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A thermodynamic theory of the Soret effect in a multicomponent liquid

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A phenomenological theory of the Soret effect in a multicomponent mixture is presented. The theory is applicable to mixtures in which the Soret effect is determined mainly by the energetic interaction between the molecules, such as liquids and dense gases, and it is based on the assumption that the steady state has a maximum number of possible microstates. The equations derived for the separation enable the thermal diffusion factor α_T of each component to be calculated using only an equation of state for the mixture and the standard state enthalpy. With a sufficiently accurate equation of state, the calculated α_T values correspond well with the data on measured α_T values of liquids and dense gases and show a better correspondence than Haase's theory. The method presented may be applicable to other coupled transport phenomena in the steady state.

I. LITERATURE

The Soret effect (also called thermal diffusion) is the well-known tendency for a mixture to separate under a temperature gradient in the absence of convection. The separation by the Soret effect is usually small, but it can be large if the mixture is at a near-critical condition (such as the natural state of some underground oil reservoirs). In the steady state, which is characterized by a zero mass flux, the set of equations between the compositional gradient in a N-component mixture and the temperature gradient applied is[1–3]

$$\overline{\nabla} x_i = -x_i(1-x_i)\alpha_{Ti}\frac{\overline{\nabla} T}{T} \quad (i=1,\ldots,N-1), \qquad (1)$$

where x_i is the mole fraction of component i, T is the absolute temperature, α_{Ti} is the thermal diffusion factor of component i. (We denote α_{T1} as α_T in bindary mixtures.) Components with a positive α_{Ti} concentrate in the colder region. The thermal diffusion factor depends on temperature, pressure, and mole fractions. At low pressure the thermal diffusion factor of gaseous binary mixtures is roughly independent of the mole fractions of the components.

For gaseous mixtures, kinetic gas theory enables accurate calculation of α_T. For liquid mixtures, however, the accuracy of the calculation methods reported to date for α_T is limited. This paper presents an alternative, more accurate, calculation method for liquids. The application of the method is not limited to the Soret effect; it may be possible to use it for other coupled transport phenomena in the steady state.

The kinetic theory of gases[3] predicts that the thermal diffusion ratio is largest for elastic spheres and that it decreases as the molecules become softer, i.e., as the exponent of the repelling forces diminishes. The theory also predicts that when two types of molecule are the same size, the molecules with the greater mass will concentrate in the low-temperature region. Similarly, if molecules have equal mass the larger molecules will concentrate in the low-temperature region. The experimental α_T values of binary gas mixtures at atmospheric pressure are of the order of 0.1 and smaller.[4]

While in gases the molecular mass or size mainly determines the thermal diffusion, in liquids the energetic interaction and, to a lesser extent, the size or form of the molecules are the main parameters. Kramers and Broeder[5] mention that components enriching at the cold side are:

(1) usually those with the smaller molecular volume for substances with equal boiling points;
(2) those with the smaller surface areas (branched compounds) for substances with nearly equal boiling points and molecular volumes;
(3) those having the higher boiling points for substances with equal molecular volume or surface;
(4) those having the greatest number of C atoms for a homologous series, and
(5) the heavier molecules of isotopes.

Kramers and Broeder used a Clusius and Dickel-type of column with a convection current to increase the separation caused by thermal diffusion. In such a column, components with a positive thermal diffusion factor concentrate at the bottom. Their experiments show that the sequence of separation of hydrocarbon mixtures from the top to the bottom is light normal paraffins, heavy normal paraffins, branched paraffins, naphthenes, and monocylic aromatics, bicyclic aromatics. This is confirmed by Jones and Milberger,[6] who observed that in several mixtures of a normal paraffin and a cycloparaffin, the normal paraffin tends towards the hot region. These authors state that this may indicate that long-chain molecules, when present together with more compact ring-structure types, concentrate in the hot region regardless of their relative molecular weight.

In addition to qualitative predictions, quantitative predictions for the thermal diffusion factor of binary liquid mixtures have also been reported in the literature[7–11] and compared with experimental data. The models are discussed briefly below to show that formulation of another model is justified.

Mortimer and Eyring[7] present a model for the Soret effect (and the Dufour effect) that is based on elementary transition state theory. The application of their model is limited to ideal mixtures of molecules of nearly equal size. The expression they derive for α_T requires values for the quantities ΔH_i, the standard-state molal enthalpy change for the activation process in which the molecule moves from the initial to the transition state of high potential energy between the initial and final states, and for ΔS_1–ΔS_2, the difference in

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entropy change for the same activation process.

Tichacek, Kmak, and Drickamer[8] derive the following expression for α_T from the theory of irreversible thermodynamics that is applied to a system fixed in the laboratory:

$$\alpha_T = \frac{v_1 v_2}{(v_1 x_1 + v_2 x_2) x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p,n}} \left[\frac{Q_1^*}{v_1} - \frac{Q_2^*}{v_2}\right],$$

where v_i is the specific volume of component i, μ_1 is the chemical potential of component 1, p is the pressure, and n is the total number of moles. The quantity Q_i^* is defined as the difference between the total enthalpy transported by one mole of moving molecules of component i in the isothermal solution and the average enthalpy of one mole of molecules of component i in the same mixture. Tichacek *et al.* state that the Q_i^* quantity is that part of the activation energy for motion of component i which is transported with the moving molecules. Having made this interpretation, they connect the activation enthalpy transported to the viscosity of the mixture and they extract values of the transport enthalpy from measurements of the viscosity and from use of Eyring's viscosity model. Further, since the partial activation enthalpy of a compound in the mixture is not available, a linear mixing rule is assumed.

Dougherty and Drickamer[9] give a similar, but slightly different, interpretation of the quantities Q_i^*, but their interpretation is no more usable than the one given by Tichacek *et al.*[8]

Rutherford and Drickamer[10] take the transport enthalpies as a starting point for further analysis, which they base on the theory of regular solutions. The expression they derive for α_T requires the value of a molecular parameter $\psi_i\,(i = 1,2)$ which is defined as the number of molecules moving into a hole left by a molecule of the type i as it jumps to another hole.

The relationship between the energy transported and the activation energy for motion remains somewhat problematic in these models. Whitaker and Pigford,[11] e.g., introduce a fitting parameter C in the theory of Tichacek *et al.* to calculate Q_i^*. As a result only the trend of α_T with mole fraction can be predicted. In some mixtures α_T is not very dependent on C and a prediction of the absolute value of α_T is possible. Dougherty and Drickamer relate the two quantities by: energy transported = 1/2 activation energy for motion. They propose this relationship because it is in good agreement with their measurements. However, even when a sound theoretical basis can be given to such a relationship, calculation of the activation energy for motion remains a problem. The introduction of a model for another transport process is required to connect the activation energy to a measurable quantity, such as viscosity.

Haase[12] follows another approach. From the phenomenological equations of irreversible thermodynamics, he derives the following expression for α_T:

$$\alpha_T = \frac{m_1 h_2 - m_2 h_1 + m_1 m_2 b/a}{(m_1 x_1 + m_2 x_2) x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p,n}},$$

where m_i is the molecular mass of component i, h_i is the molar enthalpy of component i, and a and b are unknown phenomenological parameters. To determine the ratio b/a, Haase relates it to α_T^0, the thermal diffusion factor at the standard state (in this case, the ideal gas limit $p \to 0$), as follows:

$$\alpha_T^0 = \frac{m_1 h_2^0 - m_2 h_1^0 - m_1 m_2 b^0/a^0}{(m_1 x_1 + m_2 x_2) RT},$$

where R is the gas constant and the superscript 0 refers to the standard state. Without proof, Haase then states that b/a is independent of pressure and therefore $b/a = b^0/a^0$. Haase[13] tries to validate this statement by finding an analog for the expression for thermodiffusion from that of pressure diffusion. As a result, his expression for α_T is

$$\alpha_T = \frac{m_1(h_2 - h_2^0) - m_2(h_1 - h_1^0)}{(m_1 x_1 + m_2 x_2) x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p,n}} + \frac{\alpha_T^0 RT}{x_1 \left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p,n}}. \tag{2}$$

The value of α_T^0 must be derived from kinetic gas theory or from a measurement.

The pressure independence of b/a is confirmed by measurements on gas mixtures at low pressure, but this does not necessarily imply that $b/a = b^0/a^0$. (A relationship between b/a and b^0/a^0 that contains, e.g., a ratio v_1/v_2 is also possible.) Haase[14] mentions that expression (2) was more or less a guess; it appears that Eq. (2) predicts experimental values of α_T rather well.

In summary, the most complete theory of the Soret effect in liquids is Haase's. The thermodynamic quantities in Haase's expression for α_T can be calculated with an equation of state without further assumptions and α_T^0 can be calculated with kinetic gas theory and no measurement of a physical property of the mixture is required. For this reason, Haase's theory is compared to the multicomponent theory for α_T presented in this paper.

II. NEW THEORY OF THERMAL DIFFUSION

For modeling thermal diffusion, the same system is considered as that used for measuring the thermal diffusion factor.[3] Two bulbs, A and B, with equal and constant volume V are joined by an insulated rigid tube of small diameter and filled with a multicomponent mixture (see Fig. 1). The diameter of the tube is small enough to eliminate convection currents. Initially, the temperatures of the bulbs are equal as are the mole fractions of the mixture in the bulbs. Then the valve in the tube is closed and the temperature of bulb A is changed by a small amount $\Delta T/2$ to T^A and the temperature

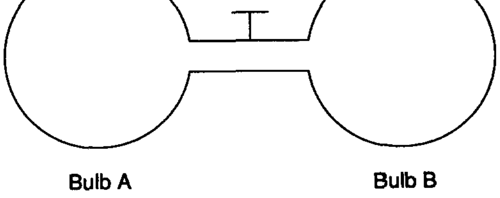

FIG. 1. Two-bulb apparatus for thermal diffusion.

of bulb B is changed by $-\Delta T/2$ to T^{B}. After the valve has been reopened, there is some interchange of mass between the bulbs until the steady state is reached. In the steady state there is a heat flux from A to B, but the net mass flux of each component is zero, while in each bulb the thermodynamic properties, such as the mole fractions x_i^A and x_i^B, are uniform and constant. The change of composition between the initial state and the steady state in bulb A and in bulb B is denoted by $\Delta x_i/2$ and $-\Delta x_i/2$, respectively.

To calculate the magnitude of the Soret effect in the two-bulb system, we determine the maximum of the canonical partition function Z of the system in the final, steady state. With this approach, the two-bulb system is characterized by a mean temperature T, a volume V for each bulb, a uniform pressure p, a mean mole number n_i $(i = 1,...,N)$ and, in addition, a small temperature difference ΔT and a small mole number difference Δn_i $(i = 1,...,N)$ between the bulbs. By maximizing the partition function, an expression for Δn_i can be derived in terms of, among other things, the given quantities $T,p,n_1,...,n_N,\Delta T$ (Sec. II A). The result is an expression for α_T that differs from Haase's expression. Haase's expression is derived with the same approach (in Sec. II B) to show the difference in the assumptions underlying the derivations.

A. Derivation

We start our analysis by noting that the role of the particle character of the mixture in thermal diffusion is different for gases and liquids. As mentioned in the literature review, the molecular mass or size largely determines thermal diffusion in gases and leads to a nonzero α_T in the ideal gas limit, while in liquids the energetic interaction is the main factor. By using the canonical partition function $\int d\Omega \exp(-E/kT)$, where Ω is the degree of occupation of energy level E and k is Boltzmann's constant, we cannot expect a correct description of thermal diffusion in diluted gases, since, e.g., in an ideal gas mixture the energy is not dependent on the composition. However, for liquids and dense gases the most important contribution to the Soret effect is described by the approach presented in this paper.

Having identified the application of the method, we must now find an expression for the partition function of the two-bulb system. The canonical partition function z^{A} of bulb (or subsystem) A is a function of the variables T^{A}, V^{A} $(= \mathrm{V})$, $n_1^A,...,n_N^A$ or, alternatively, it is a function of the averaged variables, $T,V,n_1,...,n_N$ and the departure variables $\Delta T/2, \Delta n_1/2,...,\Delta n_N/2$. Similarly, the partition function z^{B} of bulb B is a function of the variables T^{B}, V^{B} $(= V)$, n_1^{B}, $...,n_N^{\mathrm{B}}$ or, alternatively, like z^{A}, it is an equal function of the averaged variables $T, V, n_1,...,n_N$ and the departure variables $-\Delta T/2, -\Delta n_1/2,..., -\Delta n_N/2$. If it is assumed that the steady state is the macroscopic state accomplished by a maximum number of microstates, the steady state is treated as an equilibrium state that can be calculated from the maximum of the partition function. If we ignore for a moment the interdependence of the number of moles of a particular component in a bulb and the number of moles of the same type in the other bulb, then we may treat the bulbs as independent subsystems of the two-bulb system. If the contribution of the connecting tube is ignored, the partition function $Z(z^{\mathrm{A}}, z^{\mathrm{B}})$ of the total system is then equal to the product of the partition functions of the bulbs:

$$Z(z^{\mathrm{A}}, z^{\mathrm{B}}) = z^{\mathrm{A}} \cdot z^{\mathrm{B}}. \tag{3}$$

The value of Δn_i in the steady state can be calculated from the maximum of the partition function with the following two constraints. The first constraint is material conservation, expressed by

$$n_i^{\mathrm{A}} + n_i^{\mathrm{B}} = n_i^t \quad (i = 1,...,N), \tag{4}$$

where n_i^t are constants. The second constraint refers to mechanical equilibrium in the steady state, i.e., uniform pressure:

$$p^{\mathrm{A}} = p^{\mathrm{B}}. \tag{5}$$

Therefore, the mathematical problem is to find n_i^{A} and n_i^{B} by determining

$$\text{maximum } \{z^{\mathrm{A}} \cdot z^{\mathrm{B}}\} \tag{6}$$

$$\text{with the constraints } n_i^{\mathrm{A}} + n_i^{\mathrm{B}} = n_i^t \quad (i = 1,...,N),$$

$$p^{\mathrm{A}} = p^{\mathrm{B}}.$$

By substituting the relationship

$$z = \exp\left[-\frac{F}{kT}\right],$$

where $F(T,p,n_1,...,n_N)$ is the Helmholtz free energy of a bulb, and integrating the constraints into the extremum determination, statement (6) corresponds to

$$\text{minimum}\left\{\frac{F^{\mathrm{A}}}{T^{\mathrm{A}}} + \frac{F^{\mathrm{B}}}{T^{\mathrm{B}}} - \sum_{i=1}^{N} \lambda_i (n_i^{\mathrm{A}} + n_i^{\mathrm{B}}) - \nu(p^{\mathrm{A}} - p^{\mathrm{B}})\right\}, \tag{7}$$

where λ_i and ν are Lagrange multipliers. From differentiation of the expression between brackets in Eq. (7) with respect to the independent variables $n_i^{\mathrm{A}}, n_i^{\mathrm{B}}$ and using the thermodynamic relationship

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \mu_i,$$

where μ_i is the chemical potential of component i, and using the definition:

$$p_i = \left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}},$$

it follows that

$$\frac{\mu_i^{\mathrm{A}}}{T^{\mathrm{A}}} - \lambda_i - \nu p_i^{\mathrm{A}} = 0 \quad (i = 1,...,N), \tag{8a}$$

$$\frac{\mu_i^{\mathrm{B}}}{T^{\mathrm{B}}} - \lambda_i + \nu p_i^{\mathrm{B}} = 0 \quad (i = 1,...,N). \tag{8b}$$

Subtracting Eqs. (8a) and (8b) and eliminating ν gives

$$\frac{(\mu_i^{\mathrm{A}}/T^{\mathrm{A}}) - (\mu_i^{\mathrm{B}}/T^{\mathrm{B}})}{p_i^{\mathrm{A}} + p_i^{\mathrm{B}}} = \frac{(\mu_N^{\mathrm{A}}/T^{\mathrm{A}} - (\mu_N^{\mathrm{B}}/T^{\mathrm{B}})}{p_N^{\mathrm{A}} + p_N^{\mathrm{B}}} \quad (i = 1,...,N-1). \tag{9}$$

Developing $p_i^{\mathrm{A}} + p_i^{\mathrm{B}}$ with a Taylor expansion around the average of bulb A and bulb B and ignoring the second and higher order derivatives of p_i gives $2p_i$. Further, the ratio

$p_i/p_N = (\partial p/\partial n_i)_{T,V,n_{j\neq i}}/(\partial p/\partial n_N)_{T,V,n_{j\neq N}}$ is equal to $(\partial V/\partial n_i)_{T,p,n_{j\neq i}}/(\partial V/\partial n_N)_{T,p,n_{j\neq N}}$; this ratio is by definition equal to v_i/v_N, where v_i is the specific volume of type i. Shifting to the set of independent variables $T,V,p,x_1,\ldots,x_{N-1}$ to make use of $\Delta V = 0$ and $\Delta p = 0$, developing $(\mu_i^A/T^A) - (\mu_i^B/T^B)$ with a Taylor expansion around the average of bulb A and bulb B, and ignoring the second and higher order derivatives of μ_i/T gives

$$\left(\frac{\partial \mu_i/T}{\partial T}\right)_{p,V,x_j}\Delta T + \frac{1}{T}\sum_{j=1}^{N-1}\left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,p,V,x_{k\neq j}}\Delta x_j \qquad (i = 1,\ldots,N).$$

The above derivatives at constant V can be rewritten as derivatives at constant n because $(\partial \mu_i/\partial n)_{T,p,x_k} = 0$. Finally, we have the thermodynamic relationship

$$h_i = -T^2\left(\frac{\partial \mu_i/T}{\partial T}\right)_{p,n,x_j},$$

where h_i is the molar enthalpy of component i. Substituting the above into the set of equations (9) gives

$$-\left[\frac{h_i}{v_i} - \frac{h_N}{v_N}\right]\frac{\Delta T}{T} + \sum_{j=1}^{N-1}\left[\frac{1}{v_i}\frac{\partial \mu_i}{\partial x_j} - \frac{1}{v_N}\frac{\partial \mu_N}{\partial x_j}\right]\Delta x_j = 0 \qquad (i = 1,\ldots,N-1), \qquad (10)$$

where the partial derivatives refer to the variables $T,p,n,x_1,\ldots,x_{N-1}$. From this set of equations the unknown mole fraction variations can be determined and hence the thermal diffusion factors.

The explicit expression for α_T of a binary mixture can be derived by substituting Eq. (1) and the thermodynamic relationship

$$x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p,n} = x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,p,n}$$

into Eq. (10). The result is

$$\alpha_T = \frac{v_1 h_2 - v_2 h_1}{(v_1 x_1 + v_2 x_2)x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p,n}}. \qquad (11)$$

The magnitude of all quantities in Eq. (10) [and Eq. (11)] can be calculated with an equation of state. It is noted that the chemical potential $\mu_i(T,p,x_j)$ of a component in the state considered (temperature T, pressure p, mole fractions x_j) includes the chemical potential $\mu_i^0(T)$ of the standard state, which is mostly taken as the pure component in the ideal gas state. No general expression for μ_i^0 is available and we have to rely on experimental data. Extra measurements are not needed since existing data bases can be used (e.g., Refs. 15 and 16). However, the effect of h_i^0 on α_T is in most cases negligible.

B. Comparison with Haase's theory

Comparing expression (11) with Haase's expression (2) reveals some differences. The main difference between the expressions is that (11) contains the specific volume as a weighing factor, whereas (2) contains the molecular mass. By multiplying all specific volumes in expression (11) by the mixture density ρ, it can be shown that expression (11) does not correspond to Haase's expression (2) since $(\partial p/\partial x_i)_{T,p,n,x_{j\neq i}}$ is not usually equal to zero.

The second difference between the two expressions is that expression (11) requires the enthalpy of the standard state, while Haase's expression (2) does not require the enthalpy of the standard state but only the departure of the enthalpy from the standard state, $h_i - h_i^0$. However, Haase's expression requires the thermal diffusion factor of the standard state from kinetic theory or from an extra measurement. (The effect of α_T^0 on the value of α_T of liquids is in general small.)

In spite of the differences between the two expressions for α_T, there are also apparent agreements. The rough similarity between the two expressions for α_T and the fact that Haase uses the center of mass as a reference instead of the laboratory frame suggest that the expressions can be derived by the same approach in a different frame of reference. It is shown below that Haase's expression can indeed be derived from the maximalization of the partition function with the center of mass as a frame of reference.

Assume that the two-bulb system is not fixed to the laboratory frame but moves with the center of mass of the fluid. In the closed two-bulb system, this assumption implies that the total masses in the bulbs, M^A and M^B, stay constant. Then, since M^A and M^B are equal at the start of the thermal diffusion process, they are also equal in the steady state. Hence, the contraint on statement (6) is

$$M^A = M^B, \qquad (12)$$

where M^A and M^B are defined by

$$M^A = \sum_{i=1}^{N} n_i^A m_i \quad \text{and} \quad M^B = \sum_{i=1}^{N} n_i^B m_i.$$

with m_i the molecular mass of component i. To give the system the same number of degrees of freedom, constraint (5) on uniform pressure is dropped. The mathematical problem is now to find

$$\text{minimum}\left\{\frac{F^A}{T^A} + \frac{F^B}{T^B} - \sum_{i=1}^{N}\lambda_i\,(n_i^A + n_i^B) - \nu(M^A - M^B)\right\}, \qquad (13)$$

with respect to n_i^A, n_i^B. Hence, with a calculation similar to that in the previous section it follows from Eq. (13) that

$$-\left[\frac{h_i}{m_i} - \frac{h_N}{m_N}\right]\frac{\Delta T}{T} + \sum_{j=1}^{N-1}\left[\frac{1}{m_i}\frac{\partial \mu_i}{\partial x_j} - \frac{1}{m_N}\frac{\partial \mu_N}{\partial x_j}\right]\Delta x_j = 0 \qquad (i = 1,\ldots,N-1), \qquad (14)$$

where the partial derivatives refer to the variables $T,p,n,x_1,\ldots,x_{N-1}$.

The explicit expression for α_{T1} of a binary mixture derived from Eq. (14) is

$$\alpha_T = \frac{m_1 h_2 - m_2 h_1}{(m_1 x_1 + m_2 x_2)x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,p,n}}. \qquad (15)$$

Applying the ideal gas limit on Eq. (15) gives

$$\alpha_T^0 = \frac{m_1 h_2^0 - m_2 h_1^0}{(m_1 x_1 + m_2 x_2)RT}. \qquad (16)$$

Substitution of Eq. (16) into Eq. (15) gives Haase's expression (2). Since in a measurement the two-bulb system is fixed to the laboratory frame and not to the center of mass of the fluid and the condition of uniform pressure must be satisfied, Haase's expression cannot be expected to correspond to measured α_T values. If the density of the mixture does not depend to any great extent on the composition, Haase's theory will be a good approximation. This is in line with his remark[14] that it appears that expression (2) predicted α_T values rather well.

III. COMPARISON WITH EXPERIMENTAL DATA

The multicomponent model formulated in Sec. II A has been checked against the limited experimental data available for binary liquid mixtures. For this purpose the quantities in the set of equations (10) were calculated with the Soave equation of state and, for comparison, also with the Peng–Robinson equation of state. We actually used modified versions of the Soave equations of state that are commonly used and that contain experimentally determined correlations for the temperature-dependent interaction parameters θ_{ij} in the mixing rule for the a parameters:

$$a_{\text{mix}} = \Sigma_{i,j} x_i x_j (1 - \theta_{ij}) \sqrt{a_i} \sqrt{a_j}.$$

The correlations that we used are particularly useful for vapor/liquid calculations at pressures of the order of 1 and 10 MPa. The calculated values of the interaction parameters that were used as input for the equation of state are listed in the tables.

In addition to the calculation of α_T with expression (11), we have calculated α_T with the adapted Haase expression (15) and, for those mixtures for which an α_T^0 value is available, also with the Haase expression (2). We have compared the calculations of all liquid mixtures that are represented accurately by our phase behavior package and for which a measured α_T is available. The mixtures are:

(1) methane and propane at 346.08 K and 5.6 MPa, at six different mole fractions in the near-critical region,
(2) methane (mole fraction 0.34) and propane at 346.08 K, at seven different pressures in the near-critical region,
(3) n-hexane (mole fraction 0.55) and n-octane at 320 K and atmospheric pressure,
(4) carbon dioxide and hydrogen at four different dense-gas conditions,
(5) cyclohexane (mole fraction 0.5) and benzene at 313 K, atmospheric pressure and three different mole fractions,
(6) various liquid mixtures of a normal paraffin with a naphthene, at 313 K and atmospheric pressure (only qualitative measured data available),
(7) idem for various mixtures of a branched paraffin with a naphthene, a naphthene with a monocyclic aromat, and a monocyclic aromat with a multicyclic aromat.

TABLE I. Comparison of α_T values as calculated and as measured for a mixture of methane and propane at 346.08 K and 5.6 MPa at various mole fractions (equation of state: Soave; interaction parameter: 0.009 812). Superscript K refers to the model presented here. Superscript m refers to measured values. Superscript H refers to Haase's adapted expression (15) (without α_T^0). Superscript Haase refers to Haase's expression (2) (containing α_T^0). Superscript H-BWR refers to calculations done by Haase with BWR.

x_{methane}	α_T^K	α_T^m	α_T^H	α_T^{Haase}	$\alpha_T^{\text{H-BWR}}$
0.34	8.86	12.51	8.54	8.15	10.01
0.35	7.50	12.48	7.44	7.07	9.58
0.42	3.57	2.67	3.95	3.64	4.42
0.49	1.82	1.30	2.72	2.42	2.94
0.51	1.57	0.70	2.51	2.20	2.62
0.58	0.96	0.36	1.97	1.66	2.01
0.63	0.65	0.47	1.72	1.39	1.71

In the discussion below, the measured α_T values are denoted by α_T^m, the α_T values calculated with our model by α_T^K, those calculated with Haase's adapted expression (15) with α_T^H and those calculated with Haase's expression (2) containing α_T^0 with α_T^{Haase}. The values from Ref. 16 that Haase *et al.* calculated with expression (2) and the Benedict–Webb–Rubin equation of state (BWR) are denoted by $\alpha_T^{\text{H-BWR}}$. The α_T values refer to the heaviest component of the mixture, unless an α_T value is given for each component of the mixture.

The results for the mixture of methane and propane at 346.08 K and 5.6 MPa, at various mole fractions in the near-critical region, are listed in Table I and plotted in Fig. 2. The calculated data are represented by four curves. These curves are interpolated between 12–15 data points. The four curves represent the α_T^K, the α_T^H, the α_T^{Haase}, and the $\alpha_T^{\text{H-BWR}}$ values. The α_T^m and $\alpha_T^{\text{H-BWR}}$ values come from Ref. 17. The figure shows that the α_T^K values agree best with the measured values. The figure also shows that a better agreement with the experimental data is obtained with the Soave equation of state than with the BWR equation of state. Finally, the figure shows that including α_T^0 into Haase's expression (15)

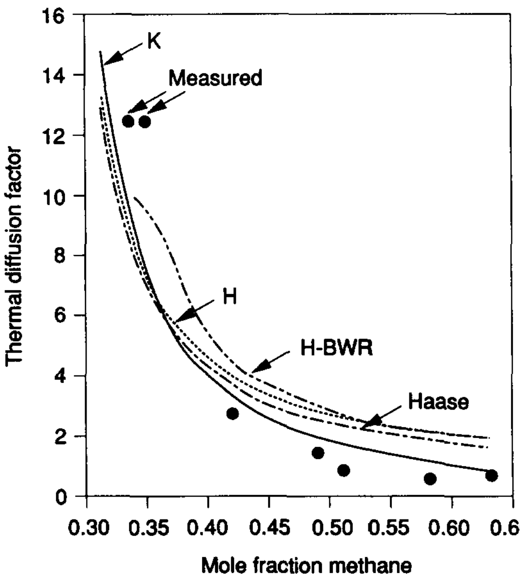

FIG. 2. Thermal diffusion factor of methane and propane at 5.6 MPa and 346.08 K as a function of composition (K: our model, Haase: Haase's expression with α_T^0, H: Haase's expression without α_T^0, H-BWR: calculated by Haase *et al.* with BWR equation of state).

results, at relatively low pressures, in a better fit with the experimental data, as expected.

The difference between the calculated and measured values can be ascribed partly to the inaccuracy in the measurements. However, Haase *et al.*[17] do not provide a value for the measurement inaccuracy, but they do mention that the temperature difference between the bulbs used in the measurements is 8 K. The effect of a finite temperature difference on the measurement of α_T can be estimated by calculating $\bar{\alpha}_T = 1/2[\alpha_T(T^A) + \alpha_T(T^B)]$ and comparing it to $\alpha_T = \alpha_T(1/2(T^A + T^B))$. For example, $\bar{\alpha}_T^K$ is 20% higher than α_T^K at $T^A - T^B = 8$ K and 0.34 methane molefraction; at 0.58 methane molefraction, i.e., far from critical condition, the difference is only 2%.

The results for a mixture of methane (mole fraction 0.34) and propane at 346.08 K and at various pressures in the near-critical region are listed in Table II. The agreement between the calculated values and the measured values (from Ref. 17) varies strongly. The agreement is poor at supercritical pressures (6.58 and 7.60 MPa) and is reasonable to good at subcritical pressures. Since all calculated values at supercritical pressures show a poor agreement with experimental data, regardless of which expression for α_T is used, the poor agreement is ascribed to the equation of state in the supercritical region. This is discussed after the next paragraph.

At subcritical pressures the best agreement with experimental data is shown by the values calculated with expression (11), as can be seen from Fig. 3. This figure also shows the effect of the equation of state used on the α_T values calculated with expression (2): the agreement with the experimental data is better with the Soave equation than with the BWR equation. Further, the Soave and the Peng–Robinson equation of state have been compared. The α_T^K values obtained with the Soave equation are no more accurate than those obtained with the Peng–Robinson equation of state. To detect an effect of the sensitivity to the interaction parameter in the Soave equation, three different values (0.009 812, 0.011 16, and 0.011 99) have been compared. No effect of the interaction parameter in the Soave equation on α_T^K has been detected.

It is not surprising that the calculated α_T values are unrealistic in the supercritical region. The equation of state used in the supercritical region is an extrapolation of the equation of state in the subcritical region and is not based on data relating to the physical properties in the supercritical region. This means that small errors in the equation of state in the supercritical region cannot be excluded, regardless of the accuracy of the equation of state in the subcritical region. The Soret effect is very sensitive to the thermodynamic properties of the components, and therefore a small error in the equation of state of the mixture may have a large effect on the calculation of α_T and thus give unrealistic α_T values in the supercritical region. Further, following this line of reasoning, it is likely that the α_T values calculated with an equation of state extrapolated in the supercritical region are more accurate in the immediate vicinity of the two-phase region than far away from it.

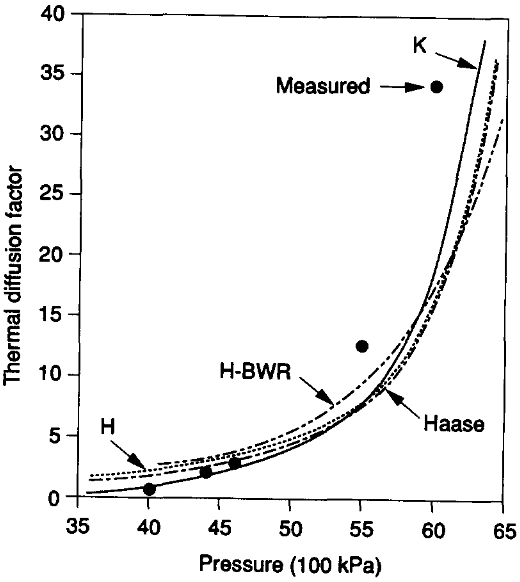

FIG. 3. Thermal diffusion factor of methane (mole fraction 0.34) and propane at 346.08 K as a function of pressure (K: our model, Haase: Haase's expression with α_T^0, H: Haase's expression without α_T^0, H-BWR: calculated by Haase *et al.* with BWR equation of state).

TABLE II. Comparison of α_T values as calculated and as measured for a mixture of methane (mole fraction 0.34) and propane at 346.08 K and at various pressures (equation of state: Soave; interaction parameter: 0.009 812).

p (100 kPa)	α_T^K	α_T^m	α_T^H	α_T^{Haase}	$\alpha_T^{\text{H-BWR}}$
40.5	1.12	0.79	2.23	1.99	2.50
44.6	1.95	2.01	2.95	2.69	3.42
46.6	2.53	2.88	3.44	3.18	4.05
55.7	8.86	12.51	8.54	8.15	10.01
60.8	21.88	34.24	18.42	17.80	19.82
65.8	72.41	18.26	54.78	53.32	37.18
76.0	97.53	8.96	64.36	62.70	42.80

For a mixture of n-hexane (mole fraction 0.55) and n-octane at 320 K and atmospheric pressure we calculate α_T^K to be 0.161. The measured α_T value is 0.16 (from Ref. 2; original paper is Ref. 18). The α_T^H value is markedly different: -0.142. The α_T^K values obtained with three interaction parameters in the Soave equation (0.001 573, 0.001 977, and 0.002 360) and with the Peng–Robinson equation have been compared. The effect of the interaction parameter on the thermal diffusion ratio is small (only 1.8% at maximum). However, the result obtained with the Peng–Robinson equation of state differs in sign from the measured value.

The results of the dense gas mixtures of carbon dioxide and hydrogen are shown in Table III. It is evident from the table that the agreement between the calculated α_T^K and measured α_T values (from Ref. 19) is reasonable; the agreement between the α_T^H and the α_T^m values is worse. More than a reasonable agreement could not be expected because of the inappropriate measuring procedure. In the analysis the temperature difference is assumed to be small compared to the absolute temperature, while in the measurements the temperature difference was 100 K.

TABLE III. Comparison of α_T values as calculated and as measured for a mixture of carbon dioxide and hydrogen at various conditions (equation of state: Soave).

x_{CO_2}	p (100 kPa)	T (K)	Interaction parameter	α_T^K	α_T^m	α_T^H
0.51	15.0	223	0.100 8	0.216	0.539	1.374
0.52	31.4	245	0.099 99	0.722	0.789	1.720
0.55	45.2	252	0.099 79	1.266	1.050	2.155
0.54	54.0	263	0.099 86	1.575	1.315	2.332

A large deviation between theory and measurement is shown by the calculation of α_T for a mixture of cyclohexane and benzene at 313 K, atmospheric pressure, and three different mole fractions (Table IV). The calculated values are different in sign and magnitude from the measured values of Dougherty and Drickamer. This was also the case for the values calculated with the Haase expression (15). The effect of the interaction parameter used or the equation of state on the calculated values is negligible. In the past, the mixture of cyclohexane and benzene has also been used to test the theory of Tichacek *et al.*[8] Whitaker and Pigford[11] found a difference in sign between calculated and measured α_T values, regardless of the value of the fitting parameter they used. Note that the measured values of Dougherty and Drickamer do not agree with the qualitative rules of Kramers and Broeder[5] (benzene has a smaller molar volume than cyclohexane; normal boiling points differ only 0.61 K).

Table V shows the calculated thermal diffusion factor of 7 liquid mixtures of a normal paraffin with a naphthene: methane + cyclopentane, *n*-butane + cyclopentane, *n*-decane + cyclopentane, methane + cyclohexane, propane + cyclohexane, *n*-butane + cyclohexane, *n*-decane + cyclohexane. The thermal diffusion ratio of all mixtures is positive for the naphthene regardless of the relative magnitude of the molecular masses. This means that the naphthene of these mixtures concentrates in the colder region, which is in line with Kramers and Broeder's[5] observation. Our calculation of a positive thermal diffusion factor of the heaviest paraffin in the mixtures methane + propane and *n*-hexane + *n*-octane is also confirmed by the rules of Kramers and Broeder.

For various mixtures of some arbitrary branched paraffins with some arbitrary naphthenes (Table VI), naphthenes with monocyclic aromats (Table VII), and monocyclic aromats with multicyclic aromats (Table VIII) the calculated α_T^K values are in accordance with the qualitative observa-

TABLE IV. Comparison of α_T values as calculated and as measured for a mixture of cyclohexane and benzene at 313 K and atmospheric pressure (equation of state: Soave).

x_{benzene}	Interaction parameter	α_T^K	α_T^m	α_T^H
0.2	0.000 875 5	− 3.02	0.58	− 1.63
0.5	0.000 876 1	− 3.45	0.40	− 1.85
0.8	0.000 875 5	− 3.87	0.10	− 2.03

TABLE V. Thermal diffusion factor of seven liquid mixtures of a normal paraffin and a naphthene at 293 K and atmospheric pressure.

Mixture	Mole fraction	α_T^K	α_T^H
Methane	0.0026	− 4.8	− 1.5
Cyclopentane	0.9974	4.8	1.5
n-butane	0.37	− 3.1	− 1.3
Cyclopentane	0.63	3.1	1.3
n-decane	0.50	− 3.4	− 2.3
Cyclopentane	0.50	3.4	2.3
Methane	0.0034	− 4.4	− 1.3
Cyclohexane	0.9966	4.4	1.3
Propane	0.10	− 2.7	− 0.42
Cyclohexane	0.90	2.7	0.42
n-butane	0.45	− 3.0	− 0.73
Cyclohexane	0.55	3.0	0.73
n-decane	0.50	− 3.5	− 1.6
Cyclohexane	0.50	3.5	1.6

TABLE VI. Thermal diffusion factor of four liquid mixtures of a branched paraffin and a naphthene at 293 K, atmospheric pressure and equimolar composition.

Mixture	α_T^K	α_T^H
i-butane	− 5.6	− 2.5
Methylcyclopentane	5.6	2.5
i-octane	− 4.6	− 3.4
Methylcyclopentane	4.6	3.4
i-butane	− 4.4	− 1.8
Cyclohexane	4.4	1.8
i-octane	− 4.9	− 3.9
Cyclohexane	4.9	3.9

TABLE VII. Thermal diffusion factor of five liquid mixtures of a naphthene and a monocyclic aromat at 293 K, atmospheric pressure and equimolar composition.

Mixture	α_T^K	α_T^H
Cyclohexane	− 3.7	− 1.9
Benzene	3.7	1.9
Cyclohexane	− 2.9	− 1.4
Toluene	2.9	1.4
Methylcyclopentane	− 2.2	− 1.5
m-xylene	2.2	1.5
Methylcyclohexane	− 4.5	− 3.2
Benzene	4.5	3.2
Methylcyclohexane	− 2.8	− 2.4
m-xylene	2.8	2.4

TABLE VIII. Thermal diffusion factor of four liquid mixtures of a monocyclic aromat and a multicyclic aromat at 293 K, atmospheric pressure and equimolar composition.

Mixture	α_T^K	α_T^H
Benzene	−1.6	0.12
Phenanthrene	1.6	−0.12
Benzene	−2.3	0.84
Anthracene	2.3	−0.84
m-xylene	−5.4	−1.5
Phenanthrene	5.4	1.5
m-xylene	−6.6	−0.75
Anthracene	6.6	0.75

tions of Kramers and Broeder. This is also the case for the α_T^H values but there are some exceptions (see Table VIII).

IV. CONCLUSIONS

(1) If it is assumed that the steady state is accomplished by a maximum number of microstates, the set of equations (10) for the Soret effect in a multicomponent mixture has been derived. The application of Eq. (10) is limited to mixtures such as liquids and dense gases in which the separation of the compounds is determined mainly by the energetic interaction. For a binary mixture, the thermal diffusion factor is given explicitly by expression (11).

(2) The quantities in the set of equations (10) can be calculated with the equation of state and the standard state enthalpy. The models that have been proposed in the past (except for Haase's) contain quantities that cannot be calculated practically or that must be measured. Haase's expression for α_T consists of quantities that can be calculated with an equation of state and kinetic gas theory. However, the assumption in Haase's model is weak.

(3) By comparing the new model with Haase's model for mixtures of which accurate thermodynamic data and a measured value of the thermal diffusion factor are available, it appears that for 18 mixtures a fairly good to good quantitative agreement with experimental data is obtained with both models; for all these mixtures the new model gives better agreement with the measured values of α_T than does Haase's model. For three mixtures of compounds with nearly equal normal boiling points, neither model agrees with the measured data. The qualitative rules of Kramers and Broeder (concerning mixtures of light normal paraffins, heavy normal paraffins, branched paraffins, naphtenes, monocylic aromats, bicylic aromats) are confirmed by the model of this paper and by Haase's model with a few exceptions.

(4) For mixtures at supercritical conditions far from the two-phase region, the extrapolation of an equation of state to the supercritical region is not sufficiently accurate for calculating a reliable thermal diffusion factor with the described theory and Haase's theory.

(5) The method presented in this paper is, in principle, applicable to other coupled transport phenomena in the steady state.

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