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Soret-Modified Hydrocarbon Mass Transport Across Compressed Nonisothermal Gases

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While engineering methods employed to predict mass transport rates across carrier fluids are often limited to either ideal gas mixtures or constant density liquids, we deal here with species mass transport across nonisothermal compressed gas "films", with special reference to hydrocarbon fuel vapor transport across nonisothermal N_2 or H_2O boundary layers at pressures up to ca. 300 atm, and at temperatures often above 1000 K. We show that because of the pressure sensitivity of the Soret factor (which quantifies the relative importance of mass transfer due to temperature gradients compared to that due to concentration gradients) mass transfer coefficients become far more sensitive to pressure level than would have been anticipated from the pressure sensitivity of ρD_{12}^{∞}. Motivated, in part, by combustion applications, we first examine the expected pressure dependence of the binary Soret factor, $\alpha_{T,12}$ for each of the n-alkanes (CH_4 to $C_{20}H_{42}$) dilute in compressed N_2 or H_2O, exploiting a rational formulation for "correcting" Chapman-Enskog-derived Soret factors ($\alpha_{T,12}^{0}$) to higher pressures based on the Thermodynamics of Irreversible Processes (TIP) combined with a Virial Equation of State (VES). Our TIP-VES-predicted Soret factors are used to demonstrate the pressure sensitivity of expected "Soret-modified" mass transfer coefficients (Sherwood numbers) for the illustrative case of $C_{12}H_{26}(g)$ transport across $N_2(g)$ at temperature ratios between 0.3 ("cold"-wall) and 2.0 ("hot"-wall) at pressures up to 300 atm. Because of the growing importance of compact, high-pressure systems in fields beside combustion, including supercritical fluid extraction and even distillation, our present results suggest that reliable mass transfer rate predictions in nonisothermal dense vapor systems of engineering importance will generally ***require*** *systematic inclusion of non-Fickian molecular mass transport.* *AIChE J*, 53: 1879–1890, 2007

Keywords: Soret mass transport, Soret factor, irreversible thermodynamics, hydrocarbon vapor diffusion, compressed nonisothermal gases

Introduction

In a previous article (Rosner et al.[1]) Chapman-Enskog gas kinetic theory was used to develop a convenient Soret factor estimation procedure for dilute mixtures of *n*-alkane fuel vapors in N_2 (or air) in the familiar ideal gas (IG-) limit. But, because of practical interest in combustion at high pressures (see, e.g. Refs. 2–5), and the fact that measurements in analogous systems have often demonstrated an appreciable rise in Soret factor (defined by Eq. 22 below) with increasing pressure (see, e.g., the data surveys in Refs. 6–8, we consider here the expected increase in Soret factor associated with

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such mixtures when compressed to pressures up to/above 100 atm—well above the thermodynamic critical pressures of these fuels. Since it is already known that fuel vapor Soret transport effects are important in many near-atmospheric pressure air-breathing combustion systems[1] (see also *Combustion and Flame*. Arias-Zugasti M, Rosner DE, Submitted for publication) this study takes on added practical urgency. For our rational estimates we adopt/exploit the convenient formalism of the Thermodynamics of Irreversible Processes (TIP) (see, e.g., Haase,[7] Oost et al.,[6] de Groot,[9] Kempers,[10,11] Rutherford[12] and Gonzalez-Bagnoli et al.[13]) which has been demonstrated to capture the principal effects of pressure on experimentally observed $\alpha_{T,12}$ values, at least for "simpler" binaries at $T < 410$ K and $p < 80$ atm. Because of our present interest in *n*-alkane vapors in the "solvents" N_2 and H_2O at combustion temperatures, and the considerable benefit of rigorous mixing "rules", we deliberately invoke the "virial equation of state" (hereafter VES) with binary-encounter coefficients $B_{ij}(T)$ evaluated for molecules obeying a Lennard-Jones (LJ) 12:6 intermolecular potential (for the alkane-N_2 cases), generalized to include the effects of a "polar" solvent (for the *n*-alkane/H_2O cases). Remarkably, at this level of approximation, we find that the predicted increment in Soret factor $\Delta\alpha_{T,12} \equiv \alpha_{T,12} - \alpha^0_{T,12}$ (above the IG-[or low pressure asymptote-] value) is strictly linear in pressure, with a slope easily calculated from a particular weighted sum of two dimensionless Joule-Thomson coefficients (accurate tabular values of which [written T^* $(dB^*/dT^*) - B^*$] are readily available, see, e.g., Hirschfelder et al.[14]). A convenient curve-fit to these values is used to generate our present numerical estimates, applicable to C_nH_{2n+2} hydrocarbons between CH_4 (methane) and $C_{20}H_{42}$ (eicosane) dilute in N_2 (or air) for $300 < T < 2000$ K and pressures up to 300 atm (30.4 MPa), or C_nH_{2n+2} dilute in H_2O(g) above ca. 700 K. Our effective LJ-parameters above nonane ($n = 9$) are based on a rational "corresponding-states"-based extrapolation method, but these values, which should be regarded as provisional, can readily be altered if/when trustworthy data become available.

It is interesting and important to note that even subject to the constraints imposed by accuracy of the VES truncated at the "binary interaction" level, we find that the pressure-corrections to a transport property like the binary Soret factor can be/often are over an order of magnitude in the dilute limit, especially at "low" or moderate (intermediate) temperatures. This is not the case for many other thermophysical properties of the system, such as the thermal conductivity or product of the "solvent" density with the binary diffusivity in the dilute limit, D^{∞}_{12}. We conclude this paper by showing that Soret-modified solute diffusion rates "inherit" this notable pressure sensitivity when predicting mass transport across such nonisothermal, nonideal vapor mixtures, illustrating this for the particular case of dodecane vapor transport across nonisothermal N_2-"films" representing boundary layers at temperature ratios between 0.3 ("cold" wall) and 2.0 ("hot" wall), at pressures up to 300 atm. We conclude that such effects are likely to be encountered in many nonisothermal extractions carried out using supercritical "solvents" like CO_2 and/or mixtures thereof.

In the course of our analysis we also: (a) illustrate a graphical construction on the B^* versus T^* plane which provides insight as to when the pressure sensitivity of the Soret factor will be large (or small)-and when/how the Soret factor increment will depend sensitively on solute molecular properties (mass, size and energy-well), and (b) indicate how to generalize these results to nondilute binary-, and ultimately, multicomponent systems. We conclude with a discussion of likely accuracy and upper bounds to the pressure level to ensure self-consistency of the present predictive model.

TIP + VES "Extrapolation" of Ideal Gas Soret Factors to Elevated Pressures

While Chapman-Enskog (CE-) gas kinetic theory provides a reasonable basis for predicting binary Soret factors for quasi-spherical molecules in the ideal gas state (see, e.g., Refs. 1, 14, and 15) (see also *Combustion and Flame*. Arias-Zugasti M, Rosner DE, Submitted for publication), our present interest lies in compressed gas environments for which the assumptions underlying CE theory break down. Fortunately, however, Haase et al.[7,16] and Oost et al.[6] have shown that the formalism of TIP (de Groot[9]) can be used to provide a rational, if approximate, method to extrapolate ideal gas (IG-) values of α_T, written α^0_T, to elevated pressures by correcting for thermodynamic nonideality using a suitable equation of state (EOS). While most of the systems treated by these authors (see, e.g. the experimental data of Becker[17] summarized in Fig. 9.1–3 of Hirschfelder et al.[14]) were near equi-molar binary mixtures of "simple" polyatomics or noble gases at temperatures below 410 K and pressures below 80 atm, it is encouraging and significant that this approach has been able to rationalize the large pressure sensitivity exhibited by $\alpha_{T,12}$ in some nondilute systems (e.g. for C_3H_8/CH_4, with $yC_3H_8 = 0.66$, $T = 346.1$ K, the experimental Soret factor increases by ca. 2.5 *orders of magnitude* in going to "only" ca. 50 atm-or the *drop* in $\alpha_{T,12}$ exhibited by the N_2/CH_4 system (see Becker[17]).

For our present purposes we have adopted the TIP-formulation of Haase,[7] according to which the binary Soret factor, $\alpha_{T,12} = \alpha_{T,12}(T;\ p,\ y_1)$, can be written (in our present notation):

$$\alpha_{T,12} = \frac{\alpha^0_{T,12} + \frac{M_1}{M_{\mathrm{mix}}}\frac{H_2 - H^0_2}{\mathcal{R}T} - \frac{M_2}{M_{\mathrm{mix}}}\frac{H_1 - H^0_1}{\mathcal{R}T}}{\frac{y_2}{\mathcal{R}T}\frac{\partial\mu_2}{\partial y_2}} \qquad (1)$$

Here $H_i - H_i^0$ (with $i = 1, 2$) are the nonideal corrections to the partial specific enthalpies of the vapor constituents, and the indicated derivative of the Species 2 chemical potential, $\partial\mu_2/\partial y_2$ must also be evaluated using a suitable EOS.

Virial EOS in the Limit of Infinite-Dilution

In nearly all "air-breathing" combustion applications the vapors N_2 and/or H_2O are prominent, and, moreover, temperatures and pressures are such that the so-called virial equation of state (VES), truncated at the "binary interaction" level, is quite adequate (especially in the limit $y_1 \ll 1$). This is fortunate since we are then able to invoke the rigorous mixing rule:

$$B_{\mathrm{mix}}(T) = y_1^2 B_{11}(T) + 2y_1 y_2 B_{12}(T) + y_2^2 B_{22}(T) \tag{2}$$

where B_{mix} is defined by the truncated EOS (quadratic in V):

$$\frac{pV}{\mathcal{R}T} = 1 + \frac{B}{V} \tag{3}$$

Perhaps even more important for our present work, the binary virial coefficients, $B_{ij}(T)$, can be related to binary molecular interactions according to a well-defined intermolecular potential (see e.g. Mason and Spurling[18] and Hirschfelder et al.[14]). Here, even for interactions involving long-chain n-alkane molecules, we adopt the familiar Lennard-Jones (LJ) potential, generalized (via the Stockmayer term) to include the effects of a permanent dipole moment (for the case of the "solvent" H_2O). It will be convenient to work with a dimensionless virial coefficient, $B^*_{ij}(T^*, t^*)$ defined by:

$$B_{ij}(T, \mu_i, \mu_j, \ldots) = b_{0ij} \cdot B^*_{ij}(T^*, t^*) \tag{4}$$

where we have factored out the characteristic molar volume defined by the cube of the LJ size (diameter) parameter b_{0ij}:

$$b_{0ij} = \frac{2\pi}{3} \sigma_{ij}^3 \cdot N_A \tag{5}$$

where, in general, $T^* = k_B T/\varepsilon_{ij}$. The second argument, t^*, is a dimensionless dipole moment (nonzero for polar-polar interactions), and numerical values of the function B^*_{ij} are provided in Hirschfelder et al.[14] Because of the appearance of $H_i - H_i^0$ in Eq. 1, we will also need the linear combination:

$$J^* \equiv B^* - T^* \frac{dB^*}{dT^*} \tag{6}$$

which we abbreviate as J^* since this particular combination determines the behavior of the Joule-Thomson coefficient of pure substances in the low-pressure limit. (Indeed, best-fit values of the LJ-Stockmayer parameters are sometimes inferred from the behavior of J^* rather than B^* itself.) We will also exploit the "geometric" significance of J^* as the intercept (see Figure 1) of a tangent to B^* on a linear B^* versus T^* plot.

Explicitly, in the dilute solute, VES limit we find:

$$H_2 - H_2^0 = p \cdot J_{22} \tag{7}$$

whereas:

$$H_1 - H_1^0 = p \cdot \left(J_{11} + \delta_{12} - T \frac{d\delta_{12}}{dT} \right) \tag{8}$$

where

$$\delta_{12} \equiv 2B_{12} - (B_{11} + B_{22}) \tag{9}$$

We conclude this section by noting that, consistent with VES in the dilute solute limit ($y_1 \ll 1$, $y_2 \simeq 1$, the chemical potential derivative appearing in Eq. 1 can be shown to be simply $\mathcal{R}T$.

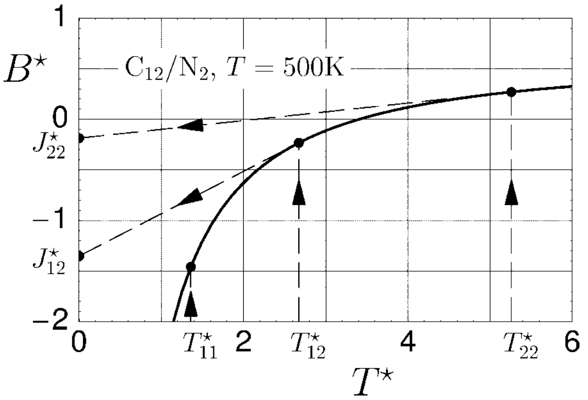

Figure 1. Graphical construction on $B^*(T^*;t^*)$ plane for $C_{12}H_{26}$ dilute in N_2 at T = 500 K; see Eq. 11.

TIP-VES ($y_1 \ll 1$) Relation Between $\Delta\alpha_{T,12}/p$ and Joule-Thomson Coefficients; Evaluation of Dimensionless J^* and Graphical Representation

Combining the results quoted above leads to a particularly transparent form of Eq. 1, viz.:

$$\alpha_{T,12} = \alpha^0_{T,12} + \Delta\alpha_{T,12} \tag{10}$$

where the T-dependent "increment in $\alpha_{T,12}$ per unit pressure (atm)" is now found to be simply:

$$\frac{\Delta\alpha_{T,12}}{p[\mathrm{atm}]} = \frac{E_{22}}{T^*} \cdot \left[\left(1 + \frac{M_1}{M_2}\right) \cdot J^*(T^*, t^*_{22}) - 2 \cdot \left(\frac{\sigma_{12}}{\sigma_{22}}\right)^3 \cdot J^*\left(\frac{\varepsilon_{22}}{\varepsilon_{12}} T^*, t^*_{12}\right) \right] \tag{11}$$

where t^*_{22} is the dimensionless dipole moment of the host gas ($t^*_{22} = 0$ for N_2, $t^*_{22} \simeq 1.2$ for H_2O) and $t^*_{12} = 0$ for the n-alkanes. In the former expression E_{22} is the dimensionless ratio of energies

$$E_{22} = \frac{p_{ref} b_{0,22}}{N_A \varepsilon_{22}} \tag{12}$$

and $p_{ref} = 1.01325 \times 10^5$ Pa. For example, when N_2 is the "solvent" we find: $E_{22} = 1.1796 \times 10^{-2}$. Here, and in what follows, $T^* \equiv T_{22}{}^* = T/(\varepsilon_{22}/k_B)$.

We note that, to this level of approximation, the increment ($\Delta\alpha_{T,12}$) is strictly linearly proportional to the pressure, and $\Delta\alpha_{T,12}/p$ [atm] for $y_1 \ll 1$ depends only on the temperature through the pre-factor E_{22}/T^* and a weighted sum of two J^*-values, one evaluated at T^*, and one evaluated at the $\varepsilon_{22}/\varepsilon_{12}$-"shifted" dimensionless temperature: $(\varepsilon_{22}/\varepsilon_{12}) \cdot T^*$. Geometrically, these J^* values are seen to be intercepts on the ordinate of the linear B^* versus T^* plot, as displayed in Figure 1 for a particular (typical) case with a nonpolar solvent. The solute/solvent molecular weight ratio is seen to explicitly enter our calculation of $\Delta\alpha_{T,12}/p$ [atm] via the weighting factor: $1 + (M_1/M_2)$ of $J^*(T^*, t^*)$, where $t^* = 0$ for the nonpolar solvent N_2. Predictions using Eq. 11 for both n-alkane/N_2 and n-alkane/H_2O systems will be presented in Section "Predicted Soret Factors Increments ...". The engineering consequences of these pressure effects on $\alpha_{T,12}$ will be illustrated in Section "Net Mass Transfer Implications and Discussion", where we explicitly consider $C_{12}H_{26}$ diffusion rates across compressed nonisothermal N_2 "films".

Prediction of $\Delta\alpha_{T,12}/p$ for Nonpolar and Polar "Solvents"; LJ-S Parameters Used for the "Solvents" N_2, H_2O

Motivated by engineering applications in which N_2 or H_2O are dominant constituents, we focus below on these two representative "solvents", one nonpolar, and one strongly polar. (We remark in passing that, considering the importance of $H_2O(g)$ as a "ubiquitous" solvent, it is remarkable how few Soret factor *experimental data* are available for binary systems involving H_2O, at any pressure!)

Summarizing, once Lennard-Jones Stockmayer (LJ-S) parameters are estimated for the dilute solute (subscript 1) (one of the *n*-alkanes; Section "Property Estimates for the *n*-Alkanes up to Eicosane", below) and solvent (subscript 2) (N_2 or H_2O; this Section, below), Eq. 11 provides a rational estimate of the increment to $\alpha_{T,12}$ at any temperature, and at any pressure for which the VES remains a valid approximation. As discussed in Section "Domain of Validity of the VES ...", for N_2 above 300 K, this pressure limit is often above 300 atm-a value more than adequate to embrace the combustion applications we have in mind. The same can be said for H_2O above ca. 1000 K.

It remains to describe the procedure we adopted to calculate numerical values of the dimensionless Joule-Thomson intercepts: $J^*(T^*, t^*)$. Rather than a table "look-up" procedure interpolating the numerical values of $-J^*$ tabulated in Hirschfelder et al.,[14] we developed the following accurate 6-parameter curve-fit for $B^* = B^*(T^*, t^*)$, based on the following functional form

$$B^* = c_1 T^{*-c_2} \cdot \exp(c_3 T^{*-c_4}) \cdot (1 - c_5 T^{*-c_6}) \tag{13}$$

for the two relevant values of t^*-i.e., $t^* = 0$ (for N_2), and $t^* = 1.2$ (for H_2O).

The best-fit dimensionless parameters $c_1, c_2, \ldots, c_6$ appearing in this relation were found to be those presented in Table 1. J^*-values efficiently calculated in this manner (cf. Eq. 6) were found to be more than sufficiently accurate for our present purposes.

We conclude this section by providing the "solvent" LJ-S parameters selected for the present illustrative calculations. While several possible internally consistent sets of values for σ_{22}, ε_{22}, and t^* may be found in the literature, we adopted those extracted from VES and/or JT-data (as opposed to pure vapor viscosity data). These values, obtained from Hirschfelder et al.[14] Tables 3.10–1 and I-A, are collected in Table 2 for the two solvents explicitly considered here; viz. N_2 and H_2O.

Table 1. Parameters Used for the Universal Function B^* in Eq. 13 (LJ-S Intermolecular Potential [HCB[14]])

t^*	c_1	c_2	c_3	c_4	c_5	c_6
0.0	1.14784	0.186005	0.137538	1.61586	2.92910	0.876608
1.2	1.07818	0.179806	1.02774	2.14412	6.71635	1.20479

Table 2. Values Adopted for the Lennard-Jones Parameters σ and ε and Dimensionless Permanent Dipole Moment t^* of Nitrogen and Water Vapor

	Nitrogen (N_2)	Water (H_2O)
σ[nm]	0.370	0.265
ε/k_B [K]	95.05	380
t^*	0.0	1.2

Property Estimates for the *n*-Alkanes up to Eicosane

Critical constants and acentric factors for the n-*alkanes*

Turning our attention to the solute species of interest (chosen here to be one of the *n*-alkanes, C_nH_{2n+2} with $n \leq 20$), to make many of the transport calculations and estimates utilized here thermodynamic critical state parameters (i.e. p_c, V_c, T_c, Z_c and the Pitzer acentric factor ω) were necessary. For the higher carbon numbers, especially those above $n = 12$, even these remain somewhat controversial (see, e.g. Lemmon and Goodwin[19]). Given our transport-oriented objectives we selected those contained in the Yaws compendium,[20] which are reproduced (with a change in pressure and volume units) in our Table 3. In any case, such values provide the basis for many rational "corresponding-states"-based estimates of other properties, including extrapolations of known LJ-parameters (as done in Section "Estimated LJ Parameters and Polarizabilities", below).

Estimated LJ parameters and polarizabilities for n-*alkanes up to* $n = 20$

There have been many independent studies which have inferred LJ-parameters for the lower alkanes, say through C_9H_{20} (for a recent tabulation see the 2nd edition of Bird et al.[21]). An early critical evaluation was contained in Galloway and Sage,[22] which already called attention to useful regularities within this homologous series, as well as to the onset of systematic departures from simple "LJ-behavior" for large carbon numbers. If the simplest LJ combining rules for σ_{12} and ε_{12} are used, (often attributed to Lorentz and Bertholet, with σ_{12} being the *arithmetic mean* of σ_{11} and σ_{22}, and ε_{12} being the *geometric mean* of ε_{11} and ε_{22}) then even for nonpolar "solvents" there may be no single set of σ_{ii} and ε_{ii} "assignments" that will accurately predict all of the transport properties of interest to us between, say, 300 and 2000 K. This in itself is an interesting and important area of research, and we suspect that our present focus on the *binary Soret factor* (rather than viscosity or D_{12}) may actually prove to be helpful, since it is known that this coefficient is more sensitive to details of the intermolecular potential than other thermodynamic or transport properties. However, to proceed we have adopted what we consider to be a reasonable set of LJ σ_{ii} and ε_{ii}/k_B parameter-assignments for each of the *n*-alkanes up to $n = 20$, and we only briefly investigate the observable consequences of departing from the geometric-mean combining rule for interaction energy by invoking the "semi-theoretical" rule mentioned by Ferzinger and Kaper[15]:

$$\varepsilon_{ij}\sigma_{ij}^6 = \sqrt{\varepsilon_{ii}\sigma_{ii}^6 \cdot \varepsilon_{jj}\sigma_{jj}^6} \tag{14}$$

Table 3. Values Adopted for the Molecular Weight, Critical Constants, and Acentric Factors of the *n*-Alkanes (After Yaws[20])

	Critical constants							
n	Substance	Formula	*M* [kg/kmol]	V_c[m^3/kmol]	T_c[K]	p_c[atm]	Z_c	ω
1	Methane	CH_4	16.040	0.0993	190.6	45.44	0.288	0.011
2	Ethane	C_2H_6	30.070	0.1479	305.4	48.16	0.284	0.099
3	Propane	C_3H_8	44.096	0.2029	369.8	41.93	0.280	0.152
4	*n*-Butane	C_4H_{10}	58.120	0.2549	425.2	37.47	0.274	0.199
5	*n*-Pentane	C_5H_{12}	72.150	0.3123	469.7	33.25	0.269	0.249
6	*n*-Hexane	C_6H_{14}	86.177	0.3699	507.4	29.73	0.264	0.305
7	*n*-Heptane	C_7H_{16}	100.20	0.4319	540.3	27.00	0.263	0.351
8	*n*-Octane	C_8H_{18}	114.23	0.4921	568.8	24.54	0.259	0.396
9	*n*-Nonane	C_9H_{20}	128.26	0.5477	595.7	22.76	0.255	0.438
10	*n*-Decane	$C_{10}H_{22}$	142.28	0.6031	618.5	20.95	0.249	0.484
12	*n*-Dodecane	$C_{12}H_{26}$	170.23	0.7178	658.1	17.93	0.237	0.515
14	*n*-Tetradecane	$C_{14}H_{30}$	198.39	0.8428	692.4	16.00	0.237	0.662
16	*n*-Hexadecane	$C_{16}H_{34}$	226.45	0.9300	720.6	14.00	0.220	0.747
18	*n*-Octadecane	$C_{18}H_{38}$	254.48	1.070	745.3	11.98	0.210	0.795
20	*n*-Eicosane	$C_{20}H_{42}$	282.55	1.190	771.4	10.26	0.194	0.876

Values adopted for the molecular weight, critical constants and acentric factors of the *n*-alkanes (after Yaws[20]).

Nor have we gone the route of Sun and Teja[23,24] who actually recommend two energy parameters for each alkane based on their "variable ε_{ii}"- fit to experimental phase equilibrium data, and invoke an EOS with no less than 32 universal dimensionless parameters.

Regarding systematic departures from the arithmetic-mean combining rule for σ_{12}, while there is some agreement on the "sign" of such departures (cf., Sun and Teja,[23,24] and Pamies and Vega[25]), in our opinion not enough information is currently available to reliably incorporate this systematic effect into our present predictions.

Summarizing, in the spirit of Tee et al.,[26] we have simply assigned effective LJ sizes (σ_{ii} is the diameter given in nanometers) in accord with the correlation (dropping subscripts):

$$\sigma[\text{nm}] = 0.820 \cdot (1 + 0.270\omega) \cdot (V_c[\text{m3/kmol}])^{1/3} \tag{15}$$

and effective LJ-energy wells in accord with the ε_{ii}/k_B-correlation:

$$\varepsilon/k_B[\text{K}] = 0.761 \cdot (1 - 0.516\omega) \cdot T_c[\text{K}] \tag{16}$$

Actual values used for the figures below are collected in Table 4, where it is noticed that there appears to be a shallow local maximum in ε_{ii}/k_B near $n = 12$. However, as already mentioned in the Introduction, "our effective LJ-parameters above nonane ($n = 9$) are based on a rational "corresponding-states"-based extrapolation method, but these values, which should be regarded as provisional, can readily be altered if/when trustworthy data become available".

When the "solvent" is polar (as in the case of H_2O) the above mentioned LJ-numbers are not sufficient to predict the effective LJ-parameters σ_{12} and ε_{12} because each of the *n*-alkanes is "polarizable". As outlined in Hirschfelder et al.,[14] this causes a slight decrease (by the factor $\xi^{-1/6}$) in σ_{12}, and a significant increase (factor of ξ^2) in ε_{12}, depending on the magnitude of ξ, where:

$$\xi = 1 + \frac{\alpha^* t^*}{\sqrt{2}} \cdot \sqrt{\frac{\varepsilon_{22}}{\varepsilon_{11}}} \tag{17}$$

Here α^* is the dimensionless polarizability of the solute molecule (actual polarizability divided by σ_{11}^3) and t^* is the above mentioned dimensionless dipole moment of the solvent molecule. Otherwise, all necessary 1–2 collision integrals, and the corresponding dimensionless second virial coefficient B^*, are calculated using $t^* = 0.0$ tables. Accordingly, our present estimates of α^* for the *n*-alkanes are also included in Table 4. In this connection it is interesting to note that, while the dimensional polarizability of the *n*-alkanes undeniably increases in a regular fashion with carbon number (see, e.g., Table 13.2–3 of Hirschfelder et al.[14]), the dimensionless polarizability decreases with *n* in accord with our above mentioned σ_{ii}-assignments. All $\Delta\alpha_T/p$ [atm] results for the "solvent" H_2O in Section "Results for $\Delta\alpha_T/p$ for *n*-Alkanes in the Polar "Solvent" H_2O" are calculated using Eq. 17 and the above mentioned parameter assignments.

This completes a concise description of the method we developed/used to plausibly "project" IG-binary Soret factors (see, e.g. Rosner, et al.[1]) into the high pressure domain, both for nonpolar and polar "solvents". Results for the *n*-alkanes (up to eicosane) dilute in either compressed N_2 and H_2O are given in Section "Predicted Soret Factor "Increments" for *n*-Alkanes . . .". We then will illustrate (Section "Net Mass

Table 4. Values Adopted for the Lennard-Jones Parameters σ and ε and Dimensionless Polarizability α* of the *n*-Alkanes

	Lennard-Jones/Stockmayer parameters				
n	Substance	Formula	σ[nm]	ε/k_B [K]	$\alpha^* \times 10^2$
1	Methane	CH_4	0.381	144	4.88
2	Ethane	C_2H_6	0.445	221	4.90
3	Propane	C_3H_8	0.502	259	4.98
4	*n*-Butane	C_4H_{10}	0.548	290	4.93
5	*n*-Pentane	C_5H_{12}	0.594	311	4.74
6	*n*-Hexane	C_6H_{14}	0.637	325	4.52
7	*n*-Heptane	C_7H_{16}	0.679	337	4.32
8	*n*-Octane	C_8H_{18}	0.717	344	4.15
9	*n*-Nonane	C_9H_{20}	0.751	351	4.07
10	*n*-Decane	$C_{10}H_{22}$	0.784	353	3.95
12	*n*-Dodecane	$C_{12}H_{26}$	0.837	368	3.87
14	*n*-Tetradecane	$C_{14}H_{30}$	0.913	347	3.45
16	*n*-Hexadecane	$C_{16}H_{34}$	0.962	337	3.36
18	*n*-Octadecane	$C_{18}H_{38}$	1.02	334	3.17
20	*n*-Eicosane	$C_{20}H_{42}$	1.08	322	3.00

Values adopted for the Lennard-Jones parameters σ and ε and dimensionless polarizability α^* of the *n*-alkanes.

Transfer Implications and Discussion") the remarkable engineering implications of pressure-sensitive Soret factors by specifically considering dodecane vapor mass transport across nonisothermal compressed N_2 "films" at pressures above 100 atm, especially in "cold-wall" situations.

Predicted Soret Factor "Increments" for *n*-Alkanes in Compressed N_2 or H_2O via TIP-VES Theory

Results for $\Delta\alpha_T/p$ for n*-alkanes in the nonpolar "solvent" N_2*

Our results for the predicted pressure sensitivity, $\Delta\alpha_{T,12}/p$, for the *n*-alkanes dilute in nitrogen are positive for all the *n*-alkanes, except at very high temperatures. This anticipated increase of $\alpha_{T,12}$ with pressure can be interpreted as being a consequence of the increasing role of attractive molecular interactions at higher pressures. Not surprisingly, this increase is larger at lower temperatures and tends to vanish only at rather high temperatures. As will be seen (Sections "Temperature-Dependence of $\alpha_T\ldots$", "Soret-Enhancement Factor F(Soret)...") the anticipated pressure sensitivity of the Soret factor for the higher alkanes, produces impressive mass transfer rate modifications, especially for "cold-wall" diffusion-controlled situations.

According to the results shown in Figure 2, at any elevated pressure $\Delta\alpha_{T,12}$ decays with temperature according to a power-law with an exponent nearly independent of the *n*-alkane under consideration. However, at very low values of $\Delta\alpha_{T,12}/p$, i.e. of order $\mathcal{O}(10^{-3})$, the decrease becomes faster than the former power law. Since in N_2 our high temperature VES predictions are actually valid to pressures approaching 1000 atm (see Section "Domain of Validity of the VES ..."), the associated increments in $\alpha_{T,12}$ may still be non-negligible.

In the special case of methane (which is lighter than N_2 and associated with a negative value of $\alpha^0_{T,12,\infty}$) the positive $\Delta\alpha_{T,12}/p$ at "low" temperatures has the effect of producing a change in sign at sufficiently high pressures. On the other hand, at very high temperatures the sign of the pressure sensitivity of $\alpha_{T,12}$ for methane becomes negative (although extremely small), eliminating this sign change.

We remind the reader that all results shown in Figure 2, and used for our subsequent numerical illustrations, are based on the "usual mixing-rules" for the effective LJ parameters (see Section "Estimated LJ Parameters ..."). In this connection it is noteworthy that the values of $\Delta\alpha_{T,12}/p$ based on an alternative mixing rule for the energy parameter ε_{ij} suggested in Ref. 15 are qualitatively similar to the former ones, although the predicted values of $\Delta\alpha_{T,12}/p$ are appreciably smaller. Indeed, the temperatures at which $\Delta\alpha_{T,12}/p$ becomes negative, based on the alternative mixing rule for ε_{ij}, are much lower than the corresponding temperatures based on the usual (geometric mean) mixing rule. This sensitivity of high pressure Soret factors to the mixing rule for ε_{ij} may be useful in future studies of such molecular interactions.

Results for $\Delta\alpha_T/p$ for n*-alkanes in the polar "solvent" H_2O*

While our principal emphasis, especially for "air-breathing" combustion applications, is on the carrier gas N_2, it is interesting to consider the major combustion product H_2O as a possible carrier gas. In the case of *n*-alkanes dilute in water vapor, an increase of pressure produces a negative correction in the Soret coefficient, which decreases in magnitude with temperature. This can be understood from a graphical construction similar to Figure 1, since now $\varepsilon_{22} > \varepsilon_{11}$ and the intercept J^*_{22} must be determined from the "dipole-shifted" function $B^*(T^*, t^* = 1.2)$.

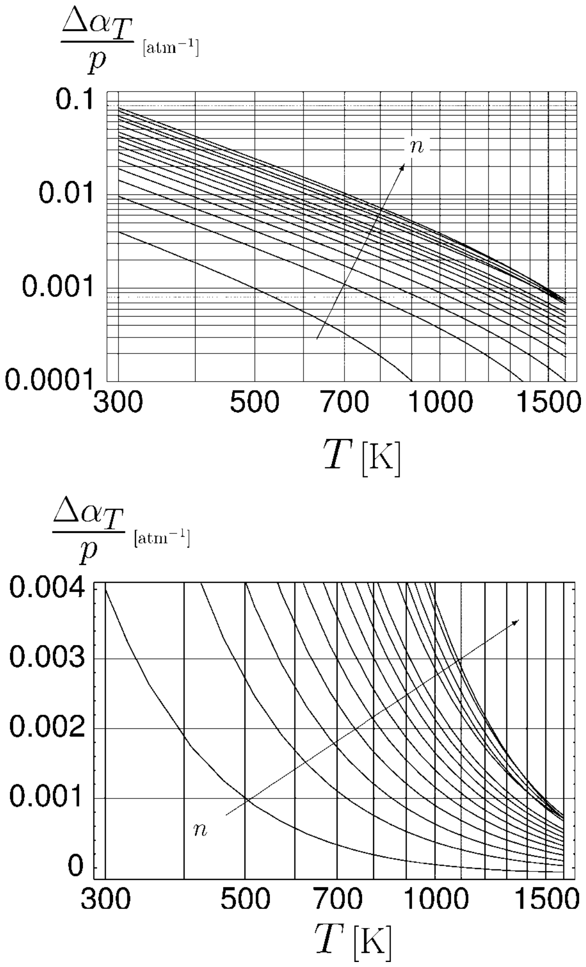

Figure 2. Increment in α_T per unit pressure (in atmospheres) for the *n*-alkanes dilute in compressed nitrogen.

Log-Log plot (top) and Log-Linear plot (bottom). $n = 1, 2, \ldots, 9, 10, 12, \ldots, 18$, and 20).

Here, too, in the limit of very high temperatures (i.e. near/above 2000 K) the predicted Soret coefficient becomes rather insensitive to pressure, whereas for moderately high temperatures ($T < 1000$ K) the dependence of $\alpha_{T,12}$ on pressure cannot be ignored. Apart from sign, the decrease in the pressure sensitivity of $\alpha_{T,12}$ with temperature at moderate temperatures follows a power law with an exponent independent of the *n*-alkane under consideration. (As higher temperatures are considered the decrease in pressure sensitivity becomes slower than the former power law). Although in the case of *n*-alkanes dilute in water vapor inevitable uncertainties in the present theoretical model and/or intermolecular LJ-S parameters may make these results of "only" semi-quantitative value, this model predicts a change in sign of the Soret factor for the n-alkanes (heavier than CH_4) dilute in water-vapor as the pressure increases. This behavior warrants further study because it could have a significant impact in many practical situations.

Net Mass Transfer Implications and Discussion

Domain of validity of the VES; N_2 above 300 K and H_2O above 700 K

As is well known, the Virial Equation of State exhibits slow convergence at very high pressures, forcing the inclusion of higher order terms in the virial expansion. But, because of its unambiguous connection to binary molecular interactions, in the present study only the first correction to the ideal gas limit (i.e., the "second" virial coefficient B) has been included. Consequently, it is incumbent upon us to provide a quantitative estimate of the maximum pressures that can be considered within the domain of validity of the present approximation. This is done here in the simplest possible fashion to provide useful guidance as to how far (from present, rather limited experience) our rational engineering mass transfer rate predictions can be extrapolated.

The value of the above mentioned maximum pressure has been estimated here as the pressure needed for the dimensionless volume ratio $|B/V|$ to become larger than a certain "tolerance" τ (where $|\ldots|$ stands for *absolute value*). According to this criterion, equivalent to Z being within 10 pct of 1.0, the maximal value of pressure within the validity domain of the VES is given as a function of temperature by

$$p_m = \tau \frac{\mathcal{R}T}{|B(T)|}\left(1 + \tau \frac{B(T)}{|B(T)|}\right) \tag{18}$$

where, because of our present focus on solutes dilute in the carrier gas (subscript 2), only $B_{22}(T)$ is required.

The estimates of p_m shown on Figure 3 for nitrogen and water vapor are based on a tolerance value of $\tau = 0.1$. As may be seen, in the case of nitrogen, quite high pressures, of considerable industrial interest, can be studied using the simple VES, especially at high temperatures. While it is clear that the present estimation of p_m is not valid at temperatures close to the so-called Boyle temperature (defined by $B(T_{\mathrm{Boyle}}) = 0$; $T_{\mathrm{Boyle}} \simeq 325$ K for N_2, and $T_{\mathrm{Boyle}} \simeq 1850$ K for H_2O), the present analysis shows that, in the case of N_2, the VES can be safely used up to pressures of 250 atm if the temperature is larger than only 300 K (see Figure 3, solid line). Values of the maximum pressure imposed by the truncated VES in the case of H_2O are much more restrictive at moderate temperatures. For instance, we find p_m is only 20 atm at $T =$ 500 K (see Figure 3, dashed line). This is a consequence of the much stronger singularity at low dimensionless temperatures of the coefficient B of a molecule with a high ε and strong permanent dipole moment (i.e. $B^*(T^*, t^* = 1.2)$ as compared to the singularity of the coefficient B corresponding to nonpolar gases (i.e. $B^*(T^*, t^* = 0)$. However, at/above intermediate temperatures ($T > 1000$ K) we find that the VES can be safely used for water vapor at pressures up to 300 atm.

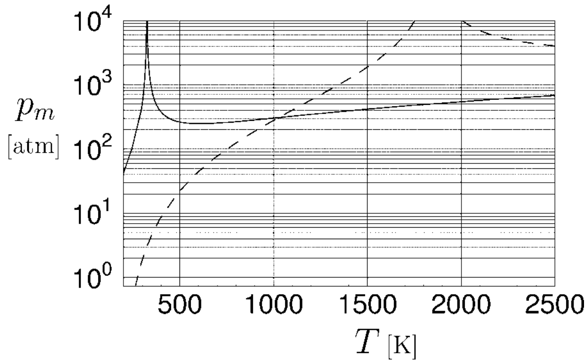

Figure 3. Maximum pressure according to Eq. 18 with $\tau = 0.1$ for the "solvents" compressed nitrogen (solid line) or water vapor (dashed line).

It should also be commented that in our view going to a VES truncated, say, at the ternary encounter level would not necessarily broaden the domain of validity of our mass transfer rate predictions since we have adopted an admittedly approximate but rational TIP-based method for extrapolating limited available binary Soret coefficient information. The simplicity of our present approach and its immediate relation to fundamental binary intermolecular interaction parameters would be compromised, and it remains to be seen whether such formal "extensions" will be justified by future experimental or theoretical investigations.

Summarizing, while more elaborate EOS-comparisons and/or the use of tighter "tolerances" may indeed lead to a more restricted domain of self-consistency for our present application of the VES, our formal mass transfer rate results at pressures above 100 atm (using a rational TIP-VES approach and realistic intermolecular potentials) should remain of considerable engineering interest because of the magnitude of the associated non-Fickian transport effects predicted (see, e.g., Figure 6 below) under such nonisothermal, compressed gas conditions.

Temperature-dependence of α_T at constant pressure up to 300 atm

A typical and quite remarkable consequence of pressure-dependent Soret factors is the "reversal" of the temperature dependence of $\alpha_{T,12}$ displayed in Figure 4 for, say, $C_{12}H_{26}$ dilute in N_2. In the ideal gas limit (see, e.g., Grew and Ibbs,[27] Rosner,[28] Rosner et al.[1]) many systems display the now-familiar T-dependence:

$$\alpha^0_{T,12}(T, y_1) = \alpha^0_{T,12,\infty}(y_1) \cdot \left(1 - \frac{C^0(y_1)}{T}\right) \tag{19}$$

where the indicated prefactor ($\alpha^0_{T,12,\infty}$) is the high-temperature asymptote *approached from below*, and C^0 is sometimes called the "cross-over" temperature. Indeed, in many applications $T > C^0$ and this "law" underlies use of the "appropriate" mean temperature:

$$\langle T \rangle = \frac{T_{\mathrm{hot}} \cdot T_{\mathrm{cold}}}{T_{\mathrm{hot}} - T_{\mathrm{cold}}} \cdot \ln\left(\frac{T_{\mathrm{hot}}}{T_{\mathrm{cold}}}\right) \tag{20}$$

familiar to experimentalists studying thermal diffusion in ideal gas mixtures. However, inspection of Figure 4 now

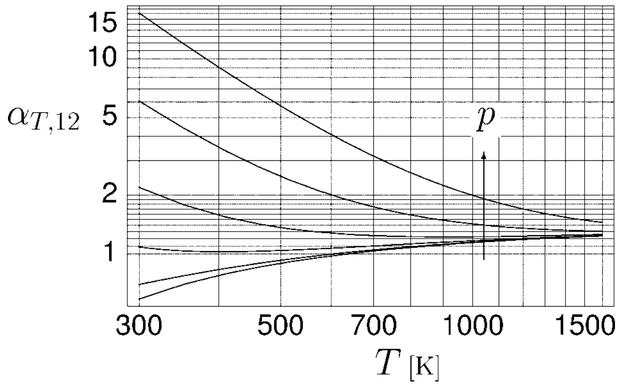

Figure 4. TIP-VES results for the binary Soret factor for *n*-dodecane dilute in nitrogen versus temperature at *p* = 1, 3, 10, 30, 100 and 300 atm, with $\alpha_{T,12}^{0}$ (*T;p*) from Ref. 1.

reveals that this particular "mean" would no longer be appropriate at high pressures. Indeed, the temperature dependence of $\alpha_{T,12}$ for $y_1 \ll 1$ becomes quite strong, requiring that $\alpha_{T,12}(T)$ be retained in (not factored out of) all integrals of the form $\int(\alpha_{T,12}(T;p)/T)dT$. As will be seen (Section "Soret-Enhancement Factor *F*(Soret)..."), such integrals play an important role in the present class of nonisothermal, dilute-solute mass transfer problems, including steady-states with no net mass transfer (see, e.g., Rosner et al.[29–31]). It is interesting to note that, irrespective of pressure (in the range considered), above ca. 1600 K all of the binary Soret coefficients (in Figure 4 for C_{12} dilute in N_2) approach a common value, which may be identified with the abovementioned high temperature asymptote, $\alpha_{T,12,\infty}^{0}$ provided by Chapman-Enskog kinetic theory in the ideal gas limit.

Soret-Enhancement Factor *F*(Soret) (Over Fick Diffusion-Controlled Net Mass Transfer Rates) in Dilute Nonisothermal Systems; Variable-Property Mass Transfer Coefficients and the (Typical) C_{12}/N_2 System

To illustrate the engineering mass-transfer consequences of pressure-sensitive Soret-factors it will be sufficient to consider purely diffusional (convection-free, isobaric) transport across a one-dimensional compressed gas "film", representing a variable-property, dilute solute but two-component "boundary layer" (in the Prandtl sense). Across such a film the net energy and dilute species mass diffusion fluxes will be a constant (first integrals), allowing the spatial variable (say *z*) to be suppressed in favor of the local mixture temperature, *T*(*z*). If $k_2(T;p)$ is the carrier gas Fourier thermal conductivity,[*] $\rho(T;p)$ the mixture mass density (*M/V* via VES), and $D_{12}^{\infty}(T;p)$ the relevant Fick diffusivity (at infinite dilution) then it is easy to show that, in the hypothetical *absence* of Soret transport, the relevant mean ρD_{12}-product (needed to calculate wall diffusion fluxes based on overall [mass-fraction] concentration differences and film thickness), written $\langle\rho D_{12}\rangle$, is given by the ratio of two definite integrals (from T_w to T_e):

$$\langle\rho D_{12}^{\infty}\rangle = \frac{\int_{T_w}^{T_e} k\,dT}{\int_{T_w}^{T_e} \frac{k}{\rho D_{12}^{\infty}}\,dT} \tag{21}$$

Division by $\rho D_{12}{}^{\infty}$ evaluated at, say, $(T_e;p)$, defines the variable thermo-physical property correction to the nondimensional mass transfer coefficient (Nusselt number for mass transfer[32] [Nu_m], or Sherwood number), written hereafter as $(Nu_m/Nu_{m,\mathrm{cp}})_{\alpha_T=0}$. We anticipate, and find (see below), that this T_w/T_e-dependent quantity will *not* be particularly pressure dependent-especially within the domain of validity of VES.[†]

We now turn our attention to binary mixture mass transfer situations in the *presence* of the additional Ludwig-Soret mass flux contribution:

$$j''_{\mathrm{LS}} = \rho D_{12}\alpha_{T,12}\cdot\omega_1\cdot(1-\omega_1)\cdot(-\nabla\ln T) \tag{22}$$

then both Fick and Soret transport contribute to the total solute (Species 1) mass flux. For brevity/simplicity, we focus below on the ("diffusion-controlled, dilute solute") limit: In terms of local mass fractions: $\omega_{1,w} \ll \omega_{1,e} \ll 1$, in which case the Fick flux "takes over" in the immediate vicinity of the wall. Under these conditions we find that the Ludwig-Soret-caused flux modification factor, written *F*(Soret; $T_w/T_e;p$) (see, e.g. Rosner et al.[28,33]) can be written in the instructive (quadrature-) form:

$$F(\mathrm{Soret};T_w/T_e;p) = \frac{A(T_e;p)\cdot\int_{T_w}^{T_e}\frac{k}{\rho D_{12}}\,dT}{\int_{T_w}^{T_e}A(T;p)\cdot\frac{k}{\rho D_{12}}\,dT} \tag{23}$$

where we have defined *A*(*T;p*) by the indefinite integral (from T_w to *T*):

$$A(T;p) \equiv \exp\left(\int_{T_w}^{T}\frac{\alpha_{T,12}(T;p)}{T}\,dT\right) \tag{24}$$

and $\alpha_{T,12} = \alpha_{T,12}(T;p)$ is the pressure-dependent binary Soret factor we have estimated (using our TIP-VES procedure; Section "TIP + VES "Extrapolation" of IG Soret Factors to Elevated Pressures") in Sections "Predicted Soret Factor "Increments" for *n*-Alkanes ..." and "Temperature-Dependence of αT ...". We anticipate from our application of TIP-VES theory, and find (see Figure 6, below), that this T_w/T_e-dependent quantity can be especially pressure dependent-even within the fortunately broad domain of validity of VES!

To make instructive illustrative calculations of both $(Nu_m/Nu_{m,\mathrm{cp}})_{\alpha_T=0}$ and *F*(Soret; $T_w/T_e;p$) using the above quadrature expressions, it remains for us to estimate the two transport properties $k_2 = k_2(T;p)$ and $D_{12}^{\infty}(T,p)$ in the compressed "solvent". The first of these was estimated using a now-familiar

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[*] While, in principle, there necessarily also exists a nonzero Dufour contribution to the energy flux, we expect that in our present (dilute-solute, highly nonisothermal) "film" examples, the Fourier contribution, $k_2(T;p)\cdot(-\nabla T)$, will completely dominate it, except, of course, for T_w/T_e-values rather close to unity (see Figs. 5 and 6).

[†] Present comments about the pressure dependence of the dimensionless mass transport coefficient (Sherwood number) actually pertain to the variable thermophysical property effect "at constant film (BL-) thickness". As is well known, in the presence of forced- or "natural"- convection, the effective "film" thickness itself depends on such parameters as Reynolds (Peclet) or Rayleigh numbers, contributing an additional dependence on pressure (see, e.g., Rosner[32] not explicitly considered here.

"corresponding-states" approach, leading to an expression of the form:

$$k(T;p) = k^0(T) + k_{ref}(T_c, p_c, Z_c) \cdot \mathrm{fct}(V_c/V) \tag{25}$$

(see, e.g., Poling et al.[34]). For $N_2(g)$ in the low pressure limit we used the simple power-law:

$$k^0(T) = (65.39 \times 10^{-3}) \cdot (T/1000)^{0.78} \tag{26}$$

where the units are W/(mK).

For the binary Fick diffusivity D_{12}^{∞} in moderately dense N_2 we invoked the rational Enskog expression[‡] (Chapman and Cowling[36,37]):

$$D_{12}^{\infty}(T;p) = \frac{D_{12\mathrm{CE}}^{\infty}}{1 + \frac{1}{2} \cdot \phi_2 \cdot \left(1 - \frac{3}{8} \cdot \frac{\sigma_{22\mathrm{HS}}}{\sigma_{12\mathrm{HS}}}\right)} \tag{27}$$

interpreting $\sigma_{12\mathrm{HS}}$ and $\sigma_{22\mathrm{HS}}$ as the appropriate effective "hard-sphere" diameters, calculated from $\sigma_{ij\mathrm{HS}} = \sigma_{ij_{\mathrm{LJ}}} \cdot [\Omega_\mu(T^*)]^{1/2}$. Here the numerator of Eq. 27 is the Fick diffusivity as given by Chapman-Enskog (IG-) theory, i.e.: $D_{12}^{0\infty}(T,p)$, and ϕ_2 is the molecular volume fraction: $N_A \pi\ \sigma_{22_{\mathrm{HS}}}^3/(6V)$. Since, in our VES-cases, $V \gg V_c$, this treatment for both k and D_{12}^{∞} is expected to be adequate to account for modest departures from IG-values. At much higher densities more complex relations would become necessary (see, e.g., Harstad and Bellan,[38] and Liu and Ruckenstein.[39]

Combining/using all of the above relations, our numerical results for the typical intermediate case of, say, $C_{12}H_{26}$ (dodecane; often used as an idealized "surrogate" for diesel engine fuel; see, e.g., Rosner and Chang[40]) dilute in compressed N_2 at $T_e = 1000$ K and pressures up to 300 atm (see also Figure 4) are shown in Figures 5 and 6.

Note that in the hypothetical absence of a Soret transport contribution, pressure would be expected to have remarkably little effect on the T_w/T_e-dependent Sherwood number (see footnote 2), whether for "cold-wall" ($T_w/T_e < 1$) or "hot-wall" ($T_w > T_e$) cases.[§]

However, because of the expected importance and pressure-sensitivity of the Ludwig-Soret contribution to solute mass transfer, especially on the "cold-wall" side of the diagram, predicted values of F(Soret; T_w/T_e;p) are seen to rise to impressive values (above a factor of 30 near $T_w/T_e = 0.3$ and $p = 300$ atm for our present parameter estimates!)-even well within the domain of validity of the virial EOS. While there are inevitable uncertainties in all present methods of predicting high pressure Soret factors, we suspect that in combustion applications, high-pressure effects (on diffusion flame temperatures and positions) due to these "transport" causes (see, e.g., Ref. 4 and Arias-Zugasti and Rosner[40] [Submitted for publication] and Palle[5]) may be far more significant than effects associated with complex homogeneous kinetics (which often dominate the combustion literature).

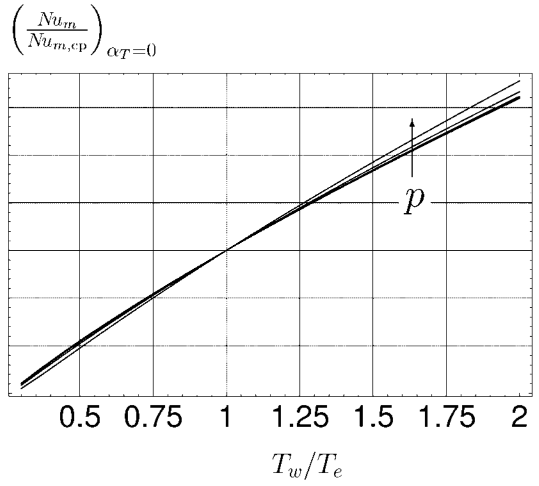

Figure 5. Variable property-induced correction factor for the "Soret-free" mass transport Nusselt number versus T_w/T_e for n-dodecane dilute in compressed nitrogen at p = 1, 3, 10, 30, 100, and 300 atm and T_e = 1000 K.

While beyond the scope of our present paper, the corresponding case of $C_{12}H_{26}$ dilute in compressed H_2O (up to 200 atm and for $0.7 \le \theta_w \le 2$) exhibited some similar features, but several intriguing new ones, including a pressure-induced change in sign of the Soret factor. Despite the increased molecular weight ratio (M_1/M_2), extreme values of F(Soret) within the range of validity of VES were more modest (nevertheless ranging between 1.2 and 0.7 at $T_w/T_e = 0.7$). Additionally, as was to be expected, the quantity $(Nu_m/Nu_{m,\mathrm{cp}})_{\alpha T=0}$ proved to be slightly more pressure-sensitive than for its N_2 counterpart (cf. Figure 5).

In spite of inevitable uncertainties in all such transport property estimates, especially those dealing with both dense fluid Soret coefficients (see, e.g. Shukla and Firoozabadi[8] and Gonzalez-Bagnoli et al.[13]) and the longest chain n-alkanes (see Section "Estimated LJ Parameters...") even in N_2 at high pressures, these considerations/illustrative calculations (Sections "Predicted Soret Factor "Increments"...", "Net Mass Transfer Implications and Discussion") force us to conclude that reliable mass transfer rate predictions in nonisothermal disparate molecular weight dense vapor systems of engineering importance will *require* systematic inclusion of the Ludwig-Soret (non-Fickian) molecular mass transport mechanism.

Generalizations (Nondilute Binary Cases [Arbitrary y_1, including "Equi-molar"], Multi-component Cases, and Even "Liquid-like" Densities)

These (and closely related) generalizations, of undeniable engineering relevance, are beyond the scope of our present

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[‡] We remark here that, while Enskog theory is sufficient for making plausible estimates of modest viscosity-, thermal conductivity-, and D_{12}-corrections from their ideal-gas limits (for monatomic vapors), it seems to be quite incapable of predicting the pressure effect on binary Soret factors of importance in our present work. Indeed, formal application of Enskog theory (see, e.g., Kincaid et al.[35]) normally leads to a *decrease* in $\alpha_{T,12}$ with an increase in system pressure, presumably because of the explicit neglect of attractive molecular interactions.

[§] In this IG-limit, if $k^0(T)$ and $D_{12}^{0,\infty}$ are represented by power-laws (with exponents κ and δ, respectively) then the variable-property correction to the Sherwood number, which we have written $(Nu_m/Nu_{m,\mathrm{cp}})_{\alpha_T} = 0$, can be shown to be given by:

$$\left(\frac{Nu_m}{Nu_{m,\mathrm{cp}}}\right)_{\alpha_{T=0}} = \left(1 - \frac{\delta - 1}{\kappa + 1}\right) \cdot \frac{1 - \theta_w^{\kappa+1}}{1 - \theta_w^{\kappa+1-(\delta-1)}} \tag{28}$$

where we have introduced: $\theta_w \equiv T_w/T_e$. In the present case (C_{12}/N_2) we estimated $\kappa = 0.78$ and $\delta = 1.74$ in the temperature range of interest.

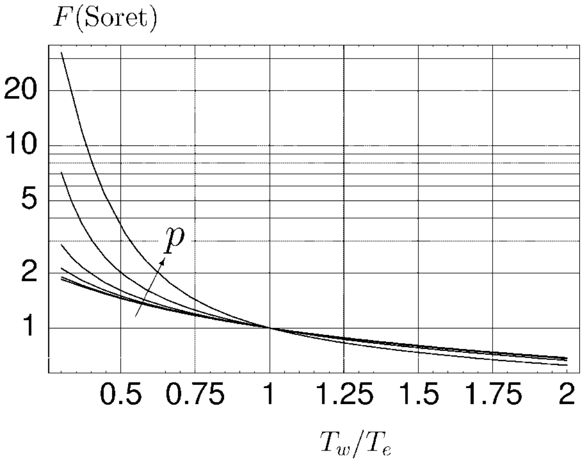

Figure 6. Soret transport-induced mass transport correction factor *F*(Soret) versus T_w/T_e for *n*-dodecane dilute in compressed nitrogen at p = 1, 3, 10, 30, 100, and 300 atm and T_e = 1000 K.

paper. However, it may be helpful to comment on them here. Indeed, in our current combustion-oriented studies (where the "solute" is often the hydrocarbon "fuel" vapor), relaxing the simplifying assumption of "infinite dilution" is of particular importance.[¶] Fortunately, this is quite straightforward within the range of validity of the virial EOS (see, e.g., Prausnitz et al.,[41] Sandler,[42] Smith and Van Ness[43]). Moreover, retaining VES has the distinct advantage of removing all uncertainties associated with the empirical "mixing-rules" appearing in more complex equations of state (see e.g. Harstad and Bellan[44]).

As it turns out, allowing y_1 to be arbitrary also enables valuable TIP-VES theory comparisons to be made with some experimental $\alpha_{T,12}$-data obtained under nearly equi-molar conditions (e.g., Becker.[17] However, we found that self-consistent treatment of much of this "low" temperature experimental data (often for $\langle T\rangle < 410$ K) also requires introduction of more complex (multi-parameter) equations of state, as was actually done by Haase, et al.[7,16] Oost et al.,[6] and Shukla and Firoozabadi.[8]

It would also be prudent to keep in mind many implicit approximations underlying our present treatment, any one of which could limit the domain of applicability of our results-especially for certain solute/solvent combinations not explicitly investigated here. Among these, mention should be made of the assumed absence of appreciable: (a) molecular clustering-e.g., solute dimer formation (creating, in effect, a ternary mixture) (Oost and DeVries[45]), (b) solute molecule "pyrolysis'", especially for the larger *n*-alkanes at the highest temperatures considered here, and (c) pressure-dependence of the relevant "heats of transport" (see, e.g., the approximate TIP-based treatments of Oost et al.[6] and Haase[7]). We recommend revisiting some of these fundamental issues, along with our approximate treatment of nonspherical molecular binary interactions (see Section "Estimated LJ Parameters . . ." discussion of effective LJ-binary interaction parameters) when the available experimental evidence warrants it. Of course, some of these uncertainties persist even in the low pressure (IG-) limit, which we presumed was (reasonably) "well-understood".

Turning to the issue of relaxing the (pseudo-) binary assumption, an attractive multi-component generalization of the diffusion flux laws is the Maxwell-Stefan TIP treatment of Standart et al.,[47] as already applied to many *liquid* systems of industrial-separations interest by Taylor and Krishna.[48] However, in our opinion, nonisothermal dense vapor multicomponent systems cry out for further experimental and theoretical study, especially with regard to the uncertain composition dependencies of the appropriate Fick- and Soret- transport coefficients (NB: In this MS formulation, in an N-component mixture ($N > 2$) there are "only" $N \cdot (N - 1)/2$ independent composition dependent D_{ij}'s and $N \cdot (N - 1)/2$ independent $\alpha_{T,ij}$'s (also composition dependent), with *no* physically relevant "diagonal" elements).

We conclude these remarks by observing that there are, indeed, important multi-component, nonisothermal engineering applications in which the vapor densities possess nearly "expanded liquid"-like values. In our view, reliable yet tractable engineering methods to deal with such situations remain to be developed.

Conclusions and Engineering Implications

The present work was motivated by the realization that many technologies dependent on rapid molecular level mixing (including vapor phase combustion for power-generation or chemical synthesis/materials processing, Rosner[31,49,50]) involve the simultaneous combination of large molecular weight disparities, appreciable temperature gradients, and (frequently for "compactness") high pressures-often well over 100 atm (10.1325 MPa). Even at 1 atm pressure we previously demonstrated significant molecular- and particle-mass transfer effects associated with combustion-generated temperature gradients rather than concentration gradients, see, e.g., our Introduction, Rosner et al.,[1] and a recent review[31]-i.e., what is now called Ludwig-Soret transport for molecules, or "thermophoresis" for suspended particles (see, e.g. Zheng,[51] Davis and Schweiger[52] and Rosner et al.[53]). These examples, coupled with the fact that most high pressure measurements of the relevant binary molecular Soret factor $\alpha_{T,12}$ over the past half-century have revealed rather significant increases with pressure (see, e.g., Figure 9.1–3 of Hirschfelder et al.[14] based on the experimental data of Becker,[17] and the more recent review/analysis of Shukla and Firoozabadi[8]) prompted the present theoretical/computational investigation of Soret (versus Fick) mass transfer effects for *n*-alkanes at "infinite dilution" across compressed N_2 or H_2O "films" (with temperature ratios from 0.3 to 2.0 when T_e = 1000 K). By rationally extrapolating our previous kinetic-theory estimates of $\alpha_{T,12}{}^0$ to high pressures (here up to ca. 300 atm) using a

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[¶] It is interesting to note that when y_1 is nonzero then there is a Second-Law imposed upper limit to the "allowable" absolute magnitude of $\alpha_{T,12}$. In our notation this limit can be written in the interesting form:

$$|\alpha_{T,12}| \le \left(\frac{C_{p_{mix}}/\mathcal{R}}{Le \cdot y_1 \cdot y_2}\right)^{1/2} \qquad (29)$$

(see, e.g., DeGroot and Mazur[46]), where values of $Le \equiv D_{12}/[k/(\rho c_p)]$ were estimated/tabulated in Rosner et al.,[1] but only in the low-density, dilute solute-limit.

convenient approximate formulation based on the Thermodynamics of Irreversible Processes (see, e.g., Haase[7]) combined with a virial equation of state (a method designated "TIP-VES" in Section "TIP + VES "Extrapolation" of IG Soret Factors to Elevated Pressures") our illustrative calculations (Sections "Predicted Soret Factor "Increments"...", "Net Mass Transfer Implications and Discussion") reveal significant pressure effects on net mass transfer rates across nonisothermal compressed gases, primarily attributable to the pressure sensitivity of the above mentioned Soret factor.

In view of our present objectives, our treatment/choice of illustrations has been deliberately focused/simplified (limited to binary systems at "infinite dilution", one-dimensional-steady compressed gas "films", an approximate TIP-based Soret factor extrapolation procedure, and VES), but these methods can be improved/tested further and extended to more realistic situations, including multicomponent convective-diffusion boundary layers (see, e.g., Rosner et al.,[30,33] and Garcia-Ybarra and Castillo[54]). Indeed, extensions of this work are the subject of follow-on studies already underway in our HTCRE-research group.

More broadly, far from being a "higher-order effect" or an erudite treatise footnote unlikely to influence the way mass-transfer equipment/processes are/should be designed, it appears from our present (rational-, if somewhat preliminary-) estimates that for nonisothermal compressed gas mixtures (e.g., *n*-alkanes dilute in N_2 or H_2O) involving high (or low-) molecular weight solutes, the non-Fickian mechanism associated with the names of Ludwig and Soret, can be responsible for order-of-magnitude mass transfer rate modifications, especially at "modest" temperatures and "high" pressures. This is confirmed by our recent ancillary results[55] for "condensation onset surface temperatures" in compressed hydrocarbon containing vapors.

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Notation

A = Soret-transport related function (Eq. 24)
B = second virial coefficient
B^* = dimensionless second virial coefficient (Eq. 4)
b_0 = characteristic molar volume (Eq. 5)
C^0 = crossover temperature (Eq. 19)
C_p = molar heat capacity at constant pressure
c_p = specific heat at constant pressure
D = Fick diffusion coefficient
E_{22} = dimensionless energy ratio (Eq. 12)
F(Soret) = Soret transport-induced correction factor (Eq. 23)
H = partial specific enthalpy
J^* = $J^* \equiv B^* - T^* \cdot dB^*/dT^*$ (Eq. 6)
j''_LS = Ludwig-Soret mass flux contribution (Eq. 22)
k = thermal conductivity
k_B = Boltzmann constant $k_B = 1.3806 \times 10^{-23}$ J/K
N_A = Avogadro"s number $N_A = 6.0221 \times 10^{26}$ Kmol^{-1}
N = number of components in mixture
n = number of carbon atoms in the *n*-alkane
Nu_m = mass transfer Nusselt number (Sherwood number)
M = molar mass
p = pressure
p_m = maximum pressure within the applicability domain of the truncated Virial EOS (Eq. 18)
p_ref = reference pressure $p_{ref} = 1.01325 \times 10^5$ Pa
$\mathcal{R}$ = ideal gas constant $\mathcal{R} = k_B \cdot N_A$
T = absolute temperature [K]
T^* = dimensionless temperature $T^* = k_B T/\varepsilon$
t^* = dimensionless dipole moment
V = molar volume
y = mole fraction
Z = "compressibility" factor $Z \equiv pV/\mathcal{R}T$

Greek letters and operators

α_T = thermal diffusion factor (Eqs. 1 and 22)
α^* = dimensionless polarizability
δ_{12} = $2B_{12} - (B_{11} + B_{22})$ (Eq. 9)
ε = well-depth parameter of the LJ potential
θ_w = dimensionless wall temperature $\theta_w = T_w/T_e$
μ = chemical potential
ξ = mixing rule parameter of the Stockmayer potential for polar/nonpolar interactions (Eq. 17)
ρ = mass density
σ = size parameter of the LJ potential
τ = maximum allowed value of $|B/V|$ within the applicability domain of the truncated VES
ϕ_2 = molecular volume fraction $\phi_2 = N_A\, \pi\sigma_{22\mathrm{HS}}{}^3/(6V)$
Ω_μ = collision integral related to viscosity (Hirschfelder et al.[14])
ω = species mass fraction
ω = acentric factor (only in Eqs. 15 and 16 and last column of Table 3)
∇ = spatial gradient operator
$\langle\ldots\rangle$ = relevant average value

Subscripts and superscripts

∞ = in the high temperature limit (subscript)
∞ = in the limit of infinite dilution (superscript)
0 = in the Ideal Gas limit
c = at the thermodynamic critical point
i/j = pertaining to component i/j
mix = pertaining to the mixture
e = at the outer "edge" (of film)
w = at the surface
ref = reference value

Abbreviations/acronyms

ACS = American Chemical Society
BL = boundary layer
CE = Chapman-Enskog theory (IG Limit)
C^n = normal alkane C_nH_{2n+2}
cp = constant property
EOS = equation of state
HCB = Hirschfelder, Curtiss and Bird[14]
HTCRE = high temperature chemical reaction engineering
HS = hard-sphere approximation
IG = ideal gas (limit $p \rightarrow 0$)
JT = Joule-Thomson
LJ = Lennard-Jones
LJ-S = Lennard-Jones-Stockmayer
L-S = Ludwig-Soret
MPa = Mega-Pascal; 1 atm = 0.101325 Mpa
MS = Maxwell-Stefan
PRF = Petroleum Research Fund
TIP = thermodynamics of irreversible processes
VES = virial equation of state (Eq. 3)
(12:6) = exponents in the LJ intermolecular potential

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