

# On the Determination of High-pressure Mass-diffusion Coefficients for Binary Mixtures<sup>1</sup>

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## Abstract

A model for high-pressure binary diffusion coefficient calculation is proposed based on considerations originating from re-casting both the low pressure kinetic theory and the Stokes-Einstein infinite dilution expressions into forms consistent with corresponding states theory. These considerations lead to an ansatz that is an expression reflecting departures from the kinetic theory relationship through a division factor that is a function of the reduced species density and that becomes unity in the limit of low pressure gases. Available high pressure data sets extracted from the literature are used to derive correlations for the factor that are eventually categorized according to the species system. The typical uncertainty in these correlations is estimated as 10 to 15 %, with a maximum uncertainty of about 30% for the high density regime.

## Introduction

The modeling of combustion phenomena occurring in Diesel, gas turbine and liquid rocket engines requires the accurate knowledge of mass diffusion,  $D_{ij}$ , and thermal diffusion,  $\alpha_{Tij}$ , coefficients. This is because despite the turbulent environment in the combustion chamber, at supercritical conditions the species molecular transport governs the dissipation (irreversible entropy production) and backscatter, as shown in a recent study [1]. In fact, the dominating effect in the dissipation is that associated with the Fick's diffusion terms, with significant contributions from the multiplied Fick's and Soret (i.e. thermal diffusion) terms. This is in sharp contrast to atmospheric flow turbulence, where viscous effects dominate. Despite the wide range of combustion applications, there are no recent systematic studies devoted to the modeling of molecular diffusion at high pressure conditions [2]; the same situation prevails for thermal diffusion effects [2].

Although kinetic theory (KT) gives a firm theoretical basis for low pressure diffusion coefficient expressions (dilute gases), there is not a similar basis for high pressure dense gases or liquids. Since high pressure fluids can have reduced densities,  $\rho_r \equiv \rho/\rho_c$  (the subscript  $c$  denotes the

critical point), comparable to those of liquids, it may be pertinent to also inquire about typical liquid diffusion calculations. Infinite dilution diffusion in liquids is usually depicted by extending the Stokes-Einstein (SE) hydrodynamic model for motion of very small particles in a liquid down to the molecular size level, but the resulting correlations have only mixed success ([3], [4], [5], [6], [7]). At a minimum, diffusion coefficient correlations should be dimensionally consistent; moreover, in conformity with results for other transport properties such as the viscosity,  $\eta$ , and the thermal conductivity,  $\lambda$ , adherence to the principle of corresponding states is deemed appropriate. In this connection, the temperature,  $T$ , and  $\rho$  (but not the pressure,  $p$ ) are here considered as the relevant primitive variables in correlations since the pure species critical values are closely related to characteristic molecular interaction potential and size. Pressure enters the calculations through the equation of state (EOS); mole fractions,  $X_i$ , or mass fractions enter through appropriate mixing rules. Particular species of interest include  $H_2$ ,  $He$  (as a safe alternative to  $H_2$  in experiments),  $O_2$ ,  $N_2$  (used in microgravity experiments, and also needed to model air), alkane hydrocarbons,  $C_nH_{2n+2}$ , as representative fuels, and the products of combustion  $H_2O$  and  $CO_2$ .

In this study we first present existing low  $p$  information in terms of corresponding states forms, as a precursor to establishing the strategy for developing a high  $p$  relationship. This relationship is next presented and used for binary species correlations based on a multitude of experimental data.

## Low pressure relationships

### Gases

Low  $p$  KT theory has been discussed in [8] and in [9] for combustion applications. The lowest order expression for the binary diffusion coefficient from KT is ([3], [6])

$$(D_{ij})_{KT} = 3(kT/(2\pi m_{ij}))^{1/2}/[8n\sigma_{ij}^2 \Omega_D(kT/\varepsilon_{ij})] \quad (1)$$

where  $i$  and  $j$  are species indices,  $k$  is the Boltzmann constant,  $m_{ij}$  is the reduced mass,  $n$  is the (average) molecular number density,  $\sigma_{ij}$  denotes the collision diameter and  $\Omega_D$  is the diffusion collision integral in terms of temperature referenced to collision potential scale,  $\varepsilon_{ij}$ . Parameters  $\sigma_{ij}$  and  $\varepsilon_{ij}$ , along with the form of the function  $\Omega_D$  are empirically determined;  $\eta$  measurements are a major source of parameter values for  $i = j$ .

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For a pure substance with  $kT \leq \varepsilon_{ii}$ , in terms of the viscosity integral  $\Omega_v$ , the  $\eta$  dependency on  $\sigma_{ii}$  and  $\varepsilon_{ii}$  is [3]

$$\eta^{-1} \sim \sigma_{ii}^2 \Omega_v (kT/\varepsilon_{ii}) \sim \sigma_{ii}^2 \sqrt{(\varepsilon_{ii}/k)}, \quad (2)$$

offering a way to determine  $\sigma_{ij}^2 \sqrt{(\varepsilon_{ij}/k)}$ . From the corresponding states rules [3],

$$\sigma_{ij} \sim (V_{c,ij}/N_A)^{1/3} \text{ and } \varepsilon_{ij} \sim kT_{c,ij} \quad (3)$$

where  $N_A$  is Avogadro's number, and the pseudocritical parameters are  $V_{c,ij} = [(V_{c,i})^{1/3} + (V_{c,j})^{1/3}]^3/8$  and  $T_{c,ij} = \sqrt{(T_{c,i}T_{c,j})}$ , where  $V$  is the molar volume. Using these rules in a relation similar to eq. 2, the empirical value of  $\sigma_{ij}^2 \sqrt{(\varepsilon_{ij}/k)}$  is herein replaced by  $6.0 \times 10^{-3} r_v (V_{c,ij})^{2/3} \sqrt{T_{c,ij}}$ , with the expectation of  $r_v \simeq \text{constant}$ . The  $r_v$  being constant is supported by  $\sigma_{ij}$  and  $\varepsilon_{ij}$  data from [10] for collisional interactions for five noble gases, air, and nine simple polyatomic gases: except for interactions with  $He$  (where  $r_v \cong 0.95$ ), the data are consistent with  $r_v = 1.0$  to within  $\simeq 2\%$  error or less. Further examination of the data reveals that aside from collisional interactions with the noble gases,  $kT_{c,ij}/\varepsilon_{ij} \cong 1.27$  to within an error of  $\simeq 5\%$  or less. (The ratio is closer to 1.05 for  $He$  and 1.17 for  $Ar$ .) The following replacements

$$\sigma_{ij} = 0.692(V_{c,ij}/N_A)^{1/3} \text{ and } \varepsilon_{ij} = kT_{c,ij}/1.27 \quad (4)$$

thus give accurate scaling of transport parameter values (e.g. for  $\eta$ ) and a good estimate of  $T$  scaling for the collision integrals.

Using the collision integrals of [10] for  $1 \leq kT/\varepsilon_{ij} \leq 10$ , augmented by Lennard-Jones functions [3] for  $kT < \varepsilon_{ij}$ ,  $\Omega_D$  is here fitted as

$$\Omega_D = 1.20(T_{c,ij}/T)^s \quad (5)$$

where  $\ln(s) = \sum_{m=0}^5 [a_m (\ln(T/T_{c,ij}))^m]$ , with  $a_m = \{-0.84211, -0.32643, -0.10053, 0.07747, 0.0127, -0.00995\}$  for  $0.2 \leq T/T_{c,ij} \leq 10$ . If  $T > 10T_{c,ij}$ ,  $s$  is here taken as a constant, 0.2304, which is its value at  $10T_{c,ij}$ . Generally,  $s$  takes values between about 1/4 to 1/2.

The final corresponding states expression for the low  $p$  binary diffusion coefficient is in  $cm^2/s$

$$(D_{ij})_{KT} = 2.81 \times 10^{-5} V [(m_i^{-1} + m_j^{-1})T]^{1/2} \times (T/T_{c,ij})^s / (r_D V_{c,ij}^{2/3}) \quad (6)$$

where  $m_i, m_j$  are molar masses ( $g/mole$ ),  $T$  is in K, and  $V$  in  $cm^3/mole$ . The factor  $r_D$  is a constant parameter of  $O(1)$ , used as an empirical adjustment for the particulars of the collisional interaction of a given pair of species. (This is especially needed for non-simple species.) Values of  $r_D$ , as obtained from diffusion data at  $p = 1 \text{ atm}$  given by [11], [3] and [12], are listed in Table 1. (Note:  $V = 82.056T$  at  $p = 1 \text{ atm}$ .) The light species  $He$  and  $H_2$  behave in a similar manner, as does benzene ( $C_6H_6$ ) and acetone ( $C_3H_6O$ ). Unfortunately, the amount and quality of data related to the heavier alkanes is less than desirable. Overall, errors in values of  $D_{ij}$  for low  $p$  gases (see in Table 1) are of order 5%; the same conclusion is reached by [10].

## Liquids

For liquid solvents with moderate  $\eta$  ( $\eta \leq 0.1$  poise), the infinite dilution (i.e.  $X_i \rightarrow 0$ ) binary diffusion coefficients,  $D_{ij}^o$ , are frequently expressed using the SE formula ([3]):

$$D_{ij}^o = kT/(\eta_j l_{ij}) \quad (7)$$

where  $l_{ij}$  is a characteristic scattering length of solute  $i$  in solvent  $j$ . An empirical correlation with lowest error is that due to Tyn and Calus [13], appropriately modified by [3]

$$l_{ij} = 1.546 \times 10^{-7} (\sigma_{b,i}/\sigma_{b,j})^{0.15} V_{b,i}^{0.4333} / V_{b,j}^{0.2667} \text{ in } cm \quad (8)$$

where  $\sigma_b$  is surface tension ( $dynes/cm$ ) and subscript  $b$  indicates the normal boiling point temperature,  $T_b$ . The average expected error with this expression is about 10% and the maximum error is about 30%. Although the modified expression is more straightforward than the original one involving parachors, the need to find  $\sigma_b$  and  $V_b$  is inconvenient. The present strategy is to use corresponding states principles and replace  $\sigma_{b,i}^{0.15} V_{b,i}^{0.4333}$  by  $0.69 r_s T_{c,i}^{0.15} V_{c,i}^{1/3}$ . Data [3] then shows that  $r_s = 1.0$  for  $N_2, O_2$ , benzene, toluene, naphthalene and the alkanes (for  $n = 4 - 16$ );  $r_s = 0.95$  for  $H_2O$ , 1.1 for  $H_2$ , and 0.88 for  $He$ . (A dimer should be used with water solutes [13], and thus the effective  $r_s$  value is 1.28) The dependency on the solvent in the form  $\sigma_{b,j}^{0.15} V_{b,j}^{0.2667} \equiv 4.88 \beta_j$  could also be expressed in terms of  $T_c$  and  $V_c$ ; however, an expression in terms of the acentric factor,  $\omega$ , is sought herein because of easy extension to mixtures. For a pure substance, the correlation  $\beta = (\omega + 0.45)^{0.4125} + 0.27 X_A$  holds with  $X_A = 1.0$  for alkanes ( $n = 6 - 16$ ), benzene and toluene, and with  $X_A = 0$  for non-hydrocarbons. This expression is easily extendable to solvent mixtures through a mole fraction average acentric factor, along with the alkane mole fraction in the mixture,  $X_A$ . The scattering length expression becomes

$$l_{ij} = 2.19 \times 10^{-8} r_s T_{c,i}^{0.15} V_{c,i}^{1/3} / \beta_j \quad (9)$$

with  $r_s = 1.0$  for most solutes. Along with  $r_s$ , details of our  $\beta$  fit give for certain solvents an additional multiplier of 1.08 ( $H_2O$ ), 0.91 ( $H_2$ ), or 1.04 ( $He$ ). However, liquid solvents with any of these species as a major constituent are not of interest. According to [3], for normal paraffin (alkane-alkane) solutions, an expression due to Hayduk and Minhas (see [3]) should be used instead of that in [13]. Calculations with this alternative expression for carbon numbers  $n = 7 - 16$  and  $300 K \leq T \leq 370 K$  lead to a solvent function dependent on its reduced temperature,  $T_r \equiv T/T_c, \beta_j = a T_r^{-b}$  where  $a = 1 - \omega_j/3$  and  $b = 1.17 \omega_j / \omega_i^{0.41}$ .

For species of interest, values from our proffered eq. 9 for  $l_{ij}$  deviate from the originals by about 3% or less, well within the accuracy of the SE correlation. This new expression is more convenient than the originals, may be used when properties at  $T_b$  are not available (e.g.  $CO_2$ ), and may readily be applied to solvents that are not pure (i.e. mixtures). Note that solvent molecular association has not

been considered in this discussion; it is not expected to be important for species combinations of interest [14].

It is well known ([15], [16], [3], [5], [17]) that for binary mixtures, the effective diffusion coefficient is  $\alpha_D D$  ( $D_{ij} = D$  for  $i, j = 1, 2$ ) where  $\alpha_D = 1 + X_k \partial(\ln \phi_k) / \partial X_k$  is the mass diffusion factor,  $\phi_k$  is the fugacity coefficient, and  $k$  denotes either species,  $i$  or  $j$ . Given expressions for the  $D_{ij}^o$ 's, the liquid binary coefficient may be obtained from the Vignes rule ([3], [17]) through

$$\ln(D_{ij}) = X_j \ln(D_{ij}^o) + X_i \ln(D_{ji}^o). \quad (10)$$

Since for low  $p$  gas, there is no distinction between  $D_{ij}$  and  $D_{ij}^o$  (see that eq. 1 is independent of  $X_i$  or  $X_j$ ), the same rule applies.

Note that  $\alpha_D = 1$  in the infinite dilution limit; measurements involve a small but finite trace amount of solute into a carrier solvent and deviations from 1 are usually neglected. In fact,  $\alpha_D$  measures departures from mixture ideality: for low  $p$  ideal gas,  $\alpha_D = 1$ , however, for liquids  $\alpha_D$  may differ substantially from 1 (e.g. see examples in [17]). Since  $\alpha_D = 0$  at the critical point ([15], [5]), there is an ambiguity in the value of  $\alpha_D$  when the solvent is near  $(T_c, \rho_c)$ . This fact, combined with the lack of accuracy in near-critical-point  $V$  values calculated from common EOS models ([3]), leads to a difficulty in the use of infinite dilution data for nearly critical solvents.

### Modeling of high-pressure diffusion coefficients

To correlate high  $p$  diffusion coefficients, the issue is the choice of a proper extension of the low pressure models to high  $p$ . Two extensions can be pursued: modify either the KT approach or the SE expressions. Since  $\rho$  is the primitive variable, it is  $\rho_r$  that is the pertinent correlation quantity at high  $p$ . As an illustration of correlations based on  $\rho_r$  rather than  $p_r$ , the data of [18] feature  $N_2$ ,  $Ar$  and  $CH_4$  as trace species in  $He$  at  $p = 1 - 6$  MPa ( $p_r > 4$ ) and  $T = 248 - 323$  K ( $T_r \gg 1$ ); however,  $\rho_r = V_c/V \leq 0.16$  is not large. The data and  $(D_{ij})_{KT}$  match to within 3% (other data for trace  $CO_2$  is not as close). A literature search shows that available data for dense gas diffusion is for  $\rho_r \leq 2$ , whereas for most liquids  $\rho_r \geq 2$  (at normal boiling, liquid  $\rho_r \approx 2.5$ ). Moreover, generally  $T_r < 1$  for liquids, while  $T_r \geq 1$  for dense vapors. These comparisons suggest that dense vapor diffusion correlations should be referenced to the KT expression, not a SE type formula, particularly since as mentioned above, SE does not hold for very high  $\eta$  solvents; indications are that it also does not hold in the low  $\eta$  limit ([5], [19]) or at  $\rho$ 's below critical ([20], [4]). Although some success has been obtained with SE based formulas for non-liquid systems with moderate  $\eta$  ([4], [7]), the idea here is to modify  $(D_{ij})_{KT}$  from eq. 6 by a factor  $w_D = 1 + \delta_D$  where  $\delta_D$  is a function of the solvent  $\rho_r$  with  $\delta_D \rightarrow 0$  as  $\rho_r \rightarrow 0$

$$D_{ij}^o = (D_{ij})_{KT} / w_{D,j}, \quad (11)$$

rendering this expression valid for all  $\rho_r$ 's; this expression is consistent with hard sphere scattering theory ([5], [20]).

The ansatz is that the  $\delta_D$  dependency on  $\rho_r$  and  $T_r$  is simple (generic), with only a few constant parameters involved. The protocol of determining the value of  $w_D$  is to use  $D_{ij}^o$  data in conjunction with calculated  $(D_{ij})_{KT}$  from eq. 6, and obtain  $\delta_D(\rho_r)$  from eq. 11. Note that at fixed (high)  $\rho_r$ , data indicates a weak dependence of diffusivity on  $T$  ([21], [5], [4]). Similarly,  $\eta$  is mostly  $\rho$  dependent ([4], [5]), so there is no advantage to using  $\eta$  as a correlation variable over  $\rho_r$ .

An example of the proposed ansatz for dense gases uses the data of [23] for light trace species ( $H_2, He$ ) in  $N_2$  or  $Ar$  carrier species;  $p = 272 - 1360$  atm (27.6 - 132 MPa),  $T = 298$  K and  $0.85 \leq \rho_r \leq 2.0$ . A very good fit to the data is with  $\delta_D = c\rho_r^{3/2}$ , where  $c = 0.42$  for  $He$  in  $Ar$  and  $c = 0.58$  for the other pairs. Figure 1 depicts the  $w_D$  data and fit curves. Note that  $T_r \geq 2$ , so that the critical point is avoided. Fit deviations are at most 10% and usually lower; the dependency on  $\rho_r$  is accurately captured. The measurement error estimate [23] is  $\simeq 5\%$  (or slightly larger).

Other data in [23] feature  $He$  as the carrier with  $N_2$ ,  $Ar$ ,  $CF_4$ , and alkanes with carbon number  $n = 1$  to 4 as solutes. The carbon based solutes display a decrease in the value of  $w_D$  at larger  $\rho_r$  and  $\delta_D$  is maximum at  $\rho_r \approx 1.2 - 1.3$ . The  $w_D$  calculated (values and fits in Fig. 2) from  $D_{ij}^o$  data yield  $\delta_D \simeq c\rho_r^{0.83}$  for the ascending part of the curves, with  $c = 0.18$  for  $N_2$  and  $Ar$ ,  $c = 0.27$  for  $CH_4$ ,  $c = 0.23$  for  $C_2H_6$ , and  $c = 0.20$  for  $n = 3$  or 4 (for  $n = 3$ ,  $r_D = 1.02$  in eq. 6). For the descending part of the alkane curves,  $\delta_D \simeq (c + \Delta c)\rho_r^{0.83}$ , with  $\Delta c = 0.48 - 0.39\rho_r^{0.83}$  for  $\rho_r \geq 1.284$  ( $p \geq 75$  MPa), changing the  $\rho_r$  dependency for those parts of the curve. Figure 2 also illustrates the  $w_D$  values for  $CF_4$ , assuming  $r_D = 1$ . The  $w_D$  values and fit for solutes  $N_2$  and  $Ar$  are given in Fig. 3, along with data for benzoic acid in  $CO_2$  (the data is from [20] with  $r_D = 3/4$  estimated from the diffusivity at  $\rho_c$ ; see Fig. 2 in [20]). The scatter in Fig. 3 ( $\simeq 10\%$  or less) is typical for high  $\rho$  measurements. Data fits are thus somewhat ambiguous; the emphasis is here on capturing data trends in the context of using generic expressions, rather than the most accurate portrayal of values for a specific data set or species pair. Considering both data scatter and the different character of solvent-solute pairs, the Fig. 3 curves are consistent with the proposed ansatz.

Umezawa and Nagashima [22] present data for  $p \simeq 10$  MPa with  $CO_2$  as solvent and alkane solutes with carbon number  $n = 5 - 14$ . This data is for  $T_r \approx 1$  and  $1.56 \leq \rho_r \leq 1.75$ . Although of considerable potential interest, use of this data faces difficulty due to lack of  $r_D$  values and possible question as to data accuracy ([7]). However, if  $r_D \sim \omega^{-1/2}$  ( $\omega$  of the alkane), then the data sets of [22] nearly overlap. This type of behavior for long chain molecules is not totally implausible ([5]); with the added assumption  $r_D \simeq 0.9$  for  $n = 5$ , the range of  $w_D$  values generally coincide with that in Fig. 2, although  $w_D$  increases strongly with  $\rho_r$ , not duplicating the dependency of Fig. 2 curves. Therefore, no conclusive results may be obtained with this data.

A recent comprehensive review of available high  $\rho$  diffusion data is that of [19]. About 80% of the data is for  $CO_2$  as the solvent. Much of the available data is for species that are not of primary interest for our ultimate purpose (highly polar species, esters, alcohols, etc.) and even when of interest, it is restricted to solvent  $1.0 \leq T_r \leq 1.1$ , with lower values dominant (see also [20]). Unfortunately, as noted before, this leads to possible difficulty in use of the data due to potential accuracy problems with  $V$  values, and also due to ambiguity in the values of  $\alpha_D$  (not being 1). This is unfortunate since Liu and Ruckenstein [7] show that when the chemical potential effect is considered in the diffusion coefficient (equivalent to our  $\alpha_{Dij}D_{ij}$ ), the correlation of data is much improved. Difficulties in accurate  $\phi$  and  $\alpha_D$  calculations, especially for near critical solvents and/or polar species, are discussed in Chapter 5 of [14]. The effect of  $\alpha_D$  values for benzene in  $CO_2$  is discussed in detail by [15], [16] who make rough estimates of  $\alpha_D$  based on Peng-Robinson or BWR EOS; large variations in  $\alpha_{Dij}D_{ij}$  are possible for  $p < 10$  MPa ( $\rho_r \lesssim 1$ ). These variations depend strongly on both the trace mole fraction and binary interaction parameter used in the EOS. The [15], [16] studies show that there is an injected quantity of solute threshold ( $\approx 1\mu l$  in their experiment) above which reduction of  $\alpha_D$  below 1 is estimated to be significant, which may lead to some very small measured  $D_{ij}^o$ .

Figure 4 presents  $w_D$  values for trace acetone in  $CO_2$  calculated using data from [4], [22] and [24]. In [24] the injected quantity is  $0.5\mu l$  and our estimated solute threshold is lower by a factor of  $\approx 2$  compared with [15], [16] because the  $CO_2$  flow rate is lower by the same factor. Only data for  $p \geq 9$  MPa are used from [24] since data fitting error and  $\rho$  fluctuations are large at lower  $p$ 's. The variation of  $\delta_D$  for  $\rho_r > 1.5$  (see Fig. 4) is well described by the curve  $\delta_D = 0.05\rho_r^{3.2}$ .

One relevant species pair for which there is considerable amount of data available is benzene in  $CO_2$ . The  $w_D$  results are presented in Fig. 5. Data from [16] is for  $0.7\mu l$  of injected solute and  $p > 9$  MPa. The effect of injected quantity of solute on measured  $D_{ij}^o$  is exhibited in [4] and [15]. The scatter is large: as much as 15% for one data set at given  $\rho_r$  and  $T_r$ , and even larger across data sets. Curve  $\delta_D = 0.06\rho_r^{3.2}$  emulates the variation for acetone in  $CO_2$ , whereas  $\delta_D = 0.23\rho_r^{0.83}$  emulates the variation with  $He$  as the solvent (Figs. 2 and 3). For  $\rho_r > 1$ , the variation (but not the value) of  $w_D$  for each of the diverse data sets roughly corresponds to one of these curves. The mean variation is thus approximately  $\delta_D \approx 0.12\rho_r^2$ . The unreasonably large  $w_D$  values for  $\rho_r < 1$  result from data of [25]. Assumed accurate  $V$  values of  $CO_2$ , taken from the NIST Chemistry WebBook, were used in this calculation, however, reductions in  $V$  would decrease  $w_D$  and increase  $\rho_r$ . Also, if  $\alpha_D \approx 0.7$ , this would shift (multiply) the  $w_D$  values for  $\rho_r < 1$  to lower values (the expected behavior). This is consistent with values of  $\alpha_D$  estimated in [15]. Finally, it is possible that the data is in error. Using the SE expression to fit the data does not resolve the apparent dis-

crepancy, as the resulting scattering length for  $\rho_r < 1$  is similarly larger than that for  $\rho_r > 1$ . No significant correlation of  $w_D$  values with  $T_r$  is apparent, although  $1 \leq T_r \leq 1.1$ , making this lack of correlation subject to future scrutiny. Overall, the scatter could have a partial explanation if different amounts of trace benzene were used in the different data sets, possibly yielding diverse  $\alpha_D$  values (below 1) and effective diffusivities. Obviously, more data, carefully obtained (especially at larger values of  $T_r$ ), would be useful.

The last data sets to be examined involve hydrocarbons for both solvent and solute. Included are octene ( $C_8H_{16}$ ) solute in solvents ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ) and hexane ( $C_6H_{14}$ ) from [26], octene in ethane from [27] and benzene ( $C_6H_6$ ), toluene ( $C_7H_8$ ) and naphthalene ( $C_{10}H_8$ ) in hexane from [28]. Values of  $r_D$  are not available, hence only  $r_D w_D$  is here determined. However,  $r_D w_D$  values for octene in ethane or propane at smaller  $\rho_r$  suggest that  $r_D \approx 2$ ;  $r_D = 2$  is adopted here for all species pairs. The resulting values of  $w_D$  are plotted in Fig. 6, along with a 'reference' curve  $w_D = [2 + \exp(-4.7\rho_r^3)]/3$  that qualitatively describes the overall behavior (most deviations  $\lesssim 10\%$ ). The data indicate a negative  $\delta_D$  with minimum  $r_D w_D = 1.0$ ; the scatter in Fig. 6 could be considerably reduced with appropriate values of  $r_D$  or  $w_D$  at large  $\rho_r$  (e.g. for  $r_D = 2$  as in Fig. 6, the asymptotic  $w_D \approx 0.9 - 0.8\omega_{solute}$ ). Having  $r_D \approx 2$  is consistent with the asymmetric, non-simple hydrocarbon molecules becoming 'entangled' (steric effect), increasing the collision cross-section, with consequent reduced diffusion. The decrease in  $w_D$  ( $\delta_D < 0$ ) could possibly then result from a forced molecular alignment ('semi-crystallization') due to packing at the higher  $\rho$ 's, leading to easier slippage of the solute molecules in the solvent. Note that octene in propane or hexane show a minimum in  $w_D$  in the vicinity of  $\rho_r \approx 1.2 - 1.3$ ; the other pairs show a leveling of  $w_D$  values at larger  $\rho_r$ . The appearance of a minimum mirrors the maximums of alkanes in  $He$  as shown in Fig. 2. Use of the SE expression to fit the data (for all  $r_s$  unity) yields a solvent  $\beta = 0.64$  for octene in ethane ( $\pm 10\%$  scatter),  $0.96$  for octene in hexane ( $\pm 7\%$  scatter) and  $0.80$  for the other pairs ( $\pm 15\%$  scatter). Setting  $r_s = 0.83$  for octene gives a consistent set of values,  $\beta = 0.53, 0.67, 0.80$  for ethane, propane, hexane respectively. For a given fit,  $\beta \propto (r_s)_{solute}$ . These values are different from those of liquids, which would be near 1. The small  $\beta$  correspond to large  $r_D$ . The accuracy of this approach is not superior to the modified KT one, especially with optimized  $r_D$  and/or asymptotic  $w_D$ . Its main drawback is the lack of uniform validity for all values of  $\rho_r$ .

From the available data, the ansatz of a generic form for  $\delta_D$  may apply for distinct classes of solvent-solute pairs, as follows:

When both solute and solvent are hydrocarbons, it appears that  $r_D \approx 2$  and  $w_D \leq 1$  (with a form similar to the reference curve of Fig. 6). It also seems possible that the (level) value of  $w_D$  for  $\rho_r > 1$  may depend on solute molecular weight or  $\omega$ ; more data are required.

For other solvent-solute pairs, the form  $\delta_D = c\rho_r^b$  seems adequate; no dependency on  $T_r$  is evident. For a light solute ( $H_2$ ,  $He$ ), the data is well fit for  $b = 3/2$ ; for  $H_2$  in  $O_2$  (rocket motor models),  $c \simeq 0.58$ . For a light solvent,  $b = 0.83$  where  $c \simeq 0.20 - 0.23$  for hydrocarbon solutes (with a possible decrease at extreme  $p$ ) and  $c \simeq 0.18$  for other solutes. For hydrocarbon solutes in air or combustion product solvents, reliance on the benzene in  $CO_2$  data suggests that  $\delta_D \approx 0.12\rho_r^2$ . This is a crude estimate; however, for conditions of interest  $\rho_r \leq 1$  and errors in  $w_D$  values will be relatively minor.

Lastly, for air or combustion products in hydrocarbons, no information is available. Fortunately, the solubility of these solutes in liquid-like hydrocarbons (i.e.  $\rho_r > 1$ ) is low and their mass fractions in such a mixture will be quite small. Thus, errors from ignorance of  $\delta_D$  values will probably have little effect on any model studies. For simplicity, convenience and caution (it is desirable to have minimal  $\delta_D$  at large  $\rho_r$ ), a linear  $\delta_D \approx 0.2\rho_r$  may be used.

Data scarcity and scatter make this ansatz provisional. Clearly more data is needed, especially for solvents with  $T_r$  well above 1 (e.g.  $N_2$ ). When the solute and/or solvent is a heavier hydrocarbon, more information on  $r_D$  values is also needed. Expected error in  $D_{ij}$  estimates is in the range 5 - 30%. Typical errors are probably 10 - 15% or less. Finally, the information derived herein can be used for multicomponent mixtures, as mixing rules give relevant diffusivities in terms of the binary coefficients (e.g. [6]).

### Summary and conclusions

An ansatz for a calculating high pressure diffusion coefficients has been derived by recasting low pressure gas relationships in a corresponding states form, which is extended at high pressures through a general dependency on the reduced density. Using available data from the literature, correlations were obtained, yielding specific dependencies on the reduced density for different classes of binary species systems. Typical errors in these correlations are  $\simeq 10 - 15\%$ , and with a range of 5 - 30%.

### ACKNOWLEDGMENT

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### References

- [1] Okong'o, N. and Bellan, J., Direct Numerical Simulation of a transitional supercritical mixing layer: heptane and nitrogen, *J. Fluid Mech.*, 464:1 (2002)
- [2] Rosner, D., *Transport Processes in Chemically Reacting Flow Systems*, Dover Publications, 2000
- [3] Reid, R. C., Prausnitz J. M. and Poling, B. E., *The Properties of Gases & Liquids*, (4th edition), McGraw-Hill Book Co., NY, 1987
- [4] Sassi, P. R., Mourier, P. Caude, M. H. and Rosset, R. H., Measurement of diffusion coefficients in supercritical carbon dioxide and correlation with the equation of Wilke and Chang, *Anal. Chem.*, 59:1164 (1987)
- [5] Liang, K. K., Wells, P. A. and Foster, N. R., Diffusion in supercritical fluids, *J. Supercrit. Fl.*, 4(2):91 (1991)
- [6] Hirschfelder, J. O., Curtiss, C. F. and Bird, R. B., *Molecular Theory of Gases and Liquids*, John Wiley and Sons, NY, 1954
- [7] Liu, H. and Ruckenstein, E., Predicting the diffusion coefficients in supercritical fluids, *Ind. Eng. Chem. Res.*, 36:888 (1997)
- [8] Ern, A. and Giovangigli, V., Structure of linear transport systems in dilute isotopic gas mixtures, *Phys. Rev. E.*, 53(1):485 (1996)
- [9] Paul, P. and Warnatz, J., A re-evaluation of the means used to calculate transport properties in reacting flows, *Proc. Comb. Inst.*, 27:495 (1998)
- [10] Bzowski, J., Kestin, E. A. Mason and Uribe, F. J., Equilibrium and transport properties of gas mixtures a low density: eleven polyatomic gases and five noble gases, *J. Phys. Chem. Ref. Data*, 19(5):1179 (1990)
- [11] Maynard, V. R. and Grushka, E., Measurement of diffusion coefficients by gas chromatography broadening techniques: a review, *Adv. in Chromatogr.*, 12: 99 (1975)
- [12] Taylor, W. L., Hurly, J. J., Meyer, B. A. and Dunlop, P. J., Binary diffusion coefficients of helium/hydrogen isotope mixtures, *J. Chem. Phys.*, 103:6959 (1995)
- [13] Tyn, M. T. and Calus, W. F., Diffusion coefficients in dilute binary liquid mixtures, *J. Chem. Eng. Data*, 20(1):106 (1975)
- [14] Prausnitz, J. M., Lichtenthaler, R. N. and de Azevedo, E. G., *Molecular Thermodynamics of Fluid-phase Equilibria*, (2nd edition) Prentice-Hall Inc., Englewood Cliffs, NJ, 1986
- [15] Ago, K. and Nishiumi, H., Calculation of mutual diffusion coefficients near the critical region from the Peng-Robinson equation of state, *Ind. Eng. Chem. Res.*, 37:1692 (1998)
- [16] Ago, K. and Nishiumi, H., Mutual diffusion coefficients of benzene in supercritical carbon dioxide, *J. Chem. Eng. Japan*, 32(5):563 (1999)
- [17] Vignes, A., Diffusion in binary solutions, *Ind. Eng. Chem. Fundam.*, 5(2):189 (1966)

- [18] Hu, A. T.-C. and Kobayashi, R., Measurements of gaseous diffusion coefficients for dilute and moderately dense gases by perturbation chromatography, *J. Chem. Engr. Data*, 15:328 (1970)
- [19] Suarez, J. J., Medina, I. and Bueno, J. L., Diffusion coefficients in supercritical fluids: available data and graphical correlations, *Fl. Phase Equilibria*, 153:167 (1998)
- [20] Catchpole, O. J. and King, M. B., Measurement and correlation of binary diffusion coefficients near critical fluids, *Ind. Eng. Chem. Res.*, 33:1828 (1994)
- [21] Suarez, J. J., Bueno, J. L. and Medina, I., Determination of binary diffusion coefficients of benzene and derivatives in supercritical carbon dioxide, *Chem. Engr. Science*, 48(13):2419 (1993)
- [22] Umezawa, S. and Nagashima, A., Measurement of the diffusion coefficients of acetone, benzene, and alkane in supercritical  $CO_2$  by the Taylor dispersion method, *J. Supercrit. Fl.*, 5(4):242 (1992)
- [23] Balenovic, Z., Myers, M. N. and Giddings, J. C., Binary diffusion in dense gases to 1360atm by the chromatographic peak-broadening method, *J. Chem. Phys.*, 52(2):915 (1970)
- [24] Funazukuri, T., Kong, C. Y. and Kagei, S., Binary diffusion coefficients of acetone in carbon dioxide at 308.2 and 313.2K in the pressure range from 7.9 to 40 MPa, *Int. J. Thermophysics*, 21(3):651 (2000)
- [25] Swaid, I. and Schneider, G. M., Determination of binary diffusion-coefficients of benzene and some alkylbenzenes in supercritical  $CO_2$  between 308-K and 328-K in the pressure range 80-bar to 160-bar with supercritical fluid chromatography (SFC), *Ber. Bunsenges Phys. Chem.*, 83:969 (1979)
- [26] Eaton, A. P. and Akgerman, A., Infinite dilution diffusion coefficients in supercritical fluids, *Ind. Eng. Chem. Res.*, 36:923 (1997)
- [27] Noel, J. M., Erkey, C., Bukur, D. B. and Akgerman, A., Infinite dilution mutual diffusion-coefficients of 1-octene and 1-tetradecene in near-critical ethane and propane, *J. Chem. Eng. Data*, 39(4):920 (1994)
- [28] Sun, C. K. and Chen, S. H., Tracer diffusion of aromatic-hydrocarbons in normal-hexane up to the supercritical region, *Chem. Eng. Science*, 40:2217 (1985)
- [29] Funazukuri, T., Ishiwata, Y. and Wakao, N., Predictive correlation for binary diffusion-coefficients in dense carbon-dioxide, *AIChE J.*, 38:1761 (1992)
- [30] Levelt-Sengers, J. M. H., Deiters, U. K., Klask, U., Swidersky, P. and Schneider, G. M., Application of the Taylor dispersion method in supercritical fluids, *Int. J. Thermophysics*, 14:893 (1993)
- [31] Harstad, K. and Bellan, J., An all-pressure fluid drop model applied to a binary mixture: heptane in nitrogen, *Int. J. of Multiphase Flow*, 26(10):1675 (2000)
- [32] Harstad, K. and Bellan, J., The d2 variation for isolated LOX drops and polydisperse clusters in hydrogen at high temperature and pressures, *Combustion and Flame*, 124:535 (2001)
- [33] Harstad, K. and Bellan, J., Evaluation of commonly used assumptions for isolated and cluster heptane drops in nitrogen at all pressures, *Combustion and Flame*, 127(1 - 2):1861 (2001)

Specie pairs	$r_D$	Approx. error
$He - H_2$	0.86	+0.005, -0.01
$He - O_2$	0.93	+0.03, -0.01
$He, H_2 - N_2, Ar$	0.93	+0.03, -0.02
$He, H_2 - CH_4$	0.92	+0.02, -0.02
$He, H_2 - C_2H_6$	1.0	
$He, H_2 - C_4H_{10}$	1.045	+0.015, -0.04
$He, H_2 - C_5H_{12}, C_6H_{14}$	1.1	+0.1, -0.1
$He, H_2 - CO_2$	0.96	+0.02, -0.02
$He, H_2 - H_2O$	0.82	+0.01, -0.02
$N_2 - O_2$	0.92	+0.01, -0.01
$N_2, O_2 - H_2O$	0.82	+0.0, -0.02
$CO_2 - H_2O$	0.93	+0.01, -0.03
$N_2 - CO_2$	0.89; 1.0	[6; 3 points]
$N_2, Ar - Alkane (n = 4-6)$	1.0	+0.08, -0.08
$N_2 - C_6H_6, C_3H_6O$	1.02	+0.03, -0.02
$Ar - C_6H_6, C_3H_6O$	0.87	+0.04, -0.02
$CO_2 - C_6H_6, C_3H_6O$	0.90	+0.02, -0.04

Table 1: Diffusivity Normalization Constants.

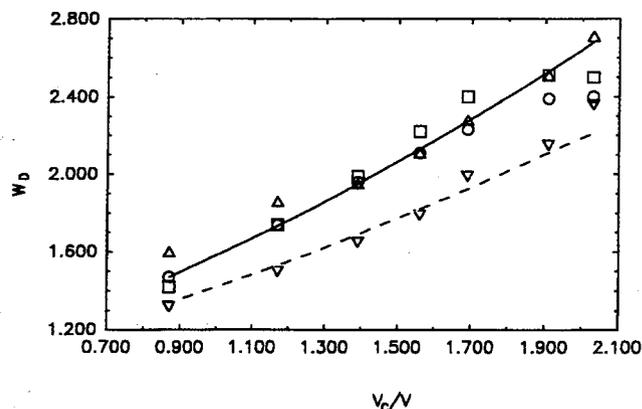
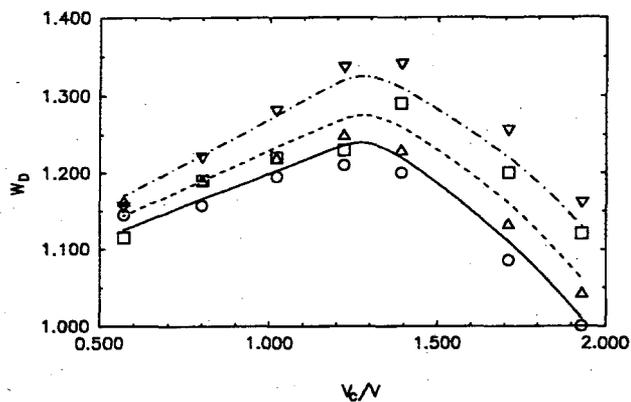
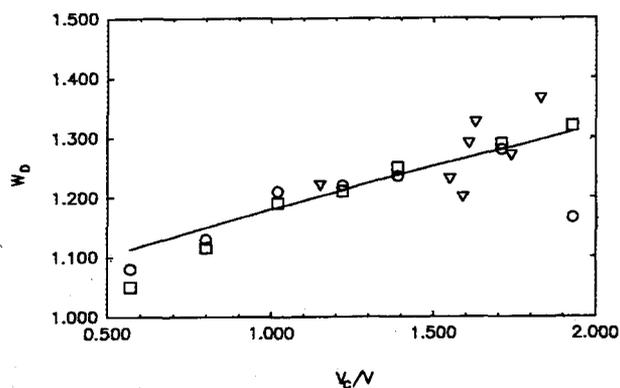


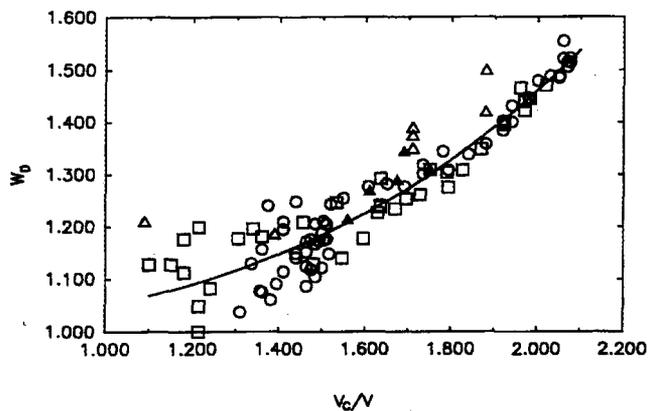
Figure 1:  $w_D$  vs.  $\rho_r = V_c/V$  for light solutes. Data from [23]:  $\circ$  for  $N_2 - H_2$ ;  $\square$  for  $N_2 - He$ ;  $\triangle$  for  $Ar - H_2$ ;  $\nabla$  for  $Ar - He$ . Curves for  $\delta_D = c\rho_r^{3/2}$ ,  $c = 0.42, 0.58$ , see text.



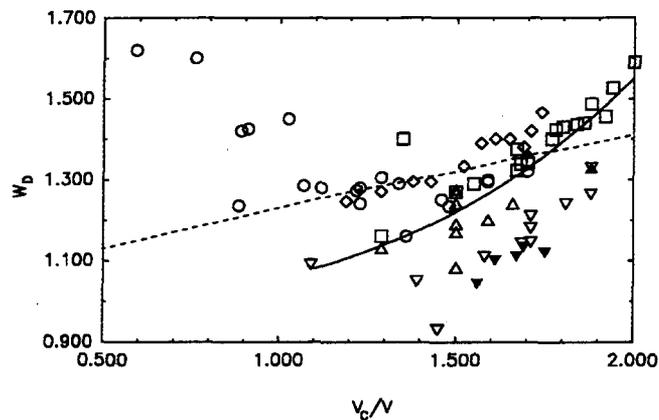
**Figure 2:**  $w_D$  vs.  $\rho_r = V_c/V$  for carbon based solutes in  $He$ . Data from [23]:  $\nabla$  for  $CH_4$ ;  $\triangle$  for  $C_2H_6$ ;  $\circ$  for  $C_3H_8, C_4H_{10}$ ;  $\square$  for  $CF_4$ . Curves for  $\delta_D = c\rho_r^{0.83}$  with variable  $c$ , see text: --- corresponds to  $\nabla$ ; -.- corresponds to  $\triangle$ ; — corresponds to  $\circ$ .



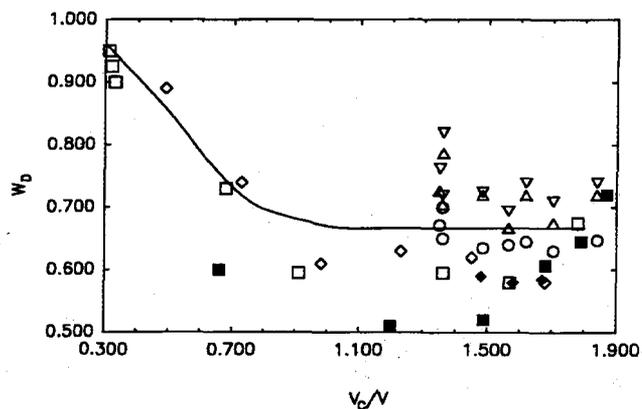
**Figure 3:**  $w_D$  vs.  $\rho_r = V_c/V$  for  $N_2$  and  $Ar$  in  $He$ , benzoic acid in  $CO_2$ . See text for data sources:  $\circ$  for  $He - N_2$ ;  $\square$  for  $He - Ar$ ;  $\nabla$  for  $CO_2 - C_7H_6O_2$ . Curve is for  $\delta_D = 0.18\rho_r^{0.83}$ .



**Figure 4:**  $w_D$  vs.  $\rho_r = V_c/V$  for acetone in  $CO_2$ . Data sources: [24]  $\circ$  for  $T = 308.2K$ ,  $\square$  for  $T = 313.2K$ ; [4]  $\triangle$ ; [22]  $\blacktriangle$ . Curve is for  $\delta_D = 0.05\rho_r^{3.2}$ .



**Figure 5:**  $w_D$  vs.  $\rho_r = V_c/V$  for benzene in  $CO_2$ . Data sources: [25]  $\circ$ ; [4]  $\nabla$ ; [30]  $\triangle$ ; [21]  $\square$ ; [22]  $\blacktriangledown$ ; [29]  $\blacktriangle$ ; [16]  $\diamond$ . Dashed curve is for  $\delta_D = 0.23\rho_r^{0.83}$ . Solid curve is for  $\delta_D = 0.06\rho_r^{3.2}$ .



**Figure 6:**  $w_D$  vs.  $\rho_r = V_c/V$  for hydrocarbon solvents and solutes,  $r_D = 2$ . See text for data sources and equation of reference curve.  $\diamond, \blacklozenge$  ethane - octene ( $\blacklozenge$  is data from [27]),  $\square$  propane - octene,  $\blacksquare$  hexane - octene,  $\nabla$  hexane - benzene,  $\triangle$  hexane - toluene,  $\circ$  hexane - naphtalene.