Theoretical Model of Thermal Diffusion Factors in Multicomponent Mixtures

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Unlike molecular diffusion, neither measured thermal diffusion coefficients nor the theoretical framework exist for the estimation of thermal diffusion coefficients in nonideal multicomponent mixtures. This work derives a theoretical model for thermal diffusion coefficients in ideal and nonideal multicomponent mixtures, based on the thermodynamics of irreversible processes and the molecular kinetic approach incorporating explicit effects of nonequilibrium properties, such as the net heat of transport and molecular diffusion coefficients, and of equilibrium properties of the mixture, which are determined by the Peng-Robinson equation of state. An interesting feature of this model is that in nonideal multicomponent mixtures thermal diffusion coefficients depend on molecular diffusion coefficients, while in binary mixtures they do not. The model successfully describes thermal diffusion factors of binary mixtures for which experimental data are available, even those in extreme nonideal conditions and close to the critical point. Since experimental data on thermal diffusion factors in multicomponent hydrocarbon mixtures are not available, testing the model's accuracy was not possible. The model, however, successfully predicted spatial variation of composition in a ternary mixture of $nC_{24}/nC_{16}/nC_{12}$*, providing an indirect verification. The six-component mixture of* $C_1/C_3/nC_5/nC_{10}/nC_{16}/C_2$ *shows significant dependency of thermal diffusion factors on the distance to the critical point. It also demonstrates for the first time that there is no need to adopt a sign convention for thermal diffusion coefficients in binary and higher mixtures. The thermodynamic stability analysis shows that when the thermal diffusion coefficient is positive, the component should go to the cold region in a binary mixture.*

Introduction

Thermal diffusion or the Soret effect is important for the study of compositional variation in hydrocarbon reservoirs (Whitson and Belery, 1994; Ghorayeb and Firoozabadi, 2000b; Ghorayeb et al., 2000) and for separating isotopic mixtures (Rabinovich et al., 1979), among other uses. In this process for a convention-free mixture a temperature gradient develops the corresponding composition gradient of the mixture constituents. Previous studies indicate that thermal diffusion factors are sensitive to the details of intermolecular interactions, size and shape of the molecules, and their magnitude is governed by thermodynamic conditions (Kincaid et al., 1987; Legros et al., 1985). In many mixtures, accurate measurement of thermal diffusion factors is difficult to perform because of the obscuring effect of natural convection. Experiments in microgravity (10^{-5} of normal gravity g) have been proposed to alleviate the difficulties with convection (Georis et al., 1998).

Thermal diffusion factor data are sparse; they are available for some binary mixtures only (Vargaftik, 1975; Ecenarro et al., 1989, 1990; Tyrrell and Harris, 1984; Wakeman et al., 1991; Ma and Beyerlein, 1983; Ma et al., 1983; Pohl et al., 1073; Eichler et al., 1986; Thyagarajan and Lallemand, 1978; Köhler, 1993; Köhler et al., 1995; Köhler and Müller, 1995).

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Recently, Zhang et al. (1996) have presented a detailed analysis of the different methods for measuring thermal diffusion factors. Again, only binary mixtures were considered.

Several theoretical approaches have been suggested in the literature to describe thermal diffusion factors in binary mixtures with varying degrees of success. Important among them are the models based on the kinetic theory of irreversible thermodynamics (Rutherford, 1963), the phenomenological theory of irreversible thermodynamics (Haase, 1950), and the maximization of the partition function of two idealized bulbs (Kempers, 1989). These models were found to describe thermal diffusion factors in some binary hydrocarbon mixtures only qualitatively because of the several approximations involved in their formulations and calculations. In fact, thermal diffusion factors from the models just described incorporate only equilibrium properties and ignore the dependence on the nonequilibrium properties. It is known that the thermal diffusion factor is a nonequilibrium property, and its proper formulation requires the knowledge of both the equilibrium and nonequilibrium properties.

Recently, Shukla and Firoozabadi (1998) developed a new theoretical model for the prediction of thermal diffusion factors in binary hydrocarbon mixtures using irreversible thermodynamics. Unlike the previous models, their work incorporates both equilibrium and nonequilibrium properties of mixtures. In that model, equilibrium properties are obtained from the volume-translated Peng-Robinson equation of state, while nonequilibrium properties are determined using the energy of viscous flow estimated from viscosity data. The Shukla and Firoozabadi model (Shukla and Firoozabadi, 1998) has been applied for the prediction of binary thermal diffusion factors of several mixtures consisting of hydrocarbon species (C_1/C_3, C_1/C_4, C_7/C_{12}, C_7/C_{16}), nonhydrocarbon species (Ar/CO_2, N_2/CO_2, H_2/N_2, H_2/CO_2), and hydrocarbon and nonhydrocarbon species (C_1/CO_2), for which experimental data were available. Comparisons of theoretical results with experimental data showed good model performance, except in the near-critical region [in the critical region due to factoring out the term $(\partial \ln f_1/\partial \ln x_1)_{P,T}$ in accordance with the practice of the experimentalists, the model should not be applied in the form presented by Haase et al. (1994)]. The model was also found to offer a significant improvement over the earlier models (Rutherford, 1963; Haase, 1950), and was able to predict the sign of thermal diffusion factors of the preceding mixtures to be consistent with the experiment.

Thermal diffusion factors in three- and higher-component nonideal mixtures may significantly differ from those in binary mixtures. For example, experimental data of thermal diffusion factors in binary mixtures C_1/C_2, C_1/C_3, and C_1/C_4 show that methane segregates toward the hot region (Sakonidou et al., 1998; Haase et al., 1971; Rutherford and Roof, 1959). In contrast, in hydrocarbon reservoirs more methane has often been seen in the cold region (top of the reservoir) (Belery and da Silva, 1990; Temeng et al., 1998) (experimental data for thermal diffusion factors in multicomponent mixtures are not available). These results show that the segregation of methane in a nonideal mixture with more than two components for a nonisothermal process cannot be determined using the binary results, and the sign of thermal diffusion factors is immaterial in defining the direction of component segregation in the hot and cold regions.

Our literature survey shows that the study of thermal diffusion factors in multicomponent mixtures has not been performed previously, probably because (1) equations of mass flux in multicomponent mixtures become too complicated to be evaluated analytically and require a special effort, and (2) no experimental data are available for thermal diffusion factors in multicomponent mixtures (more than two components) for testing the models.

The objective of this work is to derive a model for thermal diffusion factors in multicomponent nonideal mixtures. The model is derived from the thermodynamics of irreversible processes where the effects of both equilibrium and nonequilibrium properties are incorporated.

Thermal Diffusion Factors

We consider a mixture consisting of n components at a given temperature, T, and pressure, P, where the only external force, $\vec{F}$, is the gravity. If we assume that there is no heat generation, viscous dissipation, or chemical reaction, the entropy production strength can be written as (de Groot and Mazur, 1984).

$$\sigma = -\frac{1}{T^2}\left(\vec{J}_q - \sum_{k=1}^{n}\frac{\overline{H}_k}{M_k}\vec{J}_k\right)\cdot\vec{\nabla}T - \frac{1}{T}\sum_{k=1}^{n}\vec{J}_k\cdot\left(\vec{\nabla}_T\frac{\mu_k}{M_k} - \vec{F}\right), \quad (1)$$

where $\vec{J}_q$ is the heat flux, M_k, $\overline{H}_k$, μ_k, and $\vec{J}_k$ are the molecular weight, the partial molar enthalpy, the chemical potential, and the molar diffusion flux relative to the molar average velocity of component k, respectively. $\sum_{k=1}^{n}(\overline{H}_k/M_k)\vec{J}_k$ is the transfer of heat due to diffusion. By introducing a new heat-flux expression, $\vec{J}'_q$, defined as

$$\vec{J}'_q = \vec{J}_q - \sum_{k=1}^{n}\frac{\overline{H}_k}{M_k}\vec{J}_k, \quad (2)$$

and using $\sum_{k=1}^{n-1}\vec{J}_k = 0$, Eq. 1 becomes

$$\sigma = -\frac{1}{T_2}\vec{J}'_q\cdot\vec{\nabla}T - \frac{1}{T}\sum_{k=1}^{n-1}\vec{J}_k\cdot\vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right). \quad (3)$$

Another method of expressing the heat flux, $\vec{J}_q$, is based on combining the concept of irreversible thermodynamics and molecular kinetic theory involving the heat of transport (Tichacek et al., 1956; Denbigh, 1951)

$$\vec{J}_q = \sum_{k=1}^{n}\frac{Q_k}{M_k}\vec{J}_k, \quad (4)$$

where Q_k is the heat of transport of component k. The expression for $\vec{J}'_q$ then becomes

$$\vec{J}'_q = \sum_{k=1}^{n}\frac{Q_k - \overline{H}_k}{M_k}\vec{J}_k = \sum_{k=1}^{n}\frac{Q_k^*}{M_k}\vec{J}_k. \quad (5)$$

In the preceding equation $Q_k^* = Q_k - \overline{H}_k$ is the net heat of transport of component k. Consequently, Eq. 3 can be expressed in terms of the net heat of transport:

$$\sigma = -\frac{1}{T}\sum_{k=1}^{n-1}\left[\left(\frac{Q_k^*}{M_k} - \frac{Q_n^*}{M_n}\right)\frac{\vec{\nabla}T}{T} + \vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right)\right]\cdot\vec{J}_k. \quad (6)$$

Using Eqs. 3 and 6 of the entropy production strength, one can write the phenomenological equations for the diffusion flux in the following two forms:

$$\vec{J}_i = -L'_{iq}\frac{\vec{\nabla}T}{T^2} - \frac{1}{T}\sum_{k=1}^{n-1}L_{ik}\vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right), \qquad i = 1, \ldots, n-1, \quad (7)$$

and

$$\vec{J}_i = -\frac{1}{T}\sum_{k=1}^{n-1}L_{ik}\left[\left(\frac{Q_k^*}{M_k} - \frac{Q_n^*}{M_n}\right)\frac{\vec{\nabla}T}{T} + \vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right)\right], \qquad i = 1, \ldots, n-1, \quad (8)$$

respectively; L'_{iq} and L_{ik} are the phenomenological coefficients (Onsager, 1931a,b). Equations 7 and 8 imply

$$L'_{iq} = \sum_{k=1}^{n-1}L_{ik}\left(\frac{Q_k^*}{M_k} - \frac{Q_n^*}{M_n}\right), \qquad i = 1, \ldots, n-1. \quad (9)$$

At steady state, the diffusion flux vanishes and Eq. 8 implies (L_{ik}, i, $k = 1, \ldots, n-1$ are independent)

$$Q_k^*\frac{\vec{\nabla}T}{T} + \vec{\nabla}_T\mu_k = 0, \qquad i = 1, \ldots, n-1, \quad (10)$$

$$Q_n^*\frac{\vec{\nabla}T}{T} + \vec{\nabla}_T\mu_n = 0. \quad (11)$$

From the Gibbs-Duhem relation under isothermal and isobaric conditions

$$\vec{\nabla}_{T,P}\mu_n = -\frac{1}{x_n}\sum_{j=1}^{n-1}x_j\vec{\nabla}_{T,P}\mu_j. \quad (12)$$

Substituting the Gibbs-Duhem relation in Eq. 11 for the isobaric condition, one obtains

$$x_nQ_n^*\frac{\vec{\nabla}T}{T} - \sum_{k=1}^{n-1}x_k\vec{\nabla}_{T,P}\mu_k = 0; \quad (13)$$

and from Eq. 10 one obtains at isobaric conditions

$$-\sum_{k=1}^{n-1}\left[Q_k^*\frac{\vec{\nabla}T}{T} + \vec{\nabla}_{T,P}\mu_k\right]x_k = 0. \quad (14)$$

Equations 13 and 14 imply that

$$\sum_{k=1}^{n}x_kQ_k^* = 0, \quad (15)$$

which is valid only under isobaric conditions. We define the following matrix and column vectors

$$L \equiv \left[L_{ij}\right] \equiv L_{ij} \qquad i, j = 1, \ldots, n-1,$$

$$L_q \equiv \left[L'_{iq}\right] \qquad i = 1, \ldots, n-1,$$

$$Q \equiv \left[\frac{Q_k^*}{M_k} - \frac{Q_n^*}{M_n}\right] \qquad i = 1, \ldots, n-1.$$

Equation 9 can now be written in a compact form

$$L_q = L\cdot Q. \quad (16)$$

Using Eq. 7, the diffusion flux vector $J = (\vec{J}_1, \ldots, \vec{J}_{n-1})$ reads (Ghorayeb and Firoozabadi, 2000a)

$$J = -c\left(D^M\cdot\mathbf{\nabla}x + D^T\vec{\nabla}T + D^P\vec{\nabla}P\right), \quad (17)$$

where $D^M \equiv [D_{ij}]$, $D^T = (D_1^T, \ldots, D_{n-1}^T)$, $D^P = (D_1^P, \ldots, D_{n-1}^P)$, and $\nabla x = (\vec{\nabla}x_1, \ldots, \vec{\nabla}x_{n-1})$. The molecular diffusion coefficients D_{ij} ($\mathrm{m^2\cdot s^{-1}}$), the thermal diffusion coefficients D_i^T ($\mathrm{m^2\cdot s^{-1}\cdot K^{-1}}$), and the pressure diffusion coefficients D_i^P ($\mathrm{m^2\cdot s^{-1}\cdot Pa^{-1}}$) are expressed by

$$D_{ij} = a_{in}D_{in}\frac{M_ix_i}{L_{ii}}\sum_{k=1}^{n-1}L_{ik}\sum_{l=1}^{n-1}\frac{M_lx_l + M_nx_n\delta_{lk}}{M_l}\left.\frac{\partial\ln f_l}{\partial x_j}\right|_{x_j,T,P}, \qquad i, j = 1, \ldots, n-1, \quad (18)$$

$$D_i^T = a_{in}D_{in}M\frac{k_{Ti}}{T}, \qquad i = 1, \ldots, n-1, \quad (19)$$

$$D_i^P = a_{in}D_{in}\frac{M_ix_i}{RTL_{ii}}\sum_{k=1}^{n-1}L_{ik}\left[\sum_{j=1}^{n-1}x_j\overline{V}_j + \frac{M_nx_n}{M_k}\overline{V}_k - \frac{1}{c}\right] \qquad i = 1, \ldots, n-1, \quad (20)$$

respectively. The partial molar volume of component i, the fugacity of component i, the total molecular weight, and the gas constant, are $\overline{V}_i$, f_i, M, and R, respectively; $\overline{V}_i$ and f_i can be obtained using an equation of state (Firoozabadi, 1999). The subscript x_j is defined by $(x_1, \ldots, x_{j-1}, x_{j+1}, \ldots, x_{n-1})$, and δ_{lk} denotes the Kronecker delta. The coefficients a_{in}, D_{in}, and k_{Ti} are given by

$$a_{in} = \frac{M_iM_n}{M^2}, \qquad i = 1, \ldots, n-1, \quad (21)$$

$$D_{in} = \frac{M^2RL_{ii}}{cM_i^2M_n^2x_ix_n} \qquad i = 1, \ldots, n-1, \quad (22)$$

$$k_{Ti} = \frac{M_i x_i M_n x_n L'_{iq}}{MRTL_{ii}}$$

$$= \alpha_{Ti} x_i x_n, \qquad i = 1, \ldots, n-1; \tag{23}$$

where k_{Ti} and α_{Ti} are the thermal diffusion ratio and the thermal diffusion factor of component i, respectively. For binary mixtures, the diffusion flux of component 1 can be obtained from Eq. 17;

$$\vec{J}_1 = -\rho D_{12} \frac{M_1 M_2}{M^2} \left[\left. \frac{\partial \ln f_1}{\partial \ln x_1} \right|_{P,T} \vec{\nabla} x_1 + \frac{k_{T1}}{T} \vec{\nabla} T + \frac{x_1}{RT} \left(\bar{V}_1 - \frac{M_1}{\rho} \right) \vec{\nabla} P \right], \tag{24}$$

where ρ is the mass density and $k_{T1} = x_1(1 - x_1)\alpha_{T1}$. From Eq. 24 at steady state, under isobaric conditions, when $k_{T1} > 0$, thermal diffusion causes component 1 to segregate toward the cold region [from stability analysis $(\partial \ln f_1 / \partial \ln x_1)_{P,T} \geq 0$ (Firoozabadi, 1999)]. Note that there is no need for adopting a sign convention for k_{T1} in a binary mixture despite the practice in the literature. In a nonideal multicomponent mixture, the sign of k_{Ti} in general may have no relation with the segregation of a particular component to the hot or cold regions. At steady state under isobaric conditions, $\vec{\nabla} x_i = -\vec{\nabla} T$ det $(B_i)/\det(D^M)$, where B_i is the matrix D^M with column i replaced by column vector D^T; therefore, the sign of D_i^T (and thus k_{Ti}) alone may not determine the sign of $\vec{\nabla} x_i$. From Eq. 23 one obtains

$$L'_{iq} = \frac{MRTL_{ii}}{M_i x_i M_n x_n} k_{Ti}. \tag{25}$$

Using the following definitions

$$D \equiv \left[D_{ij} \right] \equiv a_{in} D_{in} \delta_{ij} \qquad i, j = 1, \ldots, n-1,$$

$$M \equiv \left[M_{ij} \right] \equiv \frac{M_i x_i}{L_{ii}} \delta_{ij} \qquad i, j = 1, \ldots, n-1,$$

$$W \equiv \left[W_{ij} \right] \equiv \frac{M_j x_j + M_n x_n \delta_{ij}}{M_j} \qquad i, j = 1, \ldots, n-1,$$

$$K_T \equiv \left[K_{Ti} \right] \equiv M \frac{k_{Ti}}{T} \qquad i = 1, \ldots, n-1;$$

then D^M and L_q read

$$D^M = D \cdot M \cdot L \cdot W \cdot F, \tag{26}$$

and

$$L_q = \frac{RT^2}{M_n x_n} M^{-1} \cdot K_T, \tag{27}$$

respectively. Equations 16 and 27 give

$$K_T = \frac{M_n x_n}{RT^2} M \cdot L \cdot Q, \tag{28}$$

which can be written as

$$k_{Ti} = \frac{M_i x_i M_n x_n}{MRTL_{ii}} \sum_{j=1}^{n-1} L_{ij} \left(\frac{Q_j^*}{M_j} - \frac{Q_n^*}{M_n} \right), \qquad i = 1, \ldots, n-1. \tag{29}$$

Under isobaric conditions, by combining Eqs. 15 and Eq. 29

$$k_{Ti} = \frac{M_i x_i}{MRTL_{ii}} \sum_{j=1}^{n-1} \left(\sum_{k=1}^{n-1} L_{ik} \frac{M_j x_j + M_n x_n \delta_{kj}}{M_j} \right) Q_j^*,$$

$$i = 1, \ldots, n-1. \tag{30}$$

We propose to use Eq. 29 (Eq. 30 is for isobaric systems) for estimating thermal diffusion ratios in multicomponent mixtures. For binary mixtures, Eq. 29 reduces to

$$k_{T1} = x_1(1 - x_1)\alpha_{T1} = \frac{M_1 x_1 M_2 x_2}{MRT} \left(\frac{Q_1^*}{M_1} - \frac{Q_2^*}{M_2} \right). \tag{31}$$

Combining this expression with Eq. 15,

$$k_{T1} = \frac{x_1}{RT} Q_1^*. \tag{32}$$

Equation 32 was used by Shukla and Firoozabadi (1998) for estimating the thermal diffusion ratio in binary mixtures [with the sign convention and the definition of the thermal diffusion factor from Shukla and Firoozabadi (1998)].

Equation 29 allows the estimation of the thermal diffusion factors for a given composition having, (1) the net heat of transport of all the components in the mixture, and (2) the phenomenological coefficients (which can be readily obtained from the molecular diffusion coefficients). When cross-molecular diffusion coefficients are neglected, that is, the phenomenological coefficients $L_{ij} = 0$ for $i \neq j$, then the expression for thermal diffusion ratios in multicomponent mixtures simplifies to

$$k_{Ti} = \frac{M_i x_i M_n x_n}{MRT} \left(\frac{Q_i^*}{M_i} - \frac{Q_n^*}{M_n} \right) \qquad i = 1, \ldots, n-1. \tag{33}$$

Thus, as in binaries, for a multicomponent mixture where the cross-molecular diffusion coefficients are negligible, the thermal diffusion ratios do not depend on molecular diffusion coefficients; they are functions of temperature, composition, molecular weight, and the net heat of transport. However, even in this case, thermal diffusion factors for multicomponent mixtures are different from those for binary mixtures, since the net heat of transport of each component differs from binary to multicomponent mixtures. Furthermore, for nonideal mixtures where the cross-molecular diffusion coefficients are significant in comparison with the mutual diffusion coefficients, they significantly affect the thermal diffusion factors. In the rest of this section we explain how the net heat of transport Q_i^* and the phenomenological coefficients L_{ij} can be obtained.

The net heat of transport for the ith component in an n-component mixture can be determined by generalizing the expression used by Shukla and Firoozabadi (1998)

$$Q_i^* = -\frac{\Delta \bar{U}_i}{\tau_i} + \left[\sum_{j=1}^{n} \frac{x_j \Delta \bar{U}_j}{\tau_j} \right] \frac{\bar{V}_i}{\sum_{j=1}^{n} x_j \bar{V}_j} \qquad i = 1, \ldots, n, \qquad (34)$$

where $\Delta \bar{U}_i$ is the partial molar internal energy departure of component i, and $\tau_i = \Delta U_i^{\text{vap}} / \Delta U_i^{\text{vis}}$; ΔU_i^{vap} and ΔU_i^{vis} are the energy of vaporization and the energy of viscous flow of pure component i, respectively (Glasstone et al., 1941).

From Eq. 26, the expression relating the phenomenological coefficient matrix L to the molecular diffusion coefficient matrix D^M can be obtained:

$$L = (D \cdot M)^{-1} \cdot D^M \cdot (W \cdot F)^{-1}; \qquad (35)$$

which is written as (Ghorayeb and Firoozabadi, 2000a)

$$\sum_{l=1}^{n-1} \sum_{k=1}^{n-1} \frac{M_k x_k + M_n x_n \delta_{lk}}{M_k} \left. \frac{\partial \ln f_k}{\partial x_j} \right|_{x_j, T, P} L_{li} = \frac{c M_n x_n}{R} D_{ij}^M, \qquad i, j = 1, \ldots, n-1. \qquad (36)$$

The preceding expression relates molecular diffusion coefficients and phenomenological coefficients. The molecular diffusion coefficients used in the next section are calculated using the model proposed by Kooijman and Taylor (1991). Ghorayeb and Firoozabadi (2000b) provide the details.

Results and Discussion

We start by studying our model for some binary mixtures near and far from the critical point; then we present results for ternary and higher mixtures. El Maâtaoui (1986) reports compositional data for the ternary mixture of $nC_{24}/nC_{16}/nC_{12}$ in a thermogravitational column (Furry et al., 1939; Lorenz and Emery, 1959; Jamet et al., 1992); our model is used to indirectly compare the results.

In order to obtain the thermal diffusion ratios using Eq. 28, equilibrium properties such as partial molar volumes, partial internal energies, and fugacities are estimated using the Peng-Robinson equation of state (PR EOS) (Peng and Robinson, 1976) with or without volume correction (Jhaveri and Youngren, 1988), along with the van der Waals mixing rules. For most of the cases we studied, the effect of the volume translation on the thermal diffusion factors was insignificant. For heavy components, however, the volume correction was found to be important to match the experimental volumetric data and had significant effect on the thermal diffusion factors. In the following, all the results we present for thermal diffusion factors are obtained without volume correction unless mentioned otherwise. The binary interaction parameters used in the PR EOS are taken from Katz and Firoozabadi (1978). Table 1 presents the critical temperature, critical pressure, acentric factor, and the molecular weight of the components considered in this study. The value of the parameter τ_i is assumed to be the same for all the components; $\tau_i = 4$. This value is based on the observation that at the normal boiling point, ln η, where η is the liquid viscosity, varies linearly with $1/T$ over a wide temperature range. The universal value of $\tau_i = 4$ gave satisfactory results for thermal diffusion factors for binary mixtures, as was shown by Shukla and Firoozabadi (1998) and is shown in this study.

Table 1. Properties of Pure Components Used in this Study

Component	T_c (K)	P_c ($\times 10^5$ Pa)	ω	M
C_1	190.60	46.00	0.008	16.04
C_2	305.40	48.83	0.098	30.07
C_3	369.80	41.90	0.152	44.09
nC_5	469.60	33.30	0.251	72.15
nC_6	507.40	29.30	0.296	86.18
C_7H_8	591.70	41.14	0.257	92.14
nC_{10}	617.60	20.80	0.490	142.28
nC_{12}	658.30	18.00	0.562	170.34
nC_{16}	717.00	14.00	0.742	226.45
nC_{24}	845.00	10.50	0.995	338.63
CO_2	304.20	72.80	0.225	44.01

Binary mixtures

Here we first present the thermal diffusion factors from the model and the data for binary mixtures of CO_2/C_2 (Walther, 1957), C_7H_8/nC_7 (toluene/n-hexane) (Köhler and Müller, 1995; Li et al., 1994), and nC_{24}/nC_{12} (El Maâtaoui, 1986). In order to make the comparison clear and to avoid confusion, we keep the same parameters that were obtained in the experimental work. The Soret coefficient, S_T, for binary mixtures used by some authors is defined by $S_T = D_1^T / [D_{11}^M x_1(1 - x_1)]$, where x_1 is the average mol fraction of component 1.

Figure 1 presents the thermal diffusion ratio k_{T1} vs. the molar density for the binary mixture CO_2/C_2 ($x_{CO_2} = 0.60$, $x_{C_2} = 0.40$) in the critical region. The predictions are in agreement with the Walther's data (1957). The figure also shows that as the critical point approaches, the predicted

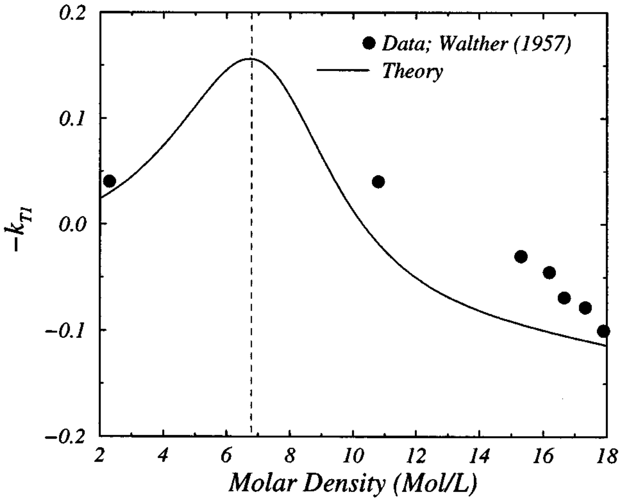

Figure 1. Thermal diffusion ratio vs. molar density at $T = 305.15$ K for the binary mixture CO_2/C_2 at composition 60/40 mol %.

The dashed line denotes the location of the critical point.

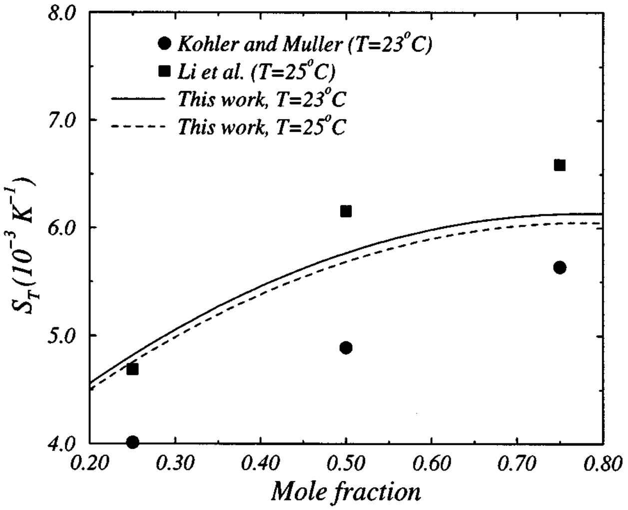

Figure 2. Soret coefficient in a toluene/*n*-hexane binary mixture vs. mol fraction of toluene at different temperatures and at atmospheric pressure.

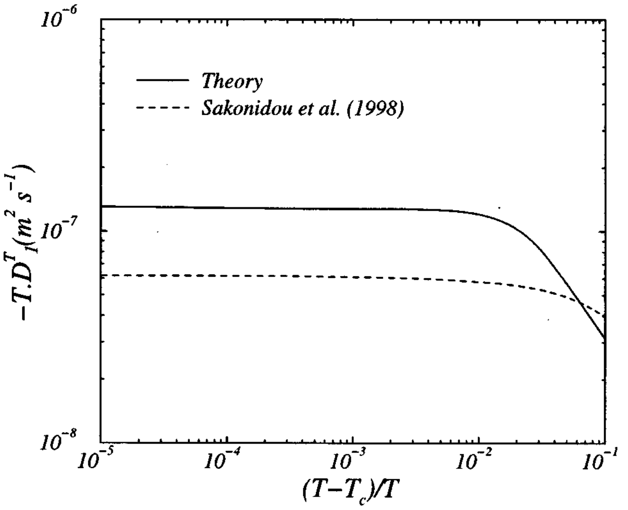

Figure 3. $-T \cdot D_1^T$ vs. $(T-T_c)/T$ for the equimolar C_1/C_2 mixture; $P=P_c=6.84\times10^6$ Pa.

thermal diffusion factor increases, as expected. Note that, depending on the molar density, CO_2 can segregate to the hot side ($k_{T1}<0$) or the cold side ($k_{T1}>0$).

Figure 2 shows the Soret coefficient in the binary mixture toluene/*n*-hexane. There is excellent agreement between the experimental data of Li et al. (1994) and Köhler and Müller (1995) and our theoretical results. Li et al. (1994) used the small-angle Rayleigh scattering method, and Köhler and Müller (1995) used the forced Rayleigh scattering method to obtain the Soret coefficients. Note that the agreement between the data and model results is very good in view of the uncertainty in the measurements of the Soret coefficients. The difference between the Soret coefficients from data at 23 and 25°C is not likely to be due to a temperature effect but to experimental differences.

El Maâtaoui (1986) reports the measured Soret coefficient in a binary mixture of nC_{24}/nC_{12} for an average composition of 8.15% nC_{24} and 91.85% nC_{12}. The average temperature for the measurements is $T_0=321.5$ K. The value of S_T reported by El Maâtaoui for these conditions is $S_T=0.90$ K^{-1}. The results from our model are in excellent agreement with the experimental data of El Maâtaoui; we obtain $S_T=0.85$ K^{-1}. This value is obtained by taking volume correction in the PR-EOS into account.

Various authors have used the mode–mode coupling analysis showing that thermal diffusion coefficients in binary mixtures exhibit a finite enhancement in the critical region (Mistura, 1972, 1975; Anisimov et al., 1995). Figure 3 depicts a plot of $-TD_1^T$ vs. $(T-T_c)/T$ near the critical point for an equimolar mixture of C_1/C_2 (at the critical pressure). This figure shows that, in view of the deficiency in the classic equations of state such as PR-EOS predictions in the critical region (Firoozabadi, 1999), our theory gives reasonable results in the critical region for this binary. The results from Sakonidou et al. (1998) are based on fitting the crossover equation of the thermal conductivity data, which allows the calculation of the molecular and thermal diffusion coefficients in the vicinity of the critical point.

Luettmer-Strathmann and Sengers (1996) investigated, using the mode–mode coupling calculations, the transport properties in a CO_2/C_2 binary mixture (25%/75%) in the critical region. They reported that (1) D_{11}^M decreases asymptotically toward zero when one approaches the critical point, and (2) k_{T1}/D_{11}^M diverges at the critical point. They also reported that D_{11}^M vanishes as ξ^{-2} (ξ is the correlation length divergent at the critical point), and k_{T1}/D_{11}^M diverges as ξ^2 when one approaches the critical point. Consequently, the product of D_{11}^M and k_{T1}/D_{11}^M, which is k_{T1}, is finite at the critical point. The results from our model for the thermal diffusion ratio, k_{T1}, for this mixture near the critical point (at the critical pressure) is depicted in Figure 4, which implies a finite value at the critical point.

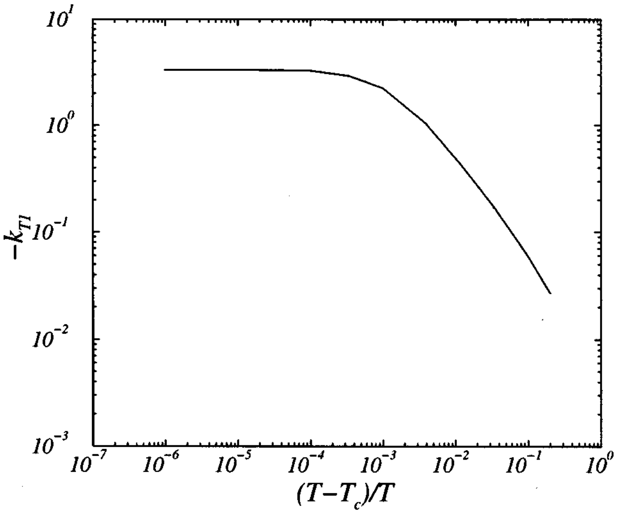

Figure 4. Thermal diffusion ratio vs. $(T-T_c)/T$ at the critical pressure for the binary mixture CO_2/C_2 at composition 25/75 mol %.

Table 2. Composition at the Top and Bottom of the Thermogravitational Column of the Ternary Mixture $nC_{24}/nC_{16}/nC_{12}$*

	$(nC_{24})_{\text{bottom}}$	$(nC_{24})_{\text{top}}$	$(nC_{16})_{\text{bottom}}$	$(nC_{16})_{\text{top}}$
Exp.	0.240	0.140	0.415	0.380
Theory	0.265	0.135	0.408	0.389

*Initial composition 12.67 (nC_{24}), 37.41 (nC_{16}), and 49.92% (nC_{12}); $T_0 = 321.5$ K, $\Delta T = 25$ K; column height = 120 cm, and permeability = 6.1×10^{-11} m^2.

Ternary mixture

The main goal of this work is to present a model for thermal diffusion factors of multicomponent mixtures. However, to the best of our knowledge there are no experimental data for multicomponent thermal diffusion factors in the literature. There are, however, spatial concentration data in ternary systems that can be used to verify the validity of our proposed model.

For the ternary mixture $nC_{24}/nC_{16}/nC_{12}$, the experimental data by El Maâtaoui (1986) in a nonisothermal 120-cm column show that nC_{24} segregates toward the bottom of the column. The data also show no significant compositional variation across the column for nC_{16}. There is excellent agreement between the measured compositional data and the results obtained using our model, where volume correction is taken into account (see Table 2). Note that without thermal diffusion there will be very little variation in the composition of nC_{12} and nC_{24} in the 120-cm column. For this mixture, the predicted Soret coefficients of components 1 (nC_{24}) and 2 (nC_{16}) from our model are $S_{T1} = 0.1552 \times 10^{-2}$ and $S_{T2} = 0.8695 \times 10^{-4}$, respectively. In addition to diffusion, thermal convection should also be considered to calculate the results in Table 2 (for details, see Ghorayeb and Firoozabadi, 2000b).

Six-component mixture

We used our model to predict the thermal diffusion factors of a mixture of $C_1/C_3/nC_5/nC_{10}/nC_{16}/C_2$ for the composition 40/12/5/2/1/40 mol % at different temperatures and pressures. The magnitude and the sign of the thermal diffusion factors obviously depend on the choice of the *n*th component (component 6 in this example). In the following, C_1, C_3, nC_5, nC_{10}, and nC_{16} represent components 1, 2, 3, 4, and 5, respectively; C_2 represents component 6. Figure 5 depicts the saturation pressure for the mixture predicted using the PR-EOS. We performed two sets of thermal diffusion factor calculations; first, we fixed the temperature equal to the critical temperature and varied the pressure. Then we fixed the pressure equal to the critical pressure and varied the temperature. The dashed lines in Figure 5 represent these two sets of calculations. The volume correction was taken into account. The predicted results are presented in Tables 3 and 4. Note that for heavier components, the thermal diffusion factor is larger than for lighter components. The thermal diffusion factor α_{T1} of the lightest component, C_1, in the mixture is negative; the others are positive. In an isobaric system when cross-molecular diffusion can be neglected, this can imply that methane can segregate toward the cold region, which may not be generally true. Similarly, component 2, C_3, may not segregate to the hot side. Tables 3 and 4 also show that, the closer the system is to the critical point, the larger is the absolute value of the thermal diffusion factors. Far from the critical point, the change of temperature (pressure) at fixed pressure (temperature) does not affect the thermal diffusion

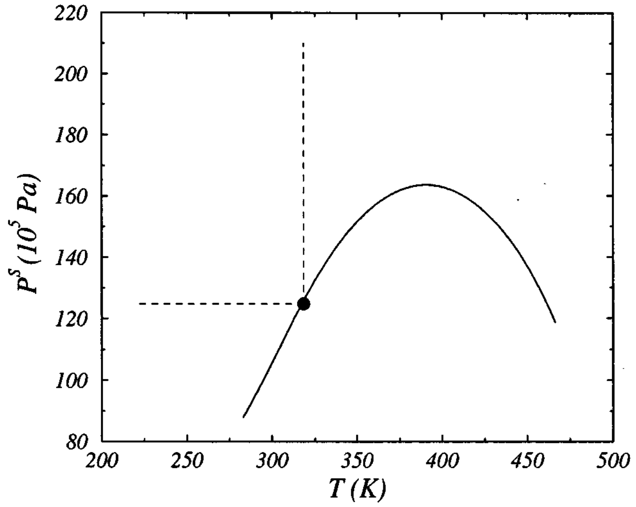

Figure 5. $P-T$ diagram for the mixture $C_1/C_2/C_3/nC_5/nC_{10}/nC_{16}$ at the composition 50/40/5/3/1/1 mol %.

The symbol ● denotes the critical point.

Table 3. Thermal Diffusion Factors for the Mixture $C_1/C_3/nC_5/nC_{10}/nC_{16}/C_2$ (40/12/5/2/1/40%, mol)*

T (K)	α_1	α_2	α_3	α_4	α_5
225	−0.8380	0.5912	1.2417	2.4412	3.2569
235	−0.8655	0.6107	1.3181	2.6466	3.6192
245	−0.8990	0.6341	1.4049	2.8774	4.0236
255	−0.9393	0.6619	1.5032	3.1377	4.4777
265	−0.9869	0.6942	1.6147	3.4323	4.9901
275	−1.0424	0.7315	1.7407	3.7656	5.5699
285	−1.1060	0.7738	1.8823	4.1415	6.2248
295	−1.1773	0.8206	2.0386	4.5602	6.9581
305	−1.2538	0.8702	2.2059	5.0147	7.7607
315	−1.3301	0.9184	2.3740	5.4825	8.5987

**Note:* $P = 1.24 \times 10^7$ Pa. C_1, C_3, nC_5, nC_{10}, and nC_{16} represent components 1, 2, 3, 4 and 5, respectively; C_2 represents component 6.

Table 4. Thermal Diffusion Factors for the Mixture $C_1/C_3/nC_5/nC_{10}/nC_{16}/C_2$ (40/12/5/2/1/40%, mol)*

$P \times 10^{-5}$ Pa	α_1	α_2	α_3	α_4	α_5
125	−1.3511	0.9312	2.4221	5.6221	8.8548
135	−1.2524	0.8647	2.2319	5.1504	8.0713
145	−1.1720	0.8105	2.0771	4.7669	7.4349
155	−1.1049	0.7653	1.9478	4.4472	6.9049
165	−1.0480	0.7267	1.8379	4.1756	6.4549
175	−0.9988	0.6935	1.7430	3.9412	6.0666
185	−0.9558	0.6644	1.6599	3.7361	5.7271
195	−0.9177	0.6387	1.5864	3.7361	5.7271
205	−0.8838	0.6157	1.5208	3.3929	5.1588

**Note:* $T = 318$ K. C_1, C_3, nC_5, nC_{10}, and nC_{16} represent components 1, 2, 3, 4, and 5, respectively; C_2 represents component 6.

factors as it does near the critical point. The distance to the critical point is the main parameter that affects the thermal diffusion factors in multicomponent mixtures.

Concluding Remarks

We have formulated a model for thermal diffusion factors for nonideal multicomponent mixtures. The model shows the explicit dependency of the thermal diffusion factors in nonideal mixtures of more than two components on molecular diffusion coefficients. The single validation of the model for a ternary mixture shows success. The model presented in this article, combined with the formalism of diffusion flux in multicomponent mixtures presented in our earlier article (Ghorayeb and Firoozabadi, 2000), provide a comprehensive theoretical framework for future experimental investigations of thermal diffusion factors in multicomponent mixtures. We believe the model also enjoys simplicity for practical applications.

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