosity ratio μ/μ^*. For the Enskog modulus $b\rho\chi$, they utilized the expression defined in terms of the generalized compressibility factor z:

$$b\rho\chi = z\,\frac{1 + \left(\dfrac{\partial \ln z}{\partial \ln T_R}\right)_{P_R}}{1 - \left(\dfrac{\partial \ln z}{\partial \ln P_R}\right)_{T_R}} - 1 \qquad (8)$$

The values of z were obtained by them from the compilation of Lydersen, Greenkorn, and Hougen (*23*). Ratios of μ/μ^* were established from the correlations of Carr, Parent, and Peck (*6*) and Comings, Mayland, and Egly (*8*). Using these relationships, Slattery and Bird (*34*) developed a correlation between the ratio $\pi\mathcal{D}_{11}/(\pi\mathcal{D}_{11})^*$ for reduced temperatures up to $T_R = 3.0$ and reduced pressures up to $P_R = 10$. Their final correlation was tested with the experimental values reported by O'Hern and Martin (*30*) and Drickamer and co-workers (*32, 40, 41*). The deviations from the data of O'Hern and Martin were found to be within 11%, while those from the data of Drickamer et al. were much higher.

It is apparent from these treatments that so far no attempt has been made to correlate self-diffusivity in a manner that does not depend on the related transport properties like viscosity and which at the same time takes into account the characteristic features of this quantity. This investigation was therefore undertaken with the objective of developing a correlation for this transport property that would satisfy these requirements. Since the self-diffusivity of dense fluids is a function of both temperature and pressure, the dependence of this property for elevated pressures can be expressed in the following manner:

$$\mathcal{D}_{11} = f(T, v, T_c, P_c, v_c, M, R) \qquad (9)$$

or

$$\mathcal{D}_{11} = \gamma\, T^a v^b T_c^{\,c} P_c^{\,d} v_c^{\,e} M^f R^g \qquad (10)$$

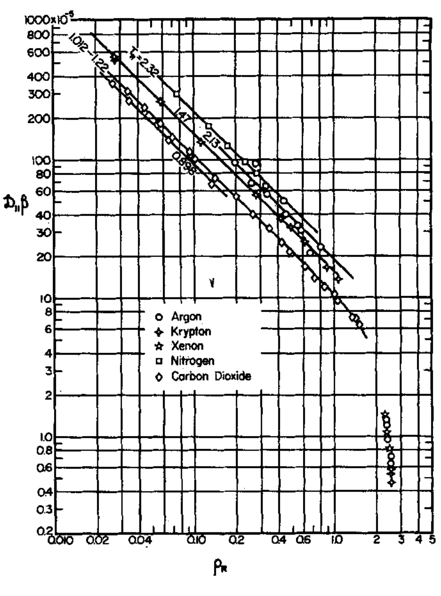

Fig. 2. Relationship between $D_{11}\ \beta$ and ρ_R for dense gases and liquids.

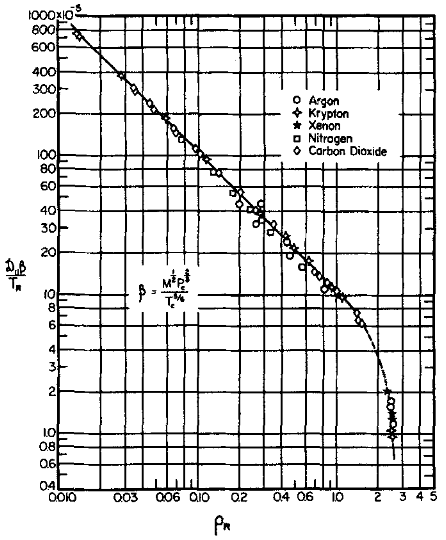

Fig. 3. Relationship between $D_{11}\ \beta/T_R$ and ρ_R for the gaseous and liquid states.

A dimensional analysis of Equation (10) yields the following:

$$\mathcal{D}_{11}\beta = \gamma' \, T_R^{\,p} \, \rho_R^{\,q} \tag{11}$$

To determine the constants of Equation (11), one approach will be to establish the behavior of $\mathcal{D}_{11}\beta$ with respect to one of the variables T_R or ρ_R, while the other is held constant. Experimental self-diffusivities presented in the literature for gaseous argon (*26*), krypton (*10*), nitrogen (*2*), and carbon dioxide (*30*), and liquid argon (*28*), krypton (*28*), and xenon (*28*) were used to establish the dependence of the modulus $\mathcal{D}_{11}\beta$ on reduced temperature and reduced density. The relationships between $\mathcal{D}_{11}\beta$ and ρ_R for these substances are presented in Figure 2. Reduced densities for the gaseous and liquid states were obtained from the compiled reduced state correlation for argon (*9*), krypton (*9*), nitrogen (*5*), and carbon dioxide (*21*). For the gaseous state the resulting isotherms are parallel with a slope of approximately −1. For the liquid state the values of $\mathcal{D}_{11}\beta$ follow a different pattern, and consequently it is to be expected that the relationship for the liquid state will be different from that of the gaseous state.

The experimental self-diffusivities of Robb and Drickamer (*32*) and Timmerhaus and Drickamer (*40, 41*) on carbon dioxide did not follow the pattern exhibited by the data of the other investigators, and consequently their values have not been included in Figure 2. This behavior was also encountered by Slattery and Bird (*34*), and the possible errors in the work of Drickamer and co-workers are discussed by O'Hern and Martin (*30*). For methane, the data of Jeffries and Drickamer (*18*) have been shown to contain a computational error (*34*), and therefore these values were also excluded. The recent data of Naghizahdeh and Rice (*28*) for liquid methane were obtained from the binary systems CH_4-CHD_3 and CH_4-CD_4, for which the difference in molecular weights of the two species is significant enough to consider the reported values as mutual diffusivities rather than self-diffusivities. For this reason these values have also been excluded from Figure 2.

A cross plot of the modulus $\mathcal{D}_{11}\beta$ vs. T_R on log-log coordinates for the gaseous state at $\rho_R = 0.10$, 0.20, 0.40, and 1.00 produced parallel lines of slope one. This behavior suggests that the exponent p of Equation (11) is $p = 1.0$, and therefore the quantity $\mathcal{D}_{11}\beta/T_R$ should be a unique function of density. In Figure 3 are presented values of $\mathcal{D}_{11}\beta/T_R$ and ρ_R for each of the substances of Figure 2. In this figure the self-diffusivities for the liquid state have also been included. The relationship of Figure 3 for the gaseous state is unique and linear with a slope of −1. This relationship can be expressed analytically as follows:

$$\frac{\mathcal{D}_{11}\beta}{T_R} = \frac{10.7 \times 10^{-5}}{\rho_R} \tag{12}$$

or

$$\mathcal{D}_{11}\beta\rho_R = 10.7 \times 10^{-5}\, T_R \tag{13}$$

Equation (13) represents the experimental values very accurately up to $\rho_R = 0.15$ and up to $\rho_R = 1.5$ with an accuracy that is comparable to the precision of the experimental data. In Figure 3 the values for the gaseous and liquid states can be blended together by a smooth curve from $\rho_R = 1.00$. However, it is apparent from this figure that the self-diffusivities for liquids are not properly described by the variables $\mathcal{D}_{11}\beta/T_R$ vs. ρ_R. The slope of the relationship representing the liquid points on this plot is much too high to permit a realistic correlation for this state.

The nature of the correlation of Figure 2 indicates that reduced density is not a convenient variable to utilize with self-diffusivities for the liquid state. Liquid diffusivities are rather strongly dependent on temperature and only weakly on pressure. Therefore, it is anticipated that the dependence of diffusivities for the liquid state can be expressed as

$$\mathcal{D}_{11} = f(T, P, T_c, P_c, v_c, M, R) \tag{14}$$

or

$$\mathcal{D}_{11} = \epsilon\, T^a P^b T_c^{\,c} P_c^{\,d} v_c^{\,e} M^f R^g \tag{15}$$

A dimensional analysis of Equation (15) produces the following:

$$\mathcal{D}_{11}\beta = \epsilon' \, T_R^{\,t} \, P_R^{\,u} \tag{16}$$

The procedure for establishing the exponents of Equation (16) is identical to that employed for the gaseous state. A plot of $\mathcal{D}_{11}\beta$ vs. T_R for lines of constant reduced pressure produced on log-log coordinates linear relationships with an average slope of $t = 3.5$. Therefore, the group $\mathcal{D}_{11}\beta/T_R^{3.5}$ was next plotted against P_R to produce the relationship of Figure 4. This relationship can be expressed analytically as follows:

$$\frac{\mathcal{D}_{11}\beta}{T_R^{\,3.5}} = 3.67 \times 10^{-5}\, P_R^{\,-0.10} \tag{17}$$

or

$$\mathcal{D}_{11}\beta = 3.67 \times 10^{-5} \frac{T_R^{\,3.5}}{P_R^{\,0.10}} \tag{18}$$

Self-diffusivities calculated with Equation (18) have been compared with the experimental values of argon, krypton, and xenon in the liquid state to produce average deviations of 5.94% for twenty-seven argon points, 4.06% for nineteen krypton points, and 12.40% for thirteen xenon points. The overall average deviation for argon, krypton, and xenon is 6.76%.

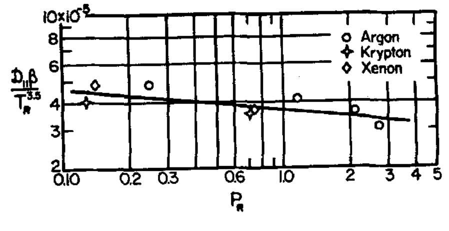

Fig. 4. Relationship between $D_{11}\ \beta/T_R^{3.5}$ and P_R for the liquid state.

CONCLUSIONS

A comprehensive analysis of self-diffusivities for the gaseous and liquid states has produced generalized relationships capable of predicting this transport property under moderate conditions of temperature and varied conditions of pressure for pure substances of a relatively simple molecular structure. Separate relationships have resulted for gases at normal pressures, for gases at elevated pressures, and for the liquid state. These relationships are summarized as follows:

Normal pressures: $$(\pi\mathcal{D}_{11})^*\delta = 44.0 \times 10^{-5}\, T_R^{1.716} \quad \text{for } T_R \geqq 1.5 \tag{5}$$

$$(\pi\mathcal{D}_{11})^*\delta = 2.427 \times 10^{-5}\, [7.907\, T_R - 1.66]^{1.538} \quad \text{for } T_R < 1.5 \tag{6}$$

Elevated pressures: $$\mathcal{D}_{11}\beta\rho_R = 10.7 \times 10^{-5}\, T_R \quad \text{for } \rho_R \leqq 1.5 \tag{13}$$

Liquid state: $$\mathcal{D}_{11}\beta = 3.67 \times 10^{-5} \frac{T_R^{3.5}}{P_R^{0.10}} \tag{18}$$

NOTATION

b = second virial coefficient for rigid spheres, $2\pi N\sigma^3/3$
m = exponent, Equation (4)
M = molecular weight
n = exponent, Equation (4)
N = Avogadro's number, 6.023×10^{23} molecules/g.-mole
p = exponent, Equation (11)
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
q = exponent, Equation (11)
R = gas constant
T = temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v = molar volume, cc./g.-mole
v_c = critical volume, cc./g.-mole
z = compressibility factor, Pv/RT
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α = constant, Equation (3)
β = self-diffusivity modulus, $M^{1/2}P_c^{1/3}/T_c^{5/6}$
γ = constant, Equation (10)
δ = self-diffusivity modulus, $M^{1/2}/P_c^{2/3}T_c^{5/6}$
$\mathcal{D}_{11}$ = self-diffusivity, sq. cm./sec.
$\mathcal{D}_c$ = self-diffusivity at critical point, sq. cm./sec.
ϵ = constant, Equation (15)
μ = viscosity, g./sec. cm.
μ^* = viscosity of gas at atmospheric pressure, g./sec. cm.
π = pressure, atm.
π = constant, 3.1416
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c
σ = collision diameter, cm.
$\Omega^{(1,1)*}(T^*)$ = reduced collision integral
χ = probability of collisions

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