A New Model of Thermal Diffusion Coefficients in Binary Hydrocarbon Mixtures

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Thermal diffusion is important for the study of composition variations in hydrocarbon reservoirs, and it can either enhance or weaken the separation in mixtures. We present a new model for the prediction of thermal diffusion coefficients in binary mixtures of reservoir fluids using the thermodynamics of irreversible processes. The model needs equilibrium properties of mixtures and energy of viscous flow. Equilibrium properties are obtained from the volume translated Peng–Robinson equation of state, and the energy of viscous flow is estimated from viscosity. The model has been applied to predict thermal diffusion coefficients of several mixtures consisting of nonhydrocarbon and hydrocarbon fluids. Comparisons of theoretical results with experimental data show a good performance of the model except in the near-critical region where all existing models are deficient. In particular, the predicted sign of thermal diffusion coefficients is consistent with experimental observations in systems investigated here, namely, C6/C8, C7/C9, C8/C10, C9/C12, C10/C16, Ar/CO2, N2/CO2, H2/N2, H2/CO2, and C7/C9, except in C7/N2, in which the values of thermal diffusion coefficients are extremely low. We have also modified some of the earlier models, such as the Kempers, Haase, and Rutherford models, which are based on phenomenological and kinetic approaches. In general, our model has been found to be most reliable and represents a significant improvement over the earlier models.

1. Introduction

A tendency of a convection-free mixture to separate under a thermal (or temperature) gradient is known as the thermal diffusion process or Soret effect. In this process, the transport of matter takes place (i.e., a concentration gradient of the mixture constituents develops) with the temperature gradient. The thermal diffusion coefficient is the measure of this effect, and its sign determines the direction of the thermal diffusion. The thermal diffusion process can occur in both liquid and gaseous mixtures and is important to (a) separate isotopic mixtures and isobaric mixtures, (b) analyze hydrodynamic instability in mixtures, (c) transport mass in living matters, (d) migrate minerals, (e) separate and characterize macromolecular (polymers) and colloidal particles by thermal field flow fractionation, and (f) study compositional variation in hydrocarbon reservoirs (oil and gas reservoirs).

The thermal diffusion coefficient, here represented by α, is an important property to be well-understood from either experiment or theory. In some mixtures due to the small magnitude of thermal diffusion coefficients and the possible obscuring effect of thermal convection, accurate measurements on α are difficult to perform. Consequently, the experimental data of α are sparse. In low-pressure gaseous mixtures and in ideal liquid mixtures, α has been found to be small, and the molecular mass and size are the main parameters to govern the magnitude of α. On the other hand, in nonideal liquid mixtures α may be large, in particular, close to the critical point. In liquids, energetic interactions, the size and shape of the molecules, and thermodynamic conditions play important roles in governing the magnitude and direction of α. Calculations based on thermodynamics of irreversible processes show that thermal diffusion can have a significant effect on the composition variation in the horizontal and vertical directions in hydrocarbon reservoirs. One requires a reliable thermal diffusion coefficient model to account for thermal diffusion.

In the past, several theoretical approaches have been advanced to describe thermal diffusion coefficients in binary mixtures with varying degrees of success. They are based on kinetic theory of dense hard spheres and its revisions, partial excess enthalpy and activity coefficient, Brownian motion and heat of transport, kinetic theory of irreversible thermodynamics, phenomenological theory of irreversible thermodynamics, and maximization of the partition function of two idealized bulbs. Expressions for α could also be obtained using different combinations of the above approaches. Among the models mentioned above, the last three models were applied to describe thermal diffusion coefficients in some hydrocarbon mixtures only qualitatively.

In this paper, we present a simple analytical model of thermal diffusion coefficients in binary mixtures and examine its accuracy by comparing theoretical results with available experimental data for hydrocarbon and nonpolar nonhydrocarbon mixtures. Our new model is based on the thermodynamics of irreversible processes. The equilibrium properties appearing in the model are evaluated from an equation of state, while the nonequilibrium properties are obtained from the knowledge of viscosity data. Also, we present the modified forms of Rutherford, Haase, and Kempers models, by incorporating in them the more accurate equation of state. Below, we present explicit forms of different theories and compare their predictions with experimental data.

In the following section, we present the general expression for diffusive mass flux and its relation with
thermal diffusion coefficients. In section 3, we present the modified forms of the Haase model, the Kempers model, and the Rutherford model. We then derive our new model using the thermodynamics of irreversible processes. In section 4, a comparison between theory and experiment is presented. Section 5 concludes the results of this work.

2. Mass Flux and Thermal Diffusion Coefficients

Here, we consider a binary mixture, in which the thermal diffusion coefficient of component 1 is given by

\[ \kappa_f \nabla T \]

\[ \nabla x_1 + \frac{M \chi_1}{RT} \left[ \nabla x_1 \right] \]

\[ \frac{\kappa_f \nabla x_1}{\kappa_f \nabla T} \]

The above expression consists of three parts: molecular diffusion, pressure diffusion, and thermal diffusion, respectively. In eq 1, \( \rho_1 \) is the total molar density, \( M \) is molecular weight, \( T \) is temperature, \( x_1 \) is the mole fraction of component 1, \( \rho \) is the mass density, \( P \) is pressure, \( R \) is a gas constant, \( V_1 \) is the partial molar volume of component 1, \( D_{12} \) is the molecular diffusion coefficient, \( \kappa_f \) is the thermal diffusion ratio of component 1, \( \nabla \) the gradient operator, and \( F_1 = (\ln f_1(\ln x_1))_T \), where \( f_1 \) is the fugacity of component 1.

The thermal diffusion coefficient \( \alpha_f \) of component 1 is defined as

\[ \alpha_f = \kappa_f/x_1 \]

Equation 1 is the Haase model.

In the second method, Kempers\textsuperscript{17} obtained an expression for \( \alpha_f \) by maximizing the partition function in a canonical ensemble of an idealized dual subsystem in a steady state, given by

\[ \alpha_f = -[(\nabla x_1 \nabla x_2)/(\nabla x_1 + \nabla x_2)] \]

where \( \nabla x_1 \) is the partial molar enthalpy of 1 at zero pressure, \( \nabla x_2 \) is the partial molar enthalpy of the standard state (pure component 1) at zero pressure, and \( \mu_1 \) is the chemical potential of component 1. Here, eq 5 is referred to as the Kempers model.

3. Theory of Thermal Diffusion Coefficients

Several attempts have been made in the past to model thermal diffusion coefficients in binary mixtures. There are mainly two theoretical approaches: the phenomenological approach and the kinetic approach, which have been the basis of modeling thermal diffusion coefficients in binary mixtures of industrial interest. Only the most important models of our interest originating from these approaches are described below.

3.1. Phenomenological Approach. In this approach, two different methods have been adopted for the derivation of \( \alpha_f \). In the first method, phenomenological equations of irreversible thermodynamics have been used to derive the following expression for \( \alpha_f \)

\[ \alpha_f = -[\alpha_f RT + (M_1(\nabla x_1 - \nabla x_2) - M_2(\nabla x_2 - \nabla x_1))/(M_1 + M_2) V(x_1(\partial \mu_1/\partial x_1)_T \nabla T)] \]

where \( \alpha_f \) is the thermal diffusion coefficient at the standard state at zero pressure, \( \nabla x_1 \) is the partial molar enthalpy of 1 at zero pressure, and \( \mu_1 \) is the chemical potential of component 1. Here, eq 5 is referred to as the Haase model.

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Both the Haase model and the Kempers model (in their original forms) have been tested previously for a few binary hydrocarbon mixtures using the Soave–Redlich–Kwong (SRK) equation of state (EOS) (Kemper\textsuperscript{17}). Agreement between theory and experiment was found to be only qualitative. Recently, the original Kempers model in combination with the Peng–Robinson (PR)\textsuperscript{20} equation of state was used to predict thermal diffusion coefficients in several binary hydrocarbons by Firoozabadi et al.\textsuperscript{19} In those calculations, partial molar enthalpies of the standard state were obtained from the Pauzaat and Danner correlations\textsuperscript{1,24} In general, comparisons of theoretical results with experimental data for hydrocarbon mixtures were found to be again only qualitative. The misinterpretation of some experimental data and the improper inclusion of the volume translation term in the equation of state could also be responsible for some misleading conclusions.\textsuperscript{19}

In order to correct the above problems, we use the volume–translated PR EOS in all our calculations presented below. Since the same equation of state is used in the modified forms of the Haase and Kemmers models, including ours presented below, our present results provide a consistent and systematic study of the thermal diffusion coefficients in binary mixtures.

3.2. Kinetic Approach. The kinetic approach of determining \( \alpha_f \) is based on irreversible thermodynamics and has been exploited by several workers.\textsuperscript{7,8,15,25–28} In
this approach, thermal diffusion coefficients are expressed in terms of the specific heats of transport of the two components in a binary mixture. The specific heats of transport are obtained from the activation energy of molecular motion, which, in turn, can be obtained from the viscosity of the mixture. However, accurate calculation of the activation energy of motion remained a problem in the past, and in those calculations, thermodynamic properties were estimated using the approximate regular solution theory.

Following the kinetic approach, several expressions for \( \alpha \) can be obtained. For example, Dougherty and Drickamer\textsuperscript{26} obtained \( \alpha \) in terms of the activation energies for molecular movements \( \Delta U_1^* \) and \( \Delta U_2^* \) for components 1 and 2, given as

\[
\alpha_{DD} = -\frac{\{M_1 \tilde{V}_2 + M_2 \tilde{V}_1 \} \Delta U_1^* \tilde{V}_2 - \Delta U_2^* \tilde{V}_1 \} \nu}{(2(M_1 x_1 + M_2 x_2) \nu (\partial \mu_1 / \partial x_1)_{T,P})} \quad (7)
\]

where the activation energy for molecular movement of the components, \( \Delta U_i^* \), is given by

\[
\Delta U_i^* = (2k n (\partial \mu_i^*/\partial x_i)_{T,P}) \quad (8)
\]

\( \Delta U_i^* \) is the total activation energy; \( n \) and \( n_i \) are the total number of moles and number of moles of component \( i \), respectively. \( \Delta U_i^* \) is a function of viscosity and thermodynamic properties of fluids. Our comparisons of theoretical results for \( \alpha_{DP} \) with experimental data show that the Dougherty–Drickamer model does not perform better than the other two models presented above. Therefore, results based on this model are not reported here.

Another simple model based on the irreversible thermodynamics was proposed by Rutherford.\textsuperscript{15} Because of the inherent approximations involved, this model, however, is identical with the Haase model\textsuperscript{21} as described above (eq 5). The thermal diffusion coefficient obtained from the modified Rutherford model is referred to as \( \alpha_{R} = \alpha_{H} \). This model was used by Rutherford\textsuperscript{15} in order to explain \( \alpha \) in the \( C_5/C_6 \) mixture using the BWR equations of state of Benedict et al.\textsuperscript{29} Theoretical predictions were found to be only qualitative. Here, we check the accuracy of the modified form of the Rutherford model against experimental data of several mixtures. The values of \( \alpha_{R} \) in the Rutherford model (or the Haase model) were determined from the kinetic theory of gases. They are tabulated by Haase\textsuperscript{18} for \( C_1/C_2 \) and by Rutherford\textsuperscript{15} for \( C_1/C_4 \). Our calculations show that the contribution of the \( \alpha_0 \) term is very small in \( C_5/C_6 \) and \( C_4/C_6 \) mixtures (less than 1% in most cases). Therefore, we do not consider \( \alpha_0 \) in mixtures other than \( C_1/C_2 \) and \( C_1/C_4 \).

In general, the models discussed above have been found to describe thermal diffusion coefficients in binary mixtures only qualitatively. In some mixtures, they are even unable to predict the correct sign of \( \alpha \). Therefore, we present below a new model based again on the irreversible thermodynamics combined with the equilibrium thermodynamics. This model is found to be more reliable than those suggested previously for the prediction of thermal diffusion coefficients in binary mixtures consisting of hydrocarbon and nonpolar nonhydrocarbon fluids.

### 3.3. Present Approach: A New Model for \( \alpha \)

Our new model is based on the method of irreversible thermodynamics. The basis of our development is the same as that proposed by Dougherty and Drickamer\textsuperscript{30} a long time ago. Following irreversible thermodynamics, Dougherty and Drickamer\textsuperscript{30} presented \( \alpha \) in terms of the properties of pure components and solubility parameters. However, their model suffers from two major defects: (a) in order to avoid the mixture property calculations, \( \alpha \) was presented in terms of the properties of pure components and solubility parameters, and (b) thermodynamic properties of the components were obtained from the approximate Scatchard–Hildebrand theory.\textsuperscript{51,52} We now know that the solubility parameters of components cannot be estimated accurately and the Scatchard–Hildebrand theory is unreliable in dealing with nonideal mixtures under different conditions.

Our new model is more rigorous than the earlier models presented in the literature and uses more accurate thermodynamic properties of mixtures obtained from the volume-translated Peng–Robinson equation of state. The effect of the nonequilibrium part in the model is accounted for by incorporating the energy of viscous flow, which can be obtained from the viscosity of the mixture components. From our approach one can even derive the Rutherford model and can obtain several other expressions for \( \alpha \) in terms of the properties of pure components and solubility parameters.

Following the thermodynamics of irreversible processes,\textsuperscript{33–35} the flux equation for the \( i \)th component in a multicomponent mixture at constant pressure is given by

\[
\mathcal{J}_i^0 = -\sum_{k=1}^{c} L_{ik}((Q_k - \tilde{H}_k) \nabla T/T) + \sum_{j=1}^{c-1} (\partial \mu_j / \partial x_j) \nabla x_j \quad (9)
\]

where \( L_{ik} \) is the phenomenological coefficient, \( Q_k \) is the heat of transport, \( \tilde{H}_k \) is the partial molar enthalpy, and \( c \) is the number of components. In fact, in the absence of a temperature gradient, \( Q_i \) is the amount of energy transported across a given reference plane per mole of the \( i \)th component.

From eq 9, in a binary mixture, the composition gradient resulting from the temperature gradient in the steady state for the first component is given by (since \( L_{12} \) and \( L_{11} \) are independent)\textsuperscript{50}

\[
\nabla x_1/x_2 = -(Q_1^* (x_1 (\partial \mu_1 / \partial x_1)) / (\nabla T/T)) \quad (10)
\]

with

\[
Q_1^* = Q_1 - \tilde{H}_1 \quad (11)
\]

where \( Q_1^* \) is the net heat of transport. A similar expression can be given for the second component,

\[
\nabla x_1/x_2 = -(Q_2^* (x_2 (\partial \mu_2 / \partial x_2)) / (\nabla T/T)) \quad (12)
\]

Using eqs 10 and 12, together with the following Gibbs-Duhem equations

\[
x_1 \partial \mu_1 / \partial x_1 + x_2 \partial \mu_2 / \partial x_2 = 0 \quad (13)
\]

we obtain a simple relation between the composition and temperature gradients as follows:
\[ \nabla x_1/x_2 = \left[ (Q_{i}^* - Q_i) \nabla x_1 (\partial \mu_i/\partial x_i) \right] (\nabla V T T) \]  
(14)

Alternatively, from the conventional flux equation for a binary mixture in the steady state (in the absence of convection and gravity), from eq 3 we obtain another relation between $\nabla x_1$ and $\nabla T$.

\[ \nabla x_1/x_2 = \alpha (\nabla V T T) \]  
(15)

Comparing eqs 14 and 15, we obtain the following new expression for the thermal diffusion coefficient in terms of the net heat of transport and chemical potential, represented by $\alpha$:

\[ \alpha = [(Q_{i}^* - Q_i) \nabla x_1 (\partial \mu_i/\partial x_i)] \]  
(16)

Equation 16 is our working expression for deriving an explicit expression for $\alpha$ in terms of the equilibrium and nonequilibrium properties of mixtures.

Since the direct evaluation of the net heat of transport, $Q_i^*$, is still not possible, following the physical interpretation of Dougherty and Drickamer\cite{30} and Denbigh\cite{35} we relate it with the energy of detaching a molecule from its neighbors in the region of the mixture, $W_{H1}$, and with the energy given up in that region when one molecule fills a hole, $W_L$, as follows:

\[ Q_{i}^* = W_{H1} - W_L \psi_i \]  
(17)

\[ Q_i^* = W_{H2} - W_L \psi_i \]  
(18)

where $\psi_i$ represents the volume fraction of molecules moving into a hole left by a molecule of type $i$ in the mixture. Note that, in the above derivation, molecules may have different sizes and shape, and the distribution of molecules to occupy holes in the mixture is completely random. Therefore, the probable energy, $W_L$, supplied to fill a hole left by the detached molecule is given by

\[ W_L = x_1 W_{H1} + x_2 W_{H2} \]  
(19)

with

\[ W_{H1} = -\bar{U}_1/\tau_1 \quad \text{and} \quad W_{H2} = -\bar{U}_2/\tau_2 \]  
(20)

where $\bar{U}_i$ is the partial molar internal energy of component $i$, and $\tau_i$ is the ratio of the energy of vaporization, $\Delta U^{vap}$, and the energy of viscous flow, $\Delta U^{visc}$.\cite{36}

\[ \tau_i = \Delta U^{vap}/\Delta U^{visc} \]  
(21)

Physical interpretation of $\tau_i$ and its evaluation are presented below and in Appendix I.

Based on the physical interpretation of the net heat of transport, $Q_i^*$, with variation of the number of molecules in the mixture, $N_i \psi_i$, where $N_i$ is the number of molecules of species $i$, we make use of the following simple relations of $\psi_i$ in terms of the partial molar volume and composition:\cite{30,35}

\[ \psi_i = \bar{V}_i (x_1 \bar{V}_1 + x_2 \bar{V}_2) \]  
(22)

with the condition that eq 22 must satisfy the Gibbs-Duhem relation following eq 13:

\[ x_1 \psi_1 + x_2 \psi_2 = 1 \]  
(23)

Detail on the characterization of $\psi_i$ is given in Appendix II. Note that in eq 22 the volume fraction is related to the partial molar volumes. This is a major deficiency of all current work including ours. In some systems close to the critical region, partial molar volume of the heavy component obtained from either theory or experiment may become negative.\cite{3} This behavior may provide unphysical values for $N_i \psi_i$. To correct this problem, we therefore use the absolute values of $\psi_i$ to count the number of molecules $N_i \psi_i$, leaving (or occupying) the holes as discussed in Appendix II. Numerically, this latter procedure has been found to offer a slight improvement over the former in the critical region of mixture C1/C3.

Using eqs 16–22, the expression for the thermal diffusion coefficient of component 1 in a binary mixture is given by

\[ \alpha = \left[ \bar{U}_1/\tau_1 - \bar{U}_2/\tau_2 \right] - \left[ (\bar{V}_2 - \bar{V}_1) x_1 W_{H1}/\tau_1 + x_2 W_{H2}/\tau_2 \right] \]  
\[ \times \left[ x_1 (\partial \mu_1/\partial x_1) \right]_{TP} \]  
\[ + \left[ x_2 V_1 + x_2 V_2 \bar{V}_i (\partial \mu_1/\partial x_1) \right]_{TP} \]  
(24)

Equation 24 represents our new model for the thermal diffusion coefficient in binary mixtures and is an explicit function of partial molar energies and volumes, energy of vaporization, and viscous flow, along with the chemical potential. Thus, the calculation based on eq 24 requires the values of $\tau_i$ and also the physically reasonable values of partial molar volumes as discussed below. Note that eq 24 cannot be applied to isotropic mixtures; it must be modified to incorporate the molecular mass dependence following ref 26.

In fact, inclusion of $\tau_i$ in the theory accounts for the energy supplied for molecular motion and cohesive energy of the liquid; the latter is approximated by the energy of vaporization. The energy of viscous flow can be determined from the viscosity data of the components. On the basis of the variation of energy of viscous flow with that of vaporization, Glassstone et al.\cite{56} suggested that under normal boiling point liquid conditions the value of $\tau_i$ may lie between 3 and 4 for most of the nonassociated liquids and hydrocarbons, which is of primary interest to us. After we modified their procedure of determining $\tau_i$, our calculation shows that, at low temperature and pressure, $\tau_i$ may range between 3 and 5. Of course, it may have even lower or higher values under different conditions of temperature and pressure. Detail on the estimation of $\tau_i$ for the mixture components is presented in Appendix I along with Figure 1. The energy of viscous flow and its relation with the energy of vaporization and viscosity is not well-defined rigorously under different conditions; we have adopted the universal values for $\tau_i$ ($\tau_1 = 4, \tau_2 = 4$) for all the fluids presented here.

4. Results and Discussion

In this section, we examine the performance of different models (our new model, a modified Kemper model, and a modified Rutherford model) in representing thermal diffusion coefficients in a number of binary mixtures for which reliable experimental data are available. We note again that the modified Rutherford model is identical with the modified Haase model $\alpha_{m}$, i.e., $\alpha_{m} = \alpha_{H}$. The systems investigated are classified in three categories: (1) hydrocarbon systems, namely, C7/C8, C9/C10, C10/C12, and C15/C16; (2) nonpolar nonhydro-
carbon systems, namely, Ar/CO₂, N₂/CO₂, H₂/N₂, and H₂/CO₂; and (3) hydrocarbon/nonhydrocarbon systems, namely, C₄/Ν₂ and C₄/CO₂. Since we are not considering the association, we apply our theory only to those mixtures, thermodynamic properties of which can be explained from the volume-translated PR EOS sufficiently accurately. In all our comparisons, the fluid indicated first signifies component 1 of the mixture.

The evaluation of thermodynamic properties requires critical parameters, anacentric factor, molecular weight, and a coefficient for the volume translation of the mixture components. Critical parameters and the acentric factor were taken from the literature. The volume translation coefficient was obtained from Jhaveri and Younghren and the Computer Modeling Group (CMG). In order to perform mixture calculations, the usual van der Waals mixing rule has been used. The binary interaction parameter kᵣ, appearing in the equation is taken to be kᵣ = 0.01 for all hydrocarbon mixtures as recommended by Katz and Tirozabadi. For non-hydrocarbon mixtures, kᵣ = 0. Our calculations based on the different reasonable values of kᵣ (other than those given above) show that kᵣ has no appreciable affect on the thermal diffusion coefficients of mixtures investigated here.

4.1. Hydrocarbon Mixtures. Figure 2 compares theoretical predictions with experimental data for C₄/C₃ at temperature T = 346 K and composition x₁(C₄) = 0.34 as a function of pressure. This mixture is close to the critical point, exhibiting a sharp maximum in α at about P = 60 bar. Results based on the three models, Kemmers, Rutherford, and our models, are included in the figure. As can be seen, all models predict the correct sign of α, suggesting that component 1, in this case CH₄, segregates in the hot region. These models also show a maximum in α close to P = 70 bar. The Kemmers model overestimates α. On the other hand, the Rutherford model gives better prediction at lower pressures, P < 55 bar, but overestimates at higher pressures. The results based on our model are given for the set of (r₁ = 4, r₂ = 4), which is based on the recommendation of Glasstone et al. and on our own calculations as described in Appendix I. In general, our model appears to be more consistent with experiment.

Figures 3 and 4 show the variation of α with composition x₁(C₄) for C₄/C₃ at temperature T = 346 K, for two pressures, P = 55 and P = 75 bar, respectively. Comparison of different theories with experiment shows that our model performs best in describing experimental data, in particular, for compositions larger than x₁ = 0.4, while both the Kempers and Rutherford models overestimate α. Again, for compositions close to the critical region, x₁ < 0.4, our model can describe experimental data for either pressure only qualitatively due to approximation by eq 22.

The above comparisons suggest that the major discrepancy between theory and experiment lies in the critical region of the mixture C₄/C₃. In order to illustrate whether the above mixture lies in the critical region and what can be the effect of critical behavior of the mixture on α, Figure 5 presents a vapor/liquid phase diagram for the C₄/C₃ mixture at T = 346 K using the
Figure 4. Comparison of theory with experiment\(^{20}\) for \(C_1/C_3\) at \(T = 346\) K and \(P = 75\) bar.

Figure 5. Vapor/liquid phase diagram of \(C_1/C_4\) at \(T = 346\) K.

PR EOS. Although none of the above state condition of Figures 2–4 lies within the phase envelope in Figure 5, the composition \(x_1 = 0.34\), with the pressure range \(P = 50–70\) bar, lies close to the critical point. The general trend of our theory is consistent with experiment even close to the critical point of the mixture. However, it appears that the critical condition effects are not properly taken into account by the model, and hence the theoretical prediction in the critical region is only qualitative, as was explained above.

Figures 6 and 7 present results of \(a\) for the nonideal mixture \(C_1/C_4\) using all three models as a function of pressure at a fixed composition, \(x_1 = 0.49\), but for two different temperatures, \(T = 344\) and 394 K, respectively. Thus, these figures provide pressure as well as temperature dependence of \(a\) at the given composition. In all cases, our model is seen to be highly reliable in describing experimental data\(^{20}\) at all conditions. As was seen before, the Kempers model fails to describe experimental results. The Rutherford model performs better than the Kempers model but is inferior to our model. In some cases, the Rutherford model follows our model because the latter model can be transformed easily into the former after some approximations. Similar results were obtained at other temperatures, \(T = 319, 361,\) and 378 K for \(x_1 = 0.49\) and \(T = 319, 344, 378,\) and 394 K for \(x_1 = 0.49,\) not shown here.

Figure 8 compares our model with experiment for \(C_1/C_4\) as a function of pressure at three different temperatures, \(T = 319, 361,\) and 394 K for \(x_1 = 0.49\). Theoretical predictions are in good agreement with experimental data at the lowest temperature, \(T = 319\) K, over the entire range of pressure. As the temperature increases from \(T = 319\) to 361 K, theoretical results still compare with experimental data very well. At the highest temperature, \(T = 394\) K, however, our model is seen to consistently underestimate experimental results at lower pressures, \(P < 120\) bar. Similar comparisons are presented in Figure 9 for a lower value of the composition, \(x_1 = 0.4,\) at \(T = 319, 378,\) and 394 K. As
shown in Figure 8, even in this case the agreement between theory and experiment is excellent at the lowest temperature, \( T = 319 \) K, for all pressures. At the other two higher temperatures (\( T = 378 \) and 394 K), especially at lower pressures (\( P < 150 \) bar), the discrepancy between theory and experiment is found to be more pronounced than in Figure 8. As in the C\(_4/C_2\) mixture, this discrepancy between theory and experiment may be due to the fact that the C\(_4/C_4\) mixture is close to the critical point under those conditions (\( x_1 = 0.4, T = 378 \) K, \( P < 140 \) bar and \( x_1 = 0.4, T = 394 \) K, and \( P < 150 \) bar). This can be clearly seen in Figure 10 using the phase diagram of C\(_4/C_4\). It should be noted that the experimental results of this system were misinterpreted previously, leading to the wrong conclusions, and the minor calculational errors in incorporating the volume translation term in PR EOS could also lead to erroneous results.\(^19\)

Figure 11 depicts results of \( \alpha \) from theory and experiment for another hydrocarbon mixture, C\(_6/C_{12}\), as a function of temperature, at fixed composition and pressure (\( x_1 = 0.5, P = 1.01325 \) bar). Experimental data are taken from Trevoy and Drickamer.\(^43\) The Kempers model is seen to provide a good prediction at low temperatures, but \( \alpha \) increases monotonically as the temperature increases. This latter behavior of the Kempers model is inconsistent with experiment. The Rutherford model fails and predicts the wrong sign of \( \alpha \). The prediction based on our model is consistent with experimental results, in particular in describing the sign of \( \alpha \). In our calculations, the volume translation term plays an important role in describing \( \alpha \) of the mixture C\(_6/C_{12}\). Since our model as well as the Kempers model depends on the partial molar volumes, volume-translated PR EOS offers a significant improvement in both theories. We have also demonstrated in the figure the explicit effect of the difference in \( x_1 \) parameters (\( r_1 = 4, r_2 = 3.5 \)) on \( \alpha \) in our model. This effect is significant and indicates that a reasonable choice of the different
$r_1$ parameters of components may lead to a successful representation of $\alpha$.

In order to further examine the reliability of our model, Figure 12 compares theoretical and experimental results of $\alpha$ for $\text{C}_2\text{C}_{18}$. Partial molar volumes are calculated again using the volume-translated PR EOS. Figure 12 shows the variation of $\alpha$ with composition of $\text{C}_2$ at $T = 308$ K and $P = 1.01325$ bar. This figure reveals that, unlike $\text{C}_2\text{C}_6$ or $\text{C}_4\text{C}_4$, the magnitude of $\alpha$ in $\text{C}_2\text{C}_{18}$ is small, but the direction of thermal diffusion in either mixture is the same. Our model can describe the direction of $\alpha$ and its magnitude reasonably well over the whole range of composition. As in Figure 11, the set ($r_1 = 4$, $r_2 = 3.5$) leads to a good prediction of $\alpha$. The modified Kempers model is greatly improved and becomes more accurate than its original form used before by Firoozabadi et al.\textsuperscript{43} (see their Figure 14). Again, the Rutherford model becomes unreliable in describing even the direction of $\alpha$.

4.2. Nonhydrocarbon Mixtures. We now present a comparison between theoretical and experimental results for $\alpha$ in a few binary nonhydrocarbon mixtures, namely, $\text{Ar}/\text{CO}_2$, $\text{N}_2\text{O}/\text{CO}_2$, $\text{H}_2\text{N}_2$, and $\text{H}_2\text{CO}_2$. Experimental values of $\alpha$ for these mixtures are available in gaseous conditions.\textsuperscript{45}

Figures 13–15 show the comparison between theoretical predictions and experimental results for $\alpha$ in mixtures $\text{Ar}/\text{CO}_2$, $\text{N}_2\text{O}/\text{CO}_2$, and $\text{H}_2\text{N}_2$, respectively, as a function of pressure at the same given temperature, $T = 357$ K. Mixtures $\text{Ar}/\text{CO}_2$ and $\text{H}_2\text{N}_2$ are equimolar at $x_1 = 0.5$. Mixture $\text{N}_2\text{O}/\text{CO}_2$ is non-equimolar at $x_1 = 0.52$. Compared to the mixtures of the previous section, the magnitude of the thermal diffusion coefficient in these mixtures is relatively small. In general, our model can describe experimental data\textsuperscript{46} of $\alpha$ in all three mixtures reasonably well. The Kempers model is seen to overestimate experimental values of $\alpha$, while the Rutherford model performs better than the former for $\text{Ar}/\text{CO}_2$ (Figure 13) and $\text{N}_2\text{O}/\text{CO}_2$ (Figure 14). For $\text{H}_2\text{N}_2$ (Figure 15), the Rutherford model becomes unreliable by predicting the large negative values of $\alpha$.

Figures 16–18 present results for $\alpha$ in the gas mixture $\text{H}_2\text{CO}_2$. In this case, our model with ($r_1 = 4$, $r_2 = 4$) can describe only the direction of $\alpha$ but not the magnitude. This is in contrast to the very good results obtained for the similar mixture $\text{H}_2\text{N}_2$ in Figure 15. However, a different set of parameters ($r_1 = 1$, $r_2 = 1$) is the better choice for the prediction of experimental data reliably, over the range of pressure (Figure 16) and temperature (Figure 17). Predictions based on the Kempers model are identical with those based on our model with ($r_1 = 1$, $r_2 = 1$), while the Rutherford model is seen to always underestimate experimental data. In Figure 18, the composition dependence of $\alpha$ cannot be described by any of the three models investigated here. It appears that $r_1$ parameters determined from the liquid state conditions are unable to explain $\alpha$ of the gaseous mixture $\text{H}_2\text{CO}_2$ very well (although the same parameters are able to describe $\alpha$ of mixture $\text{H}_2\text{N}_2$ reliably).

4.3. Hydrocarbon–Nonhydrocarbon Mixtures. Experimental values of $\alpha$ for two hydrocarbon–nonhydrocarbon (nonpolar) mixtures, $\text{C}_2\text{H}_4/\text{N}_2$ and $\text{C}_2\text{H}_4/\text{CO}_2$, are
available in gaseous conditions. Figures 19 and 20 show comparisons between theoretical predictions and experimental results for $\alpha$ in equimolar mixture C$_2$H$_6$/N$_2$ and nonequimolar mixture C$_2$H$_6$/CO$_2$, respectively, as a function of pressure at the same temperature, $T = 357$ K. As was the case with nonpolar mixtures of the previous section, the magnitude of the thermal diffusion coefficient in these mixtures is also small. Especially, in mixture C$_2$H$_6$/N$_2$, the magnitude of $\alpha$ is extremely low. Our model can describe experimental data of $\alpha$ in C$_2$H$_6$/CO$_2$ (Figure 20) well, while it predicts the small negative values of $\alpha$ in C$_2$H$_6$/N$_2$ (Figure 19). However, a choice of the set $r_1 = 4$, $r_2 = 3.5$ in Figure 19 is seen to describe experimental results more accurately. For C$_2$/N$_2$ (Figure 19), both the Kemmers and Rutherford models predict the large negative values of $\alpha$. For C$_2$/CO$_2$ (Figure 20), the Kemmers model is seen to overestimate experimental values of $\alpha$, while the Rutherford model predicts the negative values of $\alpha$.

5. Conclusion

The new model for binary mixtures of reservoir fluids uses the thermodynamics of irreversible processes. The model needs both equilibrium and nonequilibrium properties of mixtures and is more rigorous than those presented in the past. We have also modified the previously available models, the Kemmers model, the Haase model, and the Rutherford model, based on phenomenological and kinetic approaches. Theoretical results for $\alpha$ are tested against experimental data for the numerous hydrocarbon and nonhydrocarbon mixtures.

Detailed comparisons of theoretical results with experimental data for the thermal diffusion coefficients show the good performance of our model in different nonideal conditions but away from the critical region. In general, our new model has been found to be superior to the modified Kemmers and Rutherford models in describing experimental results for the thermal diffusion
coefficients in binary mixtures. In particular, the Kempers model performs only qualitatively in hydrocarbon mixtures but becomes more reliable in nonhydrocarbon mixtures. In contrast, the Rutherford model is more reliable than the Kempers model in describing thermal diffusion in hydrocarbon mixtures. However, it fails in nonhydrocarbon mixtures. Finally, accurate data for binary liquid mixtures under different conditions are needed to further test and improve the accuracy of our model. The data on thermal diffusion coefficients of hydrocarbon mixtures are so sparse that it is not possible to comment on their accuracy.

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List of Symbols

- BWR = Benedict–Webb–Rubin equation of state
- D = molecular diffusion coefficient
- EOS = equation of state
- f = fugacity
- H = enthalpy
- J = diffusion mass flux
- M = molecular weight
- MR = mixing rule
- P = pressure
- PR = Peng–Robinson
- Q = heat of transport
- Q* = net heat of transport
- R = gas constant
- SRK = Soave–Redlich–Kwong
- T = temperature
- U = internal energy
- U^* = energy of activation in mixture
- U^*_i = energy of activation of component i
- V = molar volume
- VDW = van der Waals

Greek Symbols

- \( \alpha \) = thermal diffusion coefficient
- \( \eta \) = viscosity
- \( \kappa_T \) = thermal diffusion ratio
- \( \mu \) = chemical potential
- \( \tau \) = ratio of the energy of vaporization and viscous flow
- \( \nabla \) = gradient operator

Superscripts

- C = cold
- ex = experiment
- H = hot
- vap = vaporization
- visc = viscous

Subscripts

- DD = Dougherty and Drickamer model
- ex = experiment
- H = Haase model
- i, s = indices of the species
- K = Kempers model

Appendix I. Estimation of \( \tau \) from Viscosity Data

Here, we follow the hole theory of liquid mixtures (see, for example, Glassstone et al.\(^{36}\)), in which viscosity (\( \eta \)) is related to the energy of viscous flow (\( \Delta U^{visc} \)) in the following way:

\[
\eta = \left( hN/V \right) (F/F^*) \exp(\Delta U^{visc}/RT) \tag{1.1}
\]

where the partition function \( F \) for a molecule of liquid in its initial state (\( \tau = 0 \)) is given by

\[
F = (2\pi m k_B T/h^2)^{3/2} v_i \tilde{b}_k \exp(-\Delta U^{visc}/RT) \tag{1.2}
\]

and the partition function \( F^* \) for a molecule of liquid in its activated state is given by

\[
F^* = (2\pi m k_B T/h^2)^{3/2} v_i^{23} b_k \exp(-\Delta U^{visc}/RT) \tag{1.3}
\]

where \( (2\pi m k_B T/h^2)^{3/2} \) is the translational contribution of a single molecule moving in its free volume \( v_i \), \( m = M/N \) is mass of a molecule, \( k_B \) is Boltzmann's constant, \( h \) is Planck's constant, \( b_k \) is the combined rotational and vibrational partition function, and \( U^{visc} \) is the energy of viscous flow. The free volume is defined in terms of
volume, $V$, and energy of vaporization, $\Delta U^{\text{vap}}$.

$$ u_1^{1/3} = C R T V^{1/3} (N_1^{1/2} \Delta U^{\text{vap}}) $$  \hspace{1cm} (I.4)

Assuming that partition functions ($b_k$) arising due to the rotational and vibrational degrees of freedom are the same when a molecule is in its initial and activated states, the ratio of partition functions becomes

$$ \frac{F/F^*}{} = (2\pi n k_B T)^{1/2} u_1^{1/3} $$  \hspace{1cm} (I.5)

Substituting eqs I.4 and I.5 into eq I.1, we get

$$ \eta = N_1^{1/2} C R (2\pi n k_B)^{1/2} M^{1/2} T^{0.5} \exp(\Delta U^{\text{isc}}/RT) / (V^{2/3} \Delta U^{\text{vap}}) $$  \hspace{1cm} (I.6)

The viscosity expressed by eq I.6 is in P when $R$ is in J/(mol·K), $k_B$ is in erg/K, $M$ is in gmol, $T$ is in K, and $\Delta U^{\text{isc}}$ and $\Delta U^{\text{vap}}$ are in J/mol. For a cubic packing of the lattice, $C = 2$.

Glasstone et al.\textsuperscript{36} assumed that the activation energy supplied for the molecular motion is equivalent to the cohesive energy of the liquid divided by $\tau$, which represents the size of the hole necessary for viscous flow. The cohesive energy, in turn, is approximated by the energy of vaporization $\Delta U^{\text{vap}}$. Thus,

$$ \tau = \Delta U^{\text{vap}}/\Delta U^{\text{isc}} $$  \hspace{1cm} (I.7)

Using eq I.7, eq I.6 can be written as

$$ \eta = N_1^{1/2} C R (2\pi n k_B)^{1/2} M^{1/2} T^{0.5} \exp(\Delta U^{\text{isc}}/\tau RT) / (V^{2/3} \Delta U^{\text{vap}}) $$  \hspace{1cm} (I.8)

Under normal boiling point liquid conditions, Glasstone et al.\textsuperscript{36} plotted $\ln \eta$ against $1/T$ for several substances and found that, for most nonassociated liquids, $\tau$ lies between 3 and 4. For example, for their particular values of $M = 121$ gmol, $V = 125$ cm$^3$/mol, and $\Delta U^{\text{vap}} = 20390$ J/mol, Figure 1 shows that $\ln \eta$ varies linearly with $1/T$ over a range of temperature for $\tau_1 = 3 - 5$.

Provided that molar volume and energy of vaporization are known, an alternative method of determining $\tau$ is to compare calculated values of viscosity using eq I.8 with experimental data at the given temperature and pressure. We determined the volume and energy of vaporization of some liquids using the volume-translated PR EOS and obtained $\tau$ at low temperature and pressure under liquid conditions where experimental data for $\eta$ are available. Table 1 contains the determined values of $\tau$ at two temperatures of each fluid. Overall, our results show that the value of $\tau$ can be accepted to lie in the range 3–5. This is consistent with the finding of Glasstone et al. However, our calculations at high temperature and high pressure show that $\tau$ may be even lower or higher than 3–5 depending on the condition. Since the accuracy of eq I.8 in describing viscosity is claimed to be 30%\textsuperscript{-56} and the linear relationship between energies of vaporization and viscous flow may not hold at high temperature and pressure, we use the fixed average value of $\tau_1$ ($\tau_1 = 4, \tau_2 = 4$) for all fluids investigated here.

**Appendix II. Characterization of $\psi_i$**

Evaluation of $\psi_i$ plays an important role in our model. As was noted in the text, in some mixtures close to the critical region the partial molar volume of the heavy component may become negative, giving rise to the unphysical values of $\psi_i$. This appendix discusses how to characterize $\psi_i$ and deal with the sign problem so that the number of molecules participating in the process of leaving and occupying the holes during the heat transport can be represented physically. Here, we follow the physical argument of Dougherty and Drickamer.\textsuperscript{30}

From the Gibbs–Duhem relation (eq 23), it follows that the number of molecules in the region considered in interpreting the net heat of transport is fixed. Also, the volume of this region remains constant. Suppose that $N$ molecules are removed randomly from the region. Out of $N$ molecules, $x_1N$ are species 1 and $x_2N$ are species 2 molecules. The volumes of species 1 and species 2 molecules removed from the region can be given by $x_1N\psi_1$ and $x_2N\psi_2$, respectively. The number of molecules of species 1 returning to the region will be $x_1^2N\psi_1^2 + x_2N\psi_2$, and those of species 2 will be $x_2^2N\psi_2 + x_1N\psi_1$, with their sum to be $N$. Thus, the total volume of the returning molecules becomes ($x_1^2N\psi_1^2 + x_2N\psi_2 - x_1N\psi_1 + x_2N\psi_2$). Using the Gibbs–Duhem relation (eq 23), one can readily see that the volume of the molecules returning to the region is equal to the volume of the molecules leaving the region. Equating the volume of molecules of species 1 removed from the region, $x_1N\psi_1$, and the volume of molecules of species 1 occupying the region, $x_1^2N\psi_2^1 + x_1N\psi_1^1$, we obtain eq 22, and with similar interpretation for species 2 molecules, we obtain eq 23.

Now, our major concern is that a change in the sign of the partial molar volume leads to a change in the sign of $\psi_i$. Although the Gibbs–Duhem relation (eq 23) is always satisfied and is independent of the sign of $\psi_i$, it may result in an unphysical value of $N\psi_i$. For example, let us consider the following Gibbs–Duhem relation using eq 23:

$$ N_1\psi_1 + N_2\psi_2 = N $$  \hspace{1cm} (II.1)

This relation is physically satisfied when both partial molar volumes are positive, so that the total number of molecules, $N$, is always greater than either of the two factors on the left-hand side of eq II.1. However, when
\[ \bar{V}_1 > 0 \text{ and } \bar{V}_2 < 0, \text{ the Gibbs–Duhem relation gives the equation} \]
\[ N_1 \psi_1 = N + N_2 \psi_2 \quad (II.2) \]

which is physically incorrect.

On the other hand, when we take the absolute values of the partial molar volumes, the Gibbs–Duhem relation gives the physically correct equation

\[ N_1 \psi_1 = N - N_2 \psi_2 \quad (II.3) \]

which is consistent with eq II.1. Therefore, in our model \( \psi \) are determined using eq II.3, i.e., using absolute values of the partial molar volumes.

**Literature Cited**

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