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A Corresponding States Correlation for the Infinite Dilution Binary Diffusion Coefficient of Dense Gases

S. Murad[1] and N. Bhupathiraju[1]

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The simple principle of corresponding states for the self-diffusion coefficient has been extended to binary diffusion coefficients at infinite dilution. A simple correlation based on this approach has then been developed and tested against available experimental data. For the 12 systems tested the average percentage error is less than 6% while the maximum and minimum errors are 30%, and 1%, respectively. An approximation is also suggested which permits this approach to be used for compositions other than infinite dilution.

KEY WORDS: binary diffusion coefficients; corresponding states; dense gases.

1. INTRODUCTION

The corresponding states theory is a powerful tool for predicting thermodynamic and transport properties of fluids. The simple (two parameter) theory has been widely used to predict thermodynamic and transport properties of simple compounds and has been generalized (three or four parameter forms) to study more complex molecules [1–3]. In this paper we present a corresponding states method for predicting the infinite dilution binary diffusion coefficient of dense gases. A simple approximation that permits diffusion coefficients to be estimated over the entire composition range is also presented.

2. THEORY

According to the simple principle of corresponding states, the self-diffusion coefficient of a fluid A is related to that of a reference fluid o by

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[1] Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

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the following equation [1]:

$$D_A(P,T)=\left(\frac{T_A^c}{T_o^c}\right)^{5/6}\left(\frac{P_o^c}{P_A^c}\right)^{1/3}\left(\frac{M_o}{M_A}\right)^{1/2}D_o\left(\frac{PP_o^c}{P_A^c},\frac{TT_o^c}{T_A^c}\right) \qquad (1)$$

where P and T are the pressure and temperature of fluid A, respectively. T_A^c, P_A^c, and M_A are the critical temperature, critical pressure, and molecular weight of fluid A, respectively, while T_o^c, P_o^c, and M_o refer to the reference fluid o. Equation (1) is found to be accurate for simple fluids such as argon, krypton, xenon, and methane [2], etc., and has been recently generalized to include nonconformal fluids using the shape factor approach [1].

The simple corresponding states equation for the self-diffusion coefficient is extended [3] to mutual-diffusion coefficients by the following equation:

$$D_{AB}(P,T,x_A)=\left(\frac{T_{AB}^c}{T_o^c}\right)^{5/6}\left(\frac{P_o^c}{P_{AB}^c}\right)^{1/3}\left(\frac{M_o}{M_{AB}}\right)^{1/2}D_o\left(\frac{PP_o^c}{P_{AB}^c},\frac{TT_o^c}{T_{AB}^c}\right) \qquad (2)$$

However, it is not clear in such an extension what the precise mixing rules for T_{AB}^c, P_{AB}^c, and M_{AB} should be, and therefore no definitive rules have been formulated [3]. For the extreme case when the component B is present only as a trace component ($x_B \to 0$), one can develop mixing rules based on the following argument. The probability of molecule B colliding (interacting) with another B molecule is extremely small, thus the molecular motion of B is mostly determined by the molecular interactions between a B and an A molecule (ignoring for the time being any multibody effects). In such circumstances the simple Lorentz-Berthelot mixing rules [3] can be expected to be reasonable:

$$T_{AB}^c=(T_A^c T_B^c)^{1/2} \qquad (3)$$

$$M_{AB}=2\left[M_A^{-1}+M_B^{-1}\right]^{-1} \qquad (4)$$

$$\frac{T_{AB}^c}{P_{AB}^c}=\frac{1}{8}\left[\left(\frac{T_A^c}{P_A^c}\right)^{1/3}+\left(\frac{T_B^c}{P_B^c}\right)^{1/3}\right]^3 \qquad (5)$$

The validity of Eqs. (3)–(5) can be easily tested in the limit of low density when multibody interactions are indeed negligible. Equations (3)–(5) (for our reasoning to be valid) must then also be correct when A is the trace component and B the carrier gas because of the symmetry of these equations. Experimental evidence confirms this since at low pressures D_{AB}^0

(in our notation superscript 0 implies that A is the carrier gas and B is the trace gas) $= D_{BA}^0$.

At high densities, when multibody effects become important, Eqs. (3)–(5) can no longer be expected to be valid; experimental evidence confirms this (since, in general, at high densities $D_{AB}^0 \neq D_{BA}^0$). These multibody effects consist, however, almost entirely of several molecules of the carrier gas A interacting simultaneously with a B molecule. It would thus be reasonable to assume that the effect of such multibody effects can be accounted for mostly by the properties of the carrier gas only. Such a reasoning leads to a generalized correlation of the form

$$D_{AB}^0(P,T) = F_A(\rho_A)(T_{AB}^c)^{5/6}(P_{AB}^c)^{-1/3}(M_{AB})^{-1/2}\Phi\left(\frac{T}{T_{AB}^c}, \frac{P}{P_{AB}^c}\right) \quad (6)$$

Here F_A is the correction term for multibody effects. It is a function of density and does not necessarily have to have the same functional form for all fluids. Φ, however is a universal function of reduced temperature and pressure. T_{AB}^c, P_{AB}^c, and M_{AB} are defined by Eqs. (3)–(5). For compositions other than infinite dilution, as a first approximation, D_{AB}^0 and D_{BA}^0 can be obtained, and linear interpolation can then be used for other compositions.

3. RESULTS

The corresponding states formulation given by Eq. (6) was tested using infinite dilution binary diffusion data for conformal (or nearly conformal) fluids. These data were used to obtain the functional form of Φ, and the associated constants using a least squares procedure. One simple form that was found to be very promising is:

$$D_{AB}^0 = F_A V_A^c \left(\frac{T_{AB}^c}{T_A^c}\right)^{5/6} \left(\frac{P_{AB}^c}{P_A^c}\right)^{-1/3} \left(\frac{M_{AB}}{M_A}\right)^{-1/2} T_R^a P_R^b \quad (7)$$

We investigated two cases. Initially a and b were assumed constant (case I). This constraint was then relaxed, and a and b were allowed to be functions of T_R and P_R (case II). For case I, the best set of parameters was

$$\left.\begin{aligned} a &= 1.6617 \\ b &= -1.0127 \end{aligned}\right\} \quad (8)$$

while for case II, the best set was

$$\left.\begin{aligned} a &= 1.7403 - 0.00182 T_R \\ b &= -1.0052 - 0.08648 P_R^{-1} \end{aligned}\right\} \quad (9)$$

In Eq. (7) V_A^c is the critical volume of A, F_A (defined previously) is a function of density, $T_R = T/T_{AB}^c$, and $P_R = P/P_{AB}^c$. Our tests have shown that for dense systems ($\rho \geqslant 0.7\rho_A^c$), F_A is nearly constant and equal to 1.32×10^{-7} mol · m^{-1} · s^{-1} for case I and 1.151×10^{-7} mol · m^{-1} · s^{-1} for case II. In the absence of any high density data, these default values are recommended; otherwise F_A should be estimated from any available data. It must be understood, however, that F_A will be the same for all binary systems, with the same carrier gas A. All results we are presenting in this paper are based on the default values given above.

In Fig. 1 we have tested the correlation (case II) against available experimental data for the He–Ar system. This system (He–Ar) is one of the most widely studied systems for infinite dilution binary diffusion coefficients. Consequently, we have been able to test it for a wide range of state conditions. As can be seen from the figure, the correlation agrees closely with the available experimental data [4, 5] over the entire range of state conditions studied experimentally (see also Table I). The calculated values shown are for correlation II. However, for this system correlation I gives

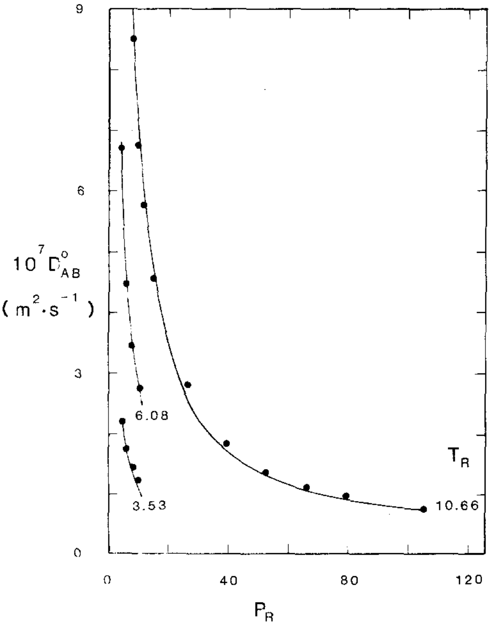

Fig. 1. Infinite dilution binary diffusion coefficients of the He–Ar system obtained from correlation II (lines) compared with available experimental data (points) at several temperatures [4, 5].

Table I. Infinite Dilution Diffusion Coefficients Calculated From Correlations Developed Compared With Experimental Data

System (carrier-trace)	No. of data points	Absolute ave. deviation+[a] (10^{-7} $m^2 \cdot s^{-1}$) I	II	Average absolute percentage deviation[a] I	II
He–N_2 [4]	5	0.13	0.08	9.4	6.0
He–Ar [4, 5]	23	0.20	0.20	7.6	7.2
He–CH_4 [4, 6]	18	0.09	0.08	1.9	1.3
He–C_2H_6 [4]	5	0.05	0.05	4.4	4.4
He–C_3H_8 [4]	5	0.04	0.04	4.4	4.1
He–C_4H_{10} [4]	5	0.04	0.04	5.0	5.0
He–CF_4 [4]	5	0.03	0.03	3.0	2.8
N_2–H_2 [4]	7	0.11	0.12	13.4	13.9
N_2–He [4]	5	0.08	0.05	6.7	3.2
Ar–He [4]	5	0.10	0.06	8.9	5.8
Ar–H_2 [4]	7	0.09	0.08	9.1	7.8
Ar–CH_4 [9]	7	0.35	0.15	16.5	7.8
Overall	97	0.13	0.11	7.11	5.7

[a] The maximum errors are generally about twice the average errors shown here.

results which are nearly as accurate as those obtained from II. Figure 2 shows the correlation (II) compared with available experimental data for He–CH_4 [4, 6], He–C_4H_{10} [4], and He–CF_4 [4]. For these three systems, the correlation again gives very good agreement over the entire pressure range. However, for these systems experimental data are not available over a very wide temperature range. Once again correlation I is only very slightly (see Table I) worse than correlation II (which is shown in Fig. 2).

Finally, in Fig. 3, we have shown results for correlation II for the system Ar–H_2 and N_2–H_2. As can be seen from the figure agreement is good for Ar–H_2. However, for N_2–H_2 agreement is not very good at high pressures (the highest pressure included in the figure for N_2–H_2 is ~140 MPa). The accuracy of the correlation starts deteriorating at approximately 85 MPa and can lead to errors of up to 30% at the highest pressure included in our comparison. We would also like to point out that this ($N_2 - H_2$) is the system which gives the poorest results amongst the 12 systems we investigated. The system N_2–H_2 has also been studied by Berry and Koeller [7]. Their experimental results appear too high compared to the

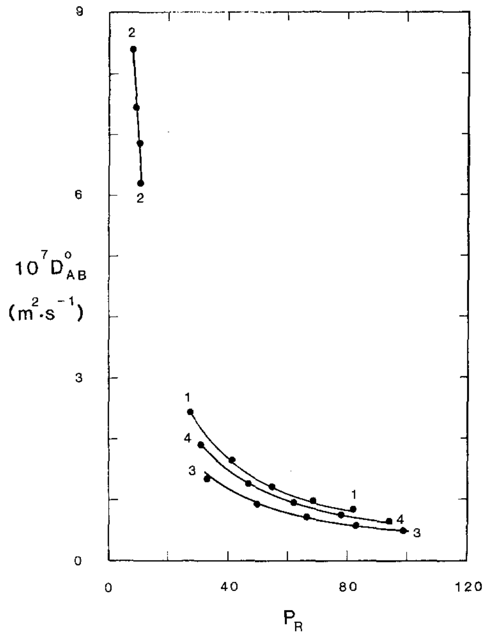

Fig. 2. Infinite dilution binary diffusion coefficients of (*1*) He–CH_4, $T_R = 9.48$; (*2*) He–CH_4, $T_R = 9.64$; (*3*) He–n–C_4H_{10}, $T_R = 6.35$; (*4*) He–CF_4, $T_R = 8.67$; using correlation II (lines) compared with available experimental data (points) [4, 6].

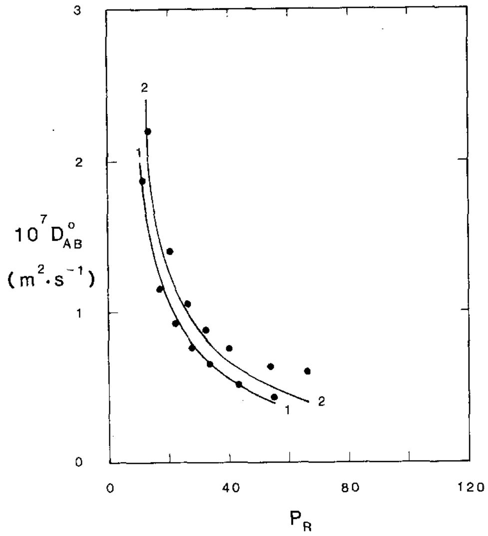

Fig. 3. Infinite dilution binary diffusion coefficients of the systems (*1*) Ar–H_2, $T_R = 4.21$, and (*2*) N_2–H_2, $T_R = 4.60$, from correlation II (lines) compared with available experimental data (points) [4].

more recent data of Balenovic et al. [4], which are believed to be more accurate [8].

A summary of all our results is given in Table I. The average absolute deviation for correlation I for all systems studied was $0.13 \times 10^{-7}\ m^2 \cdot s^{-1}$, while for correlation II it was $0.11 \times 10^{-7}\ m^2 \cdot s^{-1}$. The average absolute percentage deviation was 7.1% and 5.7% for correlations I and II, respectively. Although correlation I only involves three parameters, while correlation II has five, we still recommend II, since it does improve the accuracy of the results for almost all systems, without making the correlation a lot more difficult to use.

4. CONCLUSIONS

We have developed correlations based on the corresponding states principle that can be used to predict infinite dilution binary diffusion coefficients of conformal fluids. The functional form and the parameters are based on the limited experimental data available. As more data become available the functional form of Φ will need to be reexamined and new parameters obtained. In addition, as more experimental data become available it will be worthwhile to extend this method to nonconformal fluids. One promising approach worth investigating is the shape factor generalization. This approach has already been successfully used for viscosity [10, 11], thermal conductivity [12], and self-diffusion coefficients [1], in addition to thermodynamic properties [13], and surface tension [14].

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