

Estimating Diffusion Coefficients of Dense Fluids

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A simple and generalized correlation in terms of viscosity and molar density is proposed to estimate diffusion coefficients for hydrocarbon systems. The correlation can be used for both gases and liquids up to a pressure of about 400 bar (6000 psia). It has been shown that the proposed method may also be used to estimate effective diffusion coefficients in multicomponent systems with a reasonable degree of accuracy. Although the proposed correlation is based on experimental data in hydrocarbon systems, preliminary evaluations have shown that it is also satisfactory for non-hydrocarbon systems as well. The proposed equation predicts diffusion coefficients in gases with an absolute average deviation of 8% and in liquid systems with an absolute average deviation of 15%. The input parameters for the correlation are molecular weight, critical properties, and acentric factor of components in the system; mixture molar density; low-pressure gas viscosity; and actual viscosity. The last three properties may be predicted from appropriate correlations.

Introduction

The diffusion coefficient is an important transport property in mass-transfer calculations. Although in the past few decades many correlations and procedures have been developed for estimation of viscosity and thermal conductivity in various systems, less attention has been given to the prediction of diffusion coefficients at high pressures. This is mainly because of the difficulty in measuring diffusivity, especially in liquid systems, and reported values are not of high accuracy.

Gas injection (hydrocarbon, nitrogen, or carbon dioxide) into oil and condensate reservoirs may be attempted to recover more in situ hydrocarbons. In some cases, particularly in naturally fractured reservoirs, there has been a need for information on the rate and amount of mass transfer by diffusion. The most important property, to obtain such information, is the diffusion coefficient at reservoir conditions.

As for viscosity and thermal conductivity, kinetic theory has been shown to be adequate for estimation of molecular diffusion coefficients in low-pressure gases through Chapman-Enskog theory (Hirschfelder et al., 1954). For low-pressure liquid systems, empirical correlations are used, based on the Stokes-Einstein equation in which diffusivity and solvent viscosity are inversely related. Perhaps the most used method for liquid diffusion coefficients is the Wilke-Chang (1955) equation. Diffusivities in liquids at moderate pressures are on the order of 10^4 – 10^5 times lower than those in gases. This ratio at higher pressures reduces to less than 10 for near-critical systems.

For high-pressure systems, most theoretically based correlations fail to perform properly, and for this reason empirical correlations have been developed. From kinetic theory of gases, at low and moderate pressures, binary diffusion coefficients in gaseous systems vary inversely with pressure or density and they are independent of composition. However, this is not so at high pressures, where the gas phase may deviate significantly from an ideal gas.

In 1958, Slattery and Bird developed a chart for calculation of self-diffusion coefficients of dense gases. In their chart, reduced diffusivity, $PD/(PD)^\circ$, is correlated

to reduced temperature and pressure. The chart extends to a reduced pressure of 4 and is based on few experimental data. Later this chart was recommended in the APT Technical Data Book (1977) for estimation of binary diffusion coefficients of dense hydrocarbon systems. Mathur and Thodos (1965) developed a generalized correlation for the self-diffusivity of substances in the gaseous state and liquid state in terms of reduced density and reduced temperature. Their correlation is also based on data of only a few compounds.

Dawson et al. (1970), on the basis of the self-diffusion coefficient of methane, correlated high pressure diffusivity to reduced density in the following form:

$$\rho D/(\rho D)^\circ = a + b\rho_r + c\rho_r^2 + d\rho_r^3 \quad (1)$$

where $(\rho D)^\circ$ is the low-pressure (density) value of the density-diffusivity product estimated from Chapman-Enskog theory.

Takahashi (1974) redeveloped the Slattery and Bird chart using more data and including binary diffusivity data available in the literature. This method is also included in the Data Prediction Manual, DIPPR (Danner and Daubert, 1986).

Sigmund (1976) reported some experimental data on binary diffusion coefficients of dense hydrocarbons and for the first time combined liquid binary diffusivities with those of gases in the same form proposed by Dawson-Khoury-Kobayashi (eq 1) in terms of reduced density. Sigmund's correlation found practical applications in mass-transfer calculations in reservoir systems because it was claimed by the author that it could be used for both liquid and gaseous systems at high pressures. However, most data used in his correlation for liquid systems were at atmospheric pressure. He reported absolute average deviations of 40% for liquid diffusivities and 10% for gas diffusivities with his correlation. Although Sigmund's correlation is the most convenient correlation available in the literature for estimating high-pressure diffusivities for dense gases, for high-pressure liquid systems it grossly overpredicts values, particularly for systems in which a gas is dissolved in liquid hydrocarbons at high pressures. His correlation is valid only to a reduced density of 3, while according to his recommended method of obtaining reduced density (use of the Prausnitz and Chueh (1968) method for binary mixture critical volume) values of reduced densities of greater than 4 (especially for reservoir oils) can be obtained in practical calculations.

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The greatest disadvantage of eq 1 is its inability to predict accurate diffusion coefficients of liquids. Equation 1, with coefficients obtained from Sigmund (1976), predicts diffusivities of gases dissolved in liquid hydrocarbons at high pressures, 80–100% higher than reported experimental values. The graph of reduced diffusivity versus reduced density shows a drastic reduction in reduced diffusivity, $\rho D/(\rho D)^\circ$, when reduced density increases from 2 to 3. Therefore, a slight change in density causes a much higher deviation for predicted diffusivities in liquid systems. This high dependency of diffusivity on density becomes more important when predicted values of densities are being used. Extrapolation of Sigmund's correlation shows that diffusivity approaches zero at a reduced density of about 3.5, which is not true for reservoir oils.

Most of the methods and correlations recommended in the literature for estimating diffusion coefficients of dense fluids are based on experimental data which sometimes differ for a given system by more than 100% from one source to another. For example, Sigmund (1976) reports $30 \times 10^{-9} \text{ m}^2/\text{s}$ for C_1 – C_3 at 311 K (100 °F) and 73.7 bar (1069 psia), while Graue (1965) reports $7 \times 10^{-9} \text{ m}^2/\text{s}$ for the same system under the same conditions. This difference is even greater for the case of liquid systems at high pressures. The concentration dependency of binary diffusion coefficients is much greater for liquid systems than it is for gases. Reported experimental diffusivities for liquids may be considered reliable at very low solute concentrations. Therefore, where the concentration of the diffusing material exceeds 10 mol %, predicted values of diffusion coefficients should be used with caution.

Methods of estimating the effective diffusion coefficient of a component in a multicomponent system are important especially in hydrocarbon systems when a component such as methane is diffusing in a gas or oil mixture containing hundreds of hydrocarbon compounds. Lack of sufficient experimental data on diffusion coefficients in multicomponent systems has limited attempts to develop methods for estimating this important property. Wilke's method (1950), given in the following equation,

$$D_{A-m} = \frac{1 - y_A}{\sum_{i \neq A} y_i / D_{A,i}} \quad (2)$$

is the most commonly used method in the literature for multicomponent gas mixtures. This method is based on the theory of ideal gases and has been tested only at low and moderate pressures. Although this equation has been used for multicomponent liquid mixtures, Holmes et al. (1962) conclude that this method is not reliable for interpreting multicomponent liquid diffusion coefficient data. For multicomponent gas mixtures at high pressures, with behavior similar to liquid systems, eq 2 probably cannot be used and an alternative procedure should be developed.

In this work we attempt to develop a new method for estimating diffusion coefficients of dense gases and liquids for both binary and multicomponent systems.

Generalized Correlation for Predicting Dense Fluid Diffusion Coefficients

In the development of a new correlation for diffusivities of dense gases, several factors were considered: accuracy, simplicity, generality, extrapolability, and availability of input parameters. These goals can be achieved by developing an appropriate correlation for diffusivity in terms of the key and available parameters which influence diffusion coefficients.

In almost all theoretical and empirical correlations for estimating diffusivity in liquid systems, the viscosity of the solvent has been included as the primary parameter. The Stokes–Einstein equation, which is based on Stoke's law (Bird et al., 1960), indicates that diffusion coefficients in liquid systems are inversely proportional to viscosity. Hayduck and Cheng (1971) reported some experimental values for diffusivities in liquid systems. They also give a good review of the relation between diffusivity and solvent viscosity. In addition to the Wilke–Chang (1955) equation, other equations such as those developed by Lusis and Ratcliff (1968) also use solvent viscosity in their correlations for liquid diffusivities. On the basis of the Stokes–Einstein equation, Riazi and Daubert (1980) developed a generalized correlation between diffusion coefficient and viscosity. Hayduck and Cheng (1971) showed that for each diffusing substance the following relation between diffusivity and solvent viscosity exists:

$$D_{AB} = C_1 \mu_B^{C_2} \quad (3)$$

where constants C_1 and C_2 vary from one substance to another. For dilute solutions where experimental diffusivities are more accurate, solvent viscosity is almost the same as solute–solvent mixture viscosity. Holmes et al. (1962) discuss the relation between diffusivity and viscosity of mixed solvents. Wilke (1950) has derived a relationship between mixture viscosity and diffusivity of individual components for gas mixtures at low pressures. His correlation fails at higher pressures where the gas phase deviates from an ideal gas. Perhaps the most common relationship between diffusivity and viscosity is through Schmidt number, which is defined as the ratio of viscosity to density–diffusivity product, $\mu/\rho D$.

At high pressures, the behavior of dense gaseous systems becomes closer to that of liquid systems. Therefore, it is a sound assumption that there must exist a unique and general relation between diffusivity and viscosity for both gaseous and liquid systems. In fact it seems that the degree of deviation of viscosity of mixture from that of the low-pressure value must represent the deviation for that of diffusivity. From such analysis and preliminary investigation of diffusivity data for binary gases, the following relationship between viscosity and diffusivity of gaseous systems was observed:

$$\frac{\rho D}{(\rho D)^\circ} = \left(\frac{\mu}{\mu^\circ} \right)^n \quad (4)$$

where ρ and μ are mixture molar density and viscosity at the conditions of the system, and n is a weak function of pressure and is negative. Both eqs 3 and 4 are based on the Stokes–Einstein formula. The low-pressure density–diffusivity product, $(\rho D)^\circ$, is calculated from the Chapman–Enskog dilute gas theory (Hirschfelder et al., 1954) with molecular parameters estimated from Stiel–Thodos (1962) correlations. These equations are given in Appendix I.

The mixture low-pressure viscosity, μ° , was calculated by the Stiel–Thodos (1961) correlation. Mixture viscosity was calculated by the Jossi et al. (1962) correlation when experimental data were not available. Stiel–Thodos correlations for viscosity of gases at low and high pressures are also given in Appendix I. Experimental data used in deriving eq 4 are summarized in Table I. An evaluation of eq 4 with some experimental data for both gases and liquids is shown in Figure 1.

To generalize eq 4, more liquid diffusivity data were collected and included in the data bank, which is summarized in Table II. In using data for regression of eq 4, it was tried not to include many self-diffusivity or low-

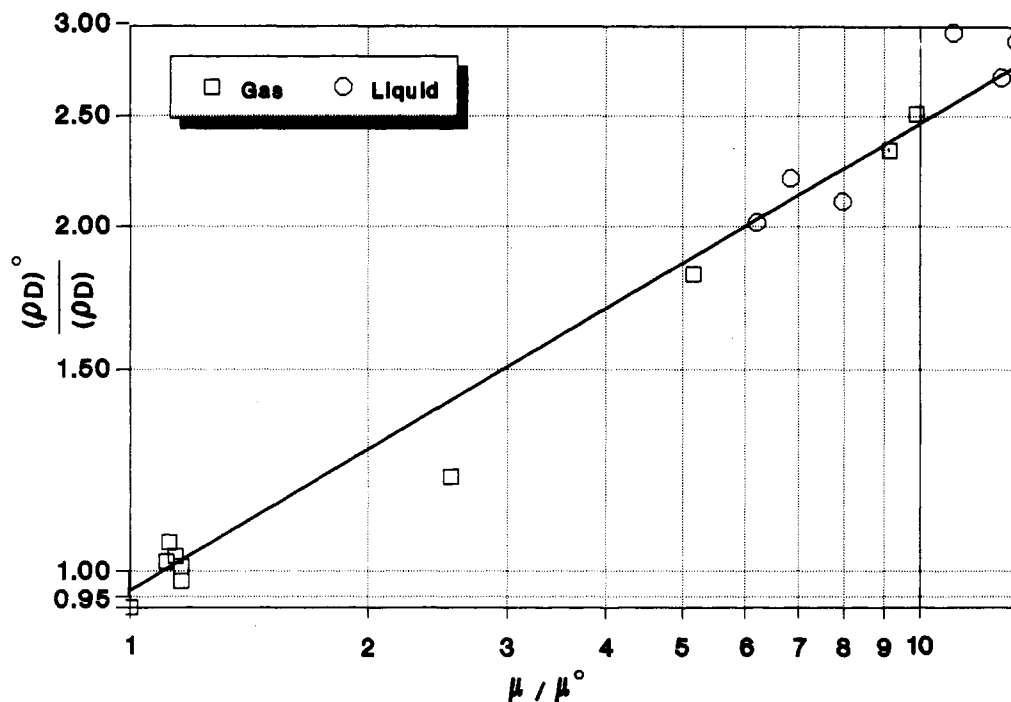


Figure 1. Evaluation of eq 4 with experimental data at 69 bar (1000 psia).

Table I. Data Bank on Diffusion Coefficients of Dense Gases

data group	binary system	mol wt of barrier (heavy comp)	no. of data points	<i>P</i> range, bar	<i>T</i> range, K	viscosity ratio range, μ/μ^0	<i>D</i> 10 ⁸ range, m ² /s	reference
1	C ₁ -C ₃	44	53	14-207	311-378	1-11	1.7-126.7	Sigmund (1976)
2	C ₁ - <i>n</i> -C ₄	58	23	14-174	311-378	1-14.5	1.4-127.5	Sigmund (1976)
3	N ₂ -C ₁	28	23	35-138	313-367	1-5	16-239.8	Sigmund (1976)
4	C ₁ -C ₂	30	11	69-275	313-351	1-5	2.7-24.9	Berry and Koeller (1960)
5	C ₁ -C ₁	16	24	10-416	155-354	1-22	7-57.6	Dawson et al. (1970)
6	N ₂ -C ₂	30	6	7-173	313	1-3	5-37	Berry and Koeller (1960)
overall	N ₂ , C ₁ -C ₄	16-58	140	7-416	155-354	1-14.5	1.4-240	

Table II. Data Bank on Diffusion Coefficients of Dense Liquids

data group	binary system	mol wt of barrier (heavy comp)	no. of data points	<i>P</i> range, bar	<i>T</i> range, K	viscosity ratio range, μ/μ^0	<i>D</i> 10 ⁸ range, m ² /s	reference
1	C ₁ - <i>n</i> -C ₅	72	41	17-155	278-411	7-37	0.97-4.97	Reamer et al. (1956)
2	C ₁ - <i>n</i> -C ₁₁ O	142	36	34-275	278-411	18-134	0.075-1.75	Reamer et al. (1956)
3	n ₂ -oil	340	40	34-310	278-411	60-20000	0.01-0.9	Reamer et al. (1956)
4	C ₁ -oil	72-322	17	20.7	303-333	25-12000	0.07-1.33	Hill and Lacy (1934)
5	C ₈ -oil	160-290	22	2-14	303-333	40-1700	0.05-0.63	Hill and Lacy (1934)
6	CO ₂ -CO ₂	44	7	70-185	274-300	4-7	1-2.0	Robinson and Stewart (1968)
overall	C ₁ , C ₃ , C ₅₊ , CO ₂ , oil	44-340	163	2-310	274-411	4-20000	0.01-5	

pressure diffusivity data so that the resulting correlation would be more accurate for dense and binary systems. However, as will be shown later, the correlation performs quite satisfactorily for those systems not included. On the basis of 283 data points listed in Tables I and II, eq 4 was revised to apply to both gas and liquid systems:

$$\frac{\rho D_{AB}}{(\rho D_{AB})^{\circ}} = a \left(\frac{\mu}{\mu^{\circ}} \right)^{b+cP_r} \quad (5)$$

$$a = 1.07 \quad b = -0.27 - 0.38\omega$$

$$c = -0.05 + 0.1\omega \quad P_r = P/P_c$$

where for a binary system of components A and B with mole fractions of x_A and x_B , pseudocritical properties are given by

$$P_c = x_A P_{c,A} + x_B P_{c,B} \quad (6)$$

$$\omega = x_A \omega_A + x_B \omega_B \quad (7)$$

For most liquid systems listed in Table II, experimental viscosity was available, and for cases where viscosity was unavailable, procedures in Chapter 11 of the API Technical Data Book (1977) were used to estimate the mixture viscosity. Equation 1 was also used with the same data bank of Tables I and II which yielded the following correlation:

$$\rho D / (\rho D)^{\circ} = 1.0644 - 0.1228\rho_r - 0.1118\rho_r^2 + 0.01983\rho_r^3 \quad (8)$$

in which the reduced density is defined as

$$\rho_r = \left(\frac{x_A V_{c,A}^{5/3} + x_B V_{c,B}^{5/3}}{x_A V_{c,A}^{2/3} + x_B V_{c,B}^{2/3}} \right) \rho \quad (9)$$

where V_c is the critical molar volume and ρ is mixture molar density.

Table III. Evaluation of Proposed Correlation for Estimating Diffusion Coefficients of Dense Fluids

data source	phase	no. of data points	AAD % ^a	
			reduced viscosity corrln (eq 5)	reduced density corrln (eq 8)
Table I	gas	140	8.1	10.2
Table II	liquid	143	15.4	48.9
overall		283	11.8	29.8

^a Absolute deviation, % = |(estimated value - experimental value) / experimental value| × 100. Absolute average deviation (AAD) % = (Σ absolute deviation, %) / no. of data points.

An evaluation of eqs 5 and 8 is given in Table III. From these evaluations, it is clear that eq 8 is not applicable to liquid systems. Although data used in the development of eq 5 were in the pressure range 14–416 bar, when eq 5 was tested against data at atmospheric pressure good results were obtained. A summary of such evaluations is given in Table IV. Application of eq 5 to some non-hydrocarbon systems is also shown in Table IV. None of the data given in Table IV were used in the regression of eq 5. The last four data points shown in Table IV for the N₂-C₁ system at 275 bar (271 atm) provided by Hanssen and Stenberg (1987) are higher than the values predicted from eq 5; those authors indicated that their experimental values are higher than values of other investigators by 5–10%.

Table V compares eq 5 with two other methods, Wilke-Chang (1955) and Lusis-Ratcliff (1968) for binary liquid systems at dilute solute solutions. Note that the other methods were specifically developed for the liquid systems at atmospheric pressure. From the results of evaluations, it is clear that eq 5 is quite comparable with other methods and even performs better, even though it was originally developed for high-pressure gas and liquid systems.

Treatment of Ternary and Multicomponent Systems

As mentioned before, the most commonly used method in the literature for calculation of effective diffusion coefficients in multicomponent systems is the method recommended by Wilke (1950), by eq 2. As discussed earlier, this method cannot be applied to liquid systems and also is not valid for high-pressure gas mixtures. For liquid systems several methods are recommended, but the one commonly used is the method of Tang and Himmelblau (1965) for mixed solvents.

Equation 5, developed in this work, can be applied to ternary and multicomponent mixtures by assuming that a multicomponent mixture behaves as a binary mixture. Then, the calculated binary diffusion coefficient may be considered as the effective diffusion coefficient in the mixture. Assume we have a mixture of *N* components and we are interested in calculating the effective diffusion coefficient of one component designated by A in the mixture. All other components in the mixture (excluding A) may be considered as a single pseudocomponent designated by B and therefore the binary diffusion coefficient of A in B would represent the diffusivity of A in the mixture. All properties of B necessary in utilizing eq 5 can be estimated using Kay's mixing rule for property *P_B*:

$$P_B = \sum_{\substack{i=1 \\ i \neq A}}^N x_i P_i / \sum_{\substack{i=1 \\ i \neq A}}^N x_i \quad (10)$$

The equation is used for all properties such as molecular weight, critical pressure, critical temperature, and acentric factor. The mole fraction of pseudocomponent B is simply 1 - *x_A*, and then eq 5 for the binary system can be used.

Table IV. Estimated Diffusion Coefficients from Eq 5 for Binary Systems Not Used in the Regression of Eq 5

no.	components		state of system	<i>T</i> , K	<i>x_A</i> , mole fracn	<i>ρ</i> (expt), kmol/m ³	<i>μ</i> (expt), mPa·s (cP)	10 ⁹ <i>D_{AB}</i> , m ² /s		% dev ^a	reference
	A	B						expt	calcd		
1	C ₁	<i>n</i> -C ₄	gas	293	0 (dilute)	0.0458	0.00727	9900 (1.06) ^b	97030	-1.9	Kestin and Yata (1968)
2	C ₁	<i>n</i> -C ₄	gas	303	0	0.04445	0.007524	10600 (1.07)	10300	-2.8	Kestin and Yata (1968)
3	CO ₂	C ₁	gas	293	0	0.0438	0.0109	16700 (1.06)	16000	-4.2	Kestin and Yata (1968)
4	CO ₂	C ₁	gas	293	0	0.0418	0.01127	17800 (1.05)	17300	-2.8	Kestin and Yata (1968)
5	C ₂	<i>n</i> -C ₆	liq	298	0.032	7.81	0.296	5.79	6.54	12.9	Hayduk and Cheng (1971)
6	C ₂	<i>n</i> -C ₇	liq	298	0.0325	6.798	0.3815	5.44	5.65	3.5	Hayduk and Cheng (1971)
7	C ₂	<i>n</i> -C ₈	liq	298	0.033	6.12	0.498	4.57	4.65	1.7	Hayduk and Cheng (1971)
8	C ₂	<i>n</i> -C ₁₂	liq	298	0.0351	4.3	1.244	2.73	2.31	-15.0	Hayduk and Cheng (1971)
9	C ₂	<i>n</i> -C ₁₆	liq	298	0.0379	3.358	2.64	1.95	1.03	-47.2	Hayduk and Cheng (1971)
10	ethanol	water	liq	288	0	55655	1.145	1.0	0.96	-4	Wilke (1949)
11	CO ₂	H ₂ O	liq	291	0	55.492	1.057	1.71	1.53	-10.5	Wilke (1949)
12	N ₂	H ₂ O	liq	295	0	55.273	0.96	2.02	1.2	3.9	Wilke (1949)
13	chloroform	benzene	liq	288	0	11.458	0.697	2.11	2.22	5.2	Wilke (1949)
14	C ₁	N ₂	gas	314.6	0.542			84 (275)	74	-11.9	Hanssen and Stenberg (1987)
15	C ₁	N ₂	gas	344.6	0.526			104 (275)	93	-10.6	Hanssen and Stenberg (1987)
16	C ₁	N ₂	gas	363.6	0.511			124 (275)	110	-11.3	Hanssen and Stenberg (1987)
17	C ₁	N ₂	gas	393	0.511			140 (275)	131	-6.4	Hanssen and Stenberg (1987)

^a Defined in Table III. ^b Numbers in parentheses indicate pressure (in bar) other than atmospheric pressure. ^c Overall AAD%.

Table V. Comparison of Eq 5 with Other Methods for Binary Liquid Systems at 298 K and 1.013 bar

solute ^a A	solvent B	10 ⁹ <i>D_{AB}</i> (expt), m ² /s	eq 5		Wilke-Chang (1955)		Lusis and Ratcliff (1968)	
			calcd	% dev ^c	calcd	% dev ^c	calcd	% dev ^c
ethane	hexane	5.79	6.54	12.9	6.44	11.2	7.66	32.3
ethane	heptane	5.44	5.63	3.5	5.25	3.5	6.14	12.9
ethane	octane	4.57	4.65	1.7	4.28	6.3	4.95	8.3
ethane	dodecane	2.73	2.32	15.0	1.98	27.5	2.22	18.7
ethane	hexadecane	1.95	1.03	47.2	1.09	44.1	1.11	43.0
overall				16.0		18.5		23.0

^a All solutions are dilute in A (*x_A* ≈ 0). ^b Experimental data from Hayduk and Cheng (1971). ^c Defined in Table III.

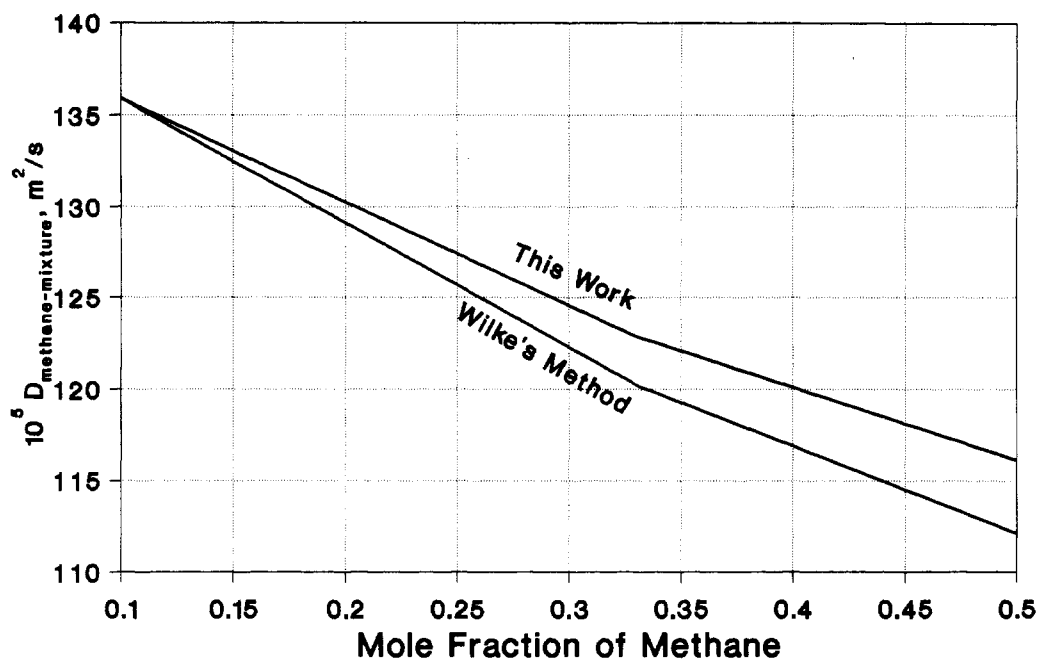


Figure 2. Evaluation of proposed method with Wilke's method for effective diffusion coefficient of CH_4 in mixture of $\text{CH}_4\text{-C}_3\text{H}_8\text{-N}_2$ at 14 bar and 311 K.

Table VI. Estimated Effective Diffusion Coefficient of Methane in Multicomponent Gas Mixture at 14 Bar and 311 K

mixture	mixture composition, mole fraction				estd effective diffusion coeff of methane, $10^8 \text{ m}^2/\text{s}$		
	CH_4	C_3H_8	N_2	$n\text{-C}_4\text{H}_{10}$	Wilke formula, eq 2 ^a	this work, eq 5	absolute dev, ^b %
1	0.5	0.3	0.2	0.0	111.9	116.0	3.7
2	0.1	0.3	0.06	0.0	136.2	135.8	2.9
3	0.05	0.05	0.9	0.0	175.6	166.3	5.8
4	0.333	0.333	0.333	0.0	120.2	123.0	2.3
5	0.25	0.25	0.25	0.25	104.3	104.6	0.3
6	0.05	0.1	0.7	0.15	141.96	134.8	5
7	0.5	0.05	0.4	0.05	151	142.5	5.6
8	0.1	0.05	0.15	0.7	91.4	90.9	0.5
total	0.05-0.5	0.05-0.33	0.15-0.7	0-0.7	91-177	91-166	3.2 ^c

^a In using Wilke's formula, the following binary diffusion coefficients from Sigmund (1976) were used at 14 bar and 311 K: $D_{\text{CH}_4\text{-C}_3\text{H}_8} = 88.3 \times 10^{-8} \text{ m}^2/\text{s}$; $D_{\text{CH}_4\text{-N}_2} = 187 \times 10^{-8} \text{ m}^2/\text{s}$; ρ = molar density of mixture = $0.551 \text{ kmol}/\text{m}^3$. ^b Defined in Table III. ^c AAD%.

Table VII. Application of Eq 5 for Some Ternary Systems

solute A	solvents B	no. of data points	T , K	P , bar	$10^8 D_{AB}$ range, m^2/s	AAD% ^a	data source
benzene	acetone + CCl_4	1	298	1.013	0.284	1.4	Danner and Dauber (1986)
methane	$\text{C}_1 + n\text{-C}_4 + n\text{-C}_{10}$	1	344	300	1.01	1	Hadiatno (1986)
toluene	$n\text{-C}_8 + n\text{-C}_{14}$	6	298	1.013	0.1-0.36	19.8	Holmes et al. (1986)
toluene	$n\text{-C}_8 + \text{cyclohexane}$	3	298	1.013	0.28-0.46	16.2	Holmes et al. (1962)
toluene	cyclohexane + $n\text{-C}_{10}$	3	298	1.013	0.19-0.2	10.1	Holmes et al. (1962)
overall		14	298-344	1-300	0.1-1	14.3	

^a Defined in Table III.

Effective diffusion coefficients calculated using this approach are compared with values obtained from Wilke's formula, eq 2, for some multicomponent gas mixtures at moderate pressures, and the results are given in Table VI. The overall difference between this technique and Wilke's method is about 3%. A graphical comparison is shown in Figure 2.

The proposed method is also evaluated with some experimental data for ternary systems, and results are given in Table VII. In analyzing results presented in Table VII, the first system is a non-hydrocarbon system. Details of this calculation are given in Appendix II. The second sample is from an IFP experiment (Hadiatno, 1986), and is an example for reservoir fluids. In this example, the solvent is a mixture of gas and liquid. Details of this calculation are also given in Appendix II. The last three systems are at atmospheric pressure. Predicted values of

diffusivity from eq 5 for these systems were all below experimental values, and relatively larger errors were observed. One of the main reasons for predicting such low values of diffusivities for these systems is the existence of compounds such as C_{10} and C_{14} . Equation 5 is based on the data given in Tables I and II which are mainly low molecular weight hydrocarbons. Therefore, eq 5 should be applied to heavy hydrocarbons with caution.

Conclusions

Based on the Stokes-Einstein equation, a simple and generalized correlation (eq 5) in terms of viscosity and density has been developed for the purpose of predicting binary diffusion coefficients in hydrocarbon systems for both gases and liquids at conditions ranging from ambient to those likely to be found in hydrocarbon-bearing reservoirs.

The proposed method can be applied to ternary and multicomponent systems for accurate prediction of effective diffusion coefficients.

Preliminary evaluations show that the proposed correlation might also be applicable to non-hydrocarbon fluids; however more experimental data must be included in the correlation for such systems.

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Nomenclature

a, b, c, d = coefficients in polynomial in reduced density (eq 1)
 C_1, C_2 = constants in eq 3
 D = mutual diffusion coefficient
 D_{AB} = binary diffusion coefficient of A in B, m²/s
 $D_{A,m}$ = effective diffusion coefficient of A in multicomponent mixture, m²/s
 M = molecular weight
 P = pressure, bar
 P_c = critical pressure, bar
 T = temperature, K
 T_c = critical temperature, K
 V_c = critical volume, m³/kmol
 x = mole fraction
 y = mole fraction in the gas phase
 Z_c = critical compressibility factor

Greek Letters

ϵ = energy parameter
 μ = viscosity of fluid, mPa·s (cP)
 μ° = low-pressure viscosity, mPa·s (cP)
 ξ = viscosity parameter
 ρ = molar density of fluid, kmol/m³
 σ = Lennard-Jones parameter, m
 Ω = collision integral

Subscripts and Superscripts

A, B = parameter corresponding to component A or B
 c = critical
 i = parameter corresponding to component i
 r = reduced parameter
 $^\circ$ = low-pressure (density) limit
 $*$ = dimensionless parameter

Appendix I

A. Low-Pressure Density-Diffusivity Products. $(\rho D)^\circ$ can be calculated from the following form of the Chapman-Enskog dilute gas theory using the Stiel-Thodos (1962) correlation for the estimation of the molecular parameters. For a binary A and B:

$$(\rho D_{AB})^\circ = \frac{2.2648 \times 10^{-6} T^{0.5} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5}}{\sigma_{AB}^2 \Omega_{AB}} \quad (\text{A-1})$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \quad (\text{A-2})$$

$$\sigma_i = 1.866 V_{c,i}^{1/3} Z_{c,i}^{-6/5} \quad (\text{A-3})$$

$$\Omega_{AB} = \frac{1.06036}{T_{AB}^{*0.1561}} + 0.193 \exp(-0.47635 T_{AB}^*) + 1.76474 \exp(-3.89411 T_{AB}^*) + 1.03587 \exp(-1.52996 T_{AB}^*) \quad (\text{A-4})$$

$$T_{AB}^* = T/\epsilon_{AB} \quad (\text{A-5})$$

$$\epsilon_{AB} = (\epsilon_A \epsilon_B)^{0.5} \quad (\text{A-6})$$

$$\epsilon_A = 65.3 T_{c,A} Z_{c,A}^{18/5} \quad (\text{A-7})$$

$$\epsilon_B = 65.3 T_{c,B} Z_{c,B}^{18/5}$$

In the above correlation, T and T_c are in K; V_c is in m³/kmol, and $(\rho D)^\circ$ is in kmol/(m·s).

B. Low-Pressure Viscosity Correlation. The Stiel and Thodos (1961) correlation is used as follows:

$$\mu_i^\circ \xi_i = 34 \times 10^{-5} T_{r,i}^{0.94} \quad (T_{r,i} < 1.5)$$

$$\mu_i^\circ \xi_i = 17.78 \times 10^{-5} (4.58 T_{r,i} - 1.67)^{5/8} \quad (T_{r,i} > 1.5) \quad (\text{A-8})$$

where

$$T_{r,i} = T/T_{c,i}$$

and

$$\xi_i = \frac{T_{c,i}^{1/6}}{M_i^{1/2} (0.987 P_{c,i})^{2/3}} \quad (\text{A-9})$$

Specific units, K and bar, must be used in eq A-9 for the pure component viscosity parameter, ξ_i . From eq A-8 for both components, μ_A° and μ_B° can be calculated.

For the mixture of A and B the following equation can be used.

$$\mu^\circ = \frac{x_A \mu_A^\circ M_A^{1/2} + x_B \mu_B^\circ M_B^{1/2}}{x_A M_A^{1/2} + x_B M_B^{1/2}} \quad (\text{A-10})$$

C. Generalized Jossi-Stiel-Thodos (1962) Correlation for Viscosity of Dense Fluids (See Also Lorenz et al. (1964)). The relation is

$$[(\mu - \mu^\circ)\xi + 10^{-4}]^{1/4} = 0.1023 + 0.023364 \rho_r + 0.058533 \rho_r^2 - 0.040758 \rho_r^3 + 0.0093324 \rho_r^4 \quad (\text{A-11})$$

For a mixture of A and B:

$$\xi = \frac{(x_A T_{c,A} + x_B T_{c,B})^{1/6}}{(x_A M_A + x_B M_B)^{0.5} [0.987 (x_A P_{c,A} + x_B P_{c,B})]^{2/3}} \quad (\text{A-12})$$

$$\rho_r = (x_A V_{c,A} + x_B V_{c,B}) \rho \quad (\text{A-13})$$

Equation A-11 predicts viscosity of dense gases, μ , very close to experimental values. However, values of liquid viscosities calculated from eq A-11 are lower than actual values. In absence of any experimental values and reliable method, eq A-11 can also be used for prediction of liquid viscosities especially for the case of mixtures.

Most recently, Chung et al. (1988) developed a generalized multiparameter correlation for viscosity of dense fluids in terms of reduced density and acentric factor. This new correlation is equivalent to eq A-11 for gases, while for liquids it seems to be more accurate.

Appendix II: Examples

A. Binary Dense Gas. Estimate the diffusion coefficient of C₁-N₂ at 313.4 K and 137.9 bar (2000 psia). The mole fraction of methane is 0.5. Experimental values reported by Sigmund (1976) are

$$\rho = 5.71 \text{ kmol/m}^3 \quad D = 1.64 \times 10^{-7} \text{ m}^2/\text{s}$$

Calculation Procedure: From Appendix I-B

$$\mu^\circ = 0.01521 \text{ mPa}\cdot\text{s (cP)}$$

From Appendix I-C

$$\mu = 0.01884 \text{ mPa}\cdot\text{s (cP)}$$

From Appendix I-A (eq A-1)

$$(\rho D)^\circ = 9.071 \times 10^{-7}$$

From eq 5

$$\rho D / (\rho D)^\circ = 0.9734$$

$$D_{\text{calc}} = 1.55 \times 10^{-7} \text{ m}^2/\text{s}$$

$$\% \text{ deviation} = \frac{(1.55 - 1.64) \times 10^{-7}}{1.64 \times 10^{-7}} = -5.4\%$$

B. Ternary System: Reservoir Conditions. Hadiatno (1986) has measured the diffusion coefficient of methane in a ternary system with the following specifications:

Composition of displacement liquid in mole fractions:

$$C_1 = 0.41 \quad n\text{-}C_4 = 0.27 \quad n\text{-}C_{10} = 0.32$$

Composition of displacement gas: pure C_1

Conditions of the system:

$$T = 344 \text{ K} \quad P = 300 \text{ bar}$$

Reported experimental diffusivity of methane (Hadiatno, 1986):

$$D = 10.1 \times 10^{-9} \text{ m}^2/\text{s}$$

Calculation Procedure: The procedure is similar to example A, except in this system the pseudocomponent B consists of three components.

$$A = C_1 \quad x_A = 0$$

$$B = 0.41C_1; 0.27C_4; 0.32C_{10} \quad x_B = 1.0$$

$$M_B = (0.41 \times 16.04) + (0.27 \times 58.12) + (0.32 \times 142.29) = 67.8$$

Similarly,

$$T_{c,B} = 390.64 \text{ K} \quad T_c = x_A T_{c,A} + x_B T_{c,B} = 390.64$$

$$P_r = 10.278 \quad \omega = 0.2133$$

From Appendix I-B

$$\mu^\circ = 8.637 \times 10^{-3} \text{ mPa}\cdot\text{s}$$

From compressibility charts in the API Technical Data Book (1977)

$$Z = 1.2699$$

$$\rho = \frac{P}{ZRT} = \frac{300}{1.2699 \times 0.08314 \times 344} = 8.26 \text{ kmol/m}^3$$

In this system, the fluid is a mixture of both gas and liquid and, due to lack of experimental viscosity, it is more convenient to use the Jossi-Stiel-Thodos correlation given in Appendix I-C for the mixture viscosity:

$$\mu = 0.124 \text{ mPa}\cdot\text{s}$$

From Appendix I-A

$$(\rho D)^\circ = 4.4082 \times 10^{-7}$$

From eq 5

$$\rho D / (\rho D)^\circ = 0.191126 \quad D_{\text{calc}} = 10.2 \times 10^{-9} \text{ m}^2/\text{s}$$

$$\% \text{ deviation} = \frac{(10.2 - 10.1) \times 10^{-9}}{10.1 \times 10^{-9}} = 1\%$$

C. Multicomponent System: A Gas Dissolved in Oil. Estimate the diffusion coefficient of methane dissolved in kerosene at 333 K (140 °F) and 20.7 bar (300

psia). The specific gravity and molecular weight of kerosene are 0.7837 and 167, respectively. The mixture molar density is 5.224 kmol/m³. The mole fraction of dissolved methane is 0.08. The experimental value of the diffusion coefficient reported by Hill and Lacy (1934) is 4.5 × 10⁻⁹ m²/s. The viscosity of kerosene at 333 K and atmospheric pressure is 1.245 mPa·s.

Calculation Procedure: In this example component B is kerosene, which is a mixture of various hydrocarbons. Critical properties of kerosene can be estimated from its molecular weight and specific gravity using Riazi and Daubert (1987) correlations:

$$T_{c,B} = 666 \text{ K} \quad V_{c,B} = 0.6681 \text{ m}^3/\text{kmol}$$

$$Z_{c,B} = 0.2403 \quad \Omega_B = 0.4613$$

$$x_A = 0.08 \quad x_B = 1 - x_A = 0.92$$

From Appendix I-A

$$(\rho D)^\circ = 2.3 \times 10^{-7} \text{ kmol}/(\text{m}\cdot\text{s})$$

To estimate mixture viscosity when a gas is dissolved in a liquid, procedure 11A7.1 in the API Technical Data Book (1981) can be used to estimate mixture viscosity from liquid viscosity at atmospheric pressure. This procedure requires the GLR (gas-liquid ratio) which may be obtained from the following relation:

$$\text{GLR} = \frac{379 x_A}{(1 - x_A)(M_B/62.4\gamma_B)}$$

where GLR is in m³/m³, x_A is the mole fraction of the dissolved gas, M_B is the molecular weight of the liquid, and γ_B is the specific gravity of the liquid at standard conditions. For this example,

$$\text{GLR} = \frac{379 \times 0.08}{0.92 \times \frac{167}{624 \times 0.7837}} = 9.7 \text{ m}^3/\text{m}^3$$

From procedure 11A7.1 in API TDB: $\mu = 1.14 \text{ mPa}\cdot\text{s}$

$$\rho D / (\rho D)^\circ = 0.1055$$

$$D_{\text{calc}} = \frac{0.1055 \times 2.3 \times 10^{-7}}{5.224} = 4.6 \times 10^{-9} \text{ m}^2/\text{s}$$

$$\% \text{ deviation} = \frac{(4.6 - 4.5) \times 10^{-9}}{4.5 \times 10^{-9}} = +2.3\%$$

D. Ternary System: Non-Hydrocarbon System. This example is directly taken from Chapter 10 in DIPPR Manual (Danner and Daubert, 1986).

Estimate the diffusivity of benzene in a binary mixture of 74.2 mol % acetone and 25.8 mol % carbon tetrachloride at 298.2 K and 1-atm pressure. The reported mixture viscosity is 0.395 mPa·s. The experimental diffusivity of benzene is 2.84 × 10⁻⁹ m²/s.

Calculation Procedure:

Assume A = benzene
B = 74.2 mol % acetone + 25.8 mol % CCl₄

The amount of benzene in the solution is small (dilute solution of A); therefore,

$$x_A = 0.0 \quad x_B = 1.0$$

From properties of acetone and carbon tetrachloride

$$M_B = 82.78 \quad T_{c,B} = 520.56 \text{ K}$$

$$V_{c,B} = 0.22626 \text{ m}^3/\text{kmol}$$

$$Z_{c,B} = 0.2423 \quad \omega_B = 0.2256$$

From Reid et al. (1987), at 298 K and 1 atm:

$$\rho_{\text{acetone}} = 784 \text{ kg/m}^3 \quad \rho_{\text{CCl}_4} = 1584 \text{ kg/m}^3$$

The weight fractions are

$$x_w = 0.5206 \text{ (acetone)}$$

$$x_w = 0.4794 \text{ (CCl}_4\text{)}$$

$$\frac{1}{\rho_B} = \frac{0.5206}{784} + \frac{0.4794}{1584}$$

$$\rho_B = 1034.466 \text{ kg/m}^3$$

$$\rho_B(\text{molar}) = \frac{1034.466}{82.78} = 12.496 \text{ kmol/m}^3$$

From Appendix I-B

$$\mu^\circ = 0.008266 \text{ mPa}\cdot\text{s}$$

From Appendix I-A

$$(\rho D)^\circ = 1.28 \times 10^{-7} \text{ kmol/(m}\cdot\text{s)}$$

From eq 5

$$\rho D / (\rho D)^\circ = 0.2698$$

$$D_{\text{calc}} = \frac{0.2698 \times 1.28 \times 10^{-7}}{12.496} = 2.8 \times 10^{-9} \text{ m}^2/\text{s}$$

$$\% \text{ deviation} = \frac{(2.8 - 2.84) \times 10^{-9}}{2.84 \times 10^{-9}} = -1.4\%$$

Using the method recommended in the DIPPR Manual (Danner and Daubert, 1986):

$$D_{\text{calc}} = 3.15 \times 10^{-9} \text{ m}^2/\text{s} \quad \% \text{ deviation} = +10.0\%$$

Literature Cited

- American Petroleum Institute. *Technical Data Book-Petroleum Refining*, 3rd ed.; API: Washington, D.C., 1977 (extant 1981); Chapter 11.
- Berry, V. J., Jr.; Koeller, R. C. Diffusion in Compressed Binary Gaseous Systems. *AIChE J.* 1960, 6, 274.
- Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; John Wiley & Sons: New York, 1960; Chapter 16.
- Chung, T. H.; Ajlan, M.; Lee, L. L.; Starling, K. E. Generalized Multiparameter Correlation for Nonpolar and Polar Transport Properties. *Ind. Eng. Chem. Res.* 1988, 27, 671.
- Danner, R. P.; Daubert, T. E. *Manual for Predicting Chemical Process Design Data*; Design Institute for Physical Property Data (DIPPR); AIChE: New York, 1986; Chapter 10, p 10K-1.
- Dawson, R.; Khoury, F.; Kobayashi, R. Self-Diffusion Measurements in Methane by Pulsed Nuclear Magnetic Resonance. *AIChE J.* 1970, 16, 725.
- Graue, D. J. A Numerical Method for Smoothing Thermodynamic Data. Ph.D. Dissertation, California Institute of Technology, 1965.
- Hadiatno, D. Etude en conditions de gisement de la diffusion et de la dispersion lors de l'injection de gaz miscible en récupération assistée du pétrole, Thèse Doctorat, l'Université de Bordeaux I, 1986.
- Hanssen, J. E.; Stenberg, D. *Experimental Diffusion Coefficients for Nitrogen at Reservoir Conditions*; PRI Report, Petroleum Research Center, Rogaland Research Institute: Stavanger, Norway, 1987.

- Hayduk, W.; Cheng, S. C. Review of Relation Between Diffusivity and Solvent Viscosity in Dilute Liquid Solutions. *Chem. Eng. Sci.* 1971, 26, 635.
- Hill, E. S.; Lacy, W. N. Rate of Solution of Methane in Quiescent Liquid Hydrocarbons. II. *Ind. Eng. Chem.* 1934, 26, 1324.
- Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; John Wiley & Sons: New York, 1954; p 539.
- Holmes, J. T.; Olander, D. R.; Wilke, R. C. Diffusion in Mixed Solvents. *AIChE J.* 1962, 8, 646.
- Jossi, J. A.; Stiel, L. I.; Thodos, G. The Viscosity of Pure Substances in the Dense Gaseous and Liquid Phases. *AIChE J.* 1962, 8, 59.
- Kestin, J.; Yata, J. J. Viscosity and Diffusion Coefficient of Six Binary Mixtures. *J. Chem. Phys.* 1968, 49, 4780.
- Lohrenz, J.; Bray, B. G.; Clark, C. R. Calculating Viscosities of Reservoir Fluids from their Compositions. *J. Pet. Technol.* 1964, October, 1171.
- Lusis, M. A.; Ratcliff, G. A. Diffusion in Binary Liquid Mixtures at Infinite Dilution. *Can. J. Chem. Eng.* 1968, 46, 385.
- Mathur, G. P.; Thodos, G. The Self-Diffusivity of Substances in the Gaseous and Liquid States. *AIChE J.* 1965, 11, 613.
- Prausnitz, J. M.; Cheue, P. L. *Computer Calculations of High-Pressure Vapor-Liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1968.
- Reamer, H. H.; Opfell, J. B.; Sage, B. H. Diffusion Coefficients in Hydrocarbon Systems: Methane-Decane in Liquid Phase. *Ind. Eng. Chem.* 1956, 48, 275.
- Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquid*, 4th ed.; McGraw-Hill: New York, 1987; Chapter 11, p 577.
- Riazi, M. R.; Daubert, T. E. Application of Corresponding States Principles for Prediction of Self-Diffusion Coefficients in Liquids. *AIChE J.* 1980, 26, 386.
- Riazi, M. R.; Daubert, T. E. Characterization Parameters for Petroleum Fraction. *Ind. Eng. Chem. Res.* 1987, 26, 755.
- Robinson, R. C.; Stewart, W. E. Self-Diffusion in Liquid Carbon Dioxide and Propane. *Ind. Eng. Chem. Fundam.* 1968, 7, 90.
- Sigmund, P. M. Prediction of Molecular Diffusion at Reservoir Conditions. Part I—Measurement and Prediction of Binary Dense Gas Diffusion Coefficients. *Can. J. Pet. Technol.* 1976, April-June, 48.
- Slattery, J. C.; Bird, R. B. Calculation of the Diffusion Coefficients of Dilute Gases and of the Self-Diffusion Coefficients of Dense Gases. *AIChE J.* 1961, 7, 611.
- Stiel, L. I.; Thodos, G. The Viscosity of Nonpolar Gases at Normal Pressures. *AIChE J.* 1958, 4, 137.
- Stiel, L. I.; Thodos, G. Lennard-Jones Force Constants Predicted from Critical Properties. *J. Chem. Eng. Data* 1962, 7, 234.
- Takahashi, S. Preparation of a Generalized Chart for the Diffusion Coefficients of Gases at High Pressures. *J. Chem. Eng. Jpn.* 1974, 7, 417.
- Tang, Y. P.; Himmelblau, D. M. Effective Binary Diffusion Coefficients in Mixed Solvents. *AIChE J.* 1965, 11, 54.
- Wilke, C. R. Estimation of Liquid Diffusion Coefficients. *Chem. Eng. Prog.* 1949, 45, 218.
- Wilke, C. R. Diffusional Properties of Multicomponent Gases. *Chem. Eng. Prog.* 1950, 46, 95.
- Wilke, C. R.; Chang, P. Correlation of Diffusion Coefficients in Dilute Solutions. *AIChE J.* 1955, 1, 264.

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