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A comprehensive thermodynamic theory of the Soret effect in a multicomponent gas, liquid, or solid

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A comprehensive theory for the Soret effect (also called thermal diffusion) is presented which incorporates both the thermodynamic contribution from selective attraction/repulsion and the kinetic contribution from selective collision interaction between the components. The new theory is an extension of a theory presented earlier in which the thermodynamic contribution only was modeled. The single assumption of the theory is that the Soret effect in the steady state is the macroscopic state accomplished by a maximum number of microstates with respect to the ideal gas state. As a result, the Soret effect in a multicomponent mixture can be calculated by using input from an equation-of-state of the mixture and kinetic gas theory without the use of matching parameters. The theory is not limited to systems with a small temperature difference and/or a small concentration difference. The methodology of the new theory can be used to model other cross-effects in irreversible thermodynamics. A test of the theory against the measured Soret effect in 18 mixtures shows agreement within a factor of 2 over four decades. Closer agreement cannot be expected since it appears that the calculation of the Soret effect is extremely sensitive to the accuracy of input from the equation-of-state. The present equations-of-state, even those that are calibrated for use in the chemical and petroleum industry, require modification for the calculation of the Soret effect, because of a higher demand in accuracy. In addition, it is also important to examine which frame of reference (center-of-volume or center-of-mass) applies to a particular measurement or practical application, because the frame of reference determines which mathematical expression for the Soret effect must be used. [DOI: 10.1063/1.1398315]

I. INTRODUCTION

The Soret effect (also called thermal diffusion) is the tendency of a mixture of two or more components to separate as a result of a spatial temperature difference. It is one of the well-known cross-effects in irreversible thermodynamics. This general theory assumes the component and heat fluxes between the hot and the cold region to be a linear function of the concentration differences and the temperature difference. In steady state, in which the component fluxes have vanished and only a heat flux remains, the Soret effect is quantified by the equation:[1]

$$\Delta x_i = -x_i(1-x_i)\alpha_{Ti}\frac{\Delta T}{T} \quad (i=1,\ldots,N), \tag{1}$$

where x_i is the mole fraction of component i,T the absolute temperature, N the number of components, and α_{Ti} the thermal diffusion factor of component i and the subject of this paper. The thermal diffusion factor is small (<0.3) in the case of dilute gases, but can be large (>10) in liquids and gases at near-critical condition (such as the natural state of some underground oil reservoirs) or in polymer solutions and colloids. For dilute gases, kinetic gas theory enables calculation of α_{Ti}. However, the thermal diffusion factor in liquids, solids, polymers, etc., is still the subject of research.

In 1989 we published a thermodynamic theory of the Soret effect for multicomponent liquids,[2] in which a common physical principle from statistical thermodynamics, i.e., ‘‘a macroscopic state is accomplished by a maximum number of possible microstates,’’ is applied to the steady nonequilibrium state. Two other assumptions were made: mechanical equilibrium and a negligible Soret effect in an ideal gas. The result was a set of equations that provides a numeric prediction of the thermal diffusion factors of a multicomponent liquid. To arrive at numeric predictions, the set of equations does not require input from measured data but needs implementation in a phase behavior computer package only. It does not contain matching parameters. For a binary mixture, the explicit expression for the thermal diffusion factor is according to that theory:

$$\alpha_{T1} = \frac{v_1 v_2}{v_1 x_1 + v_2 x_2} \frac{\dfrac{h_2}{v_2} - \dfrac{h_1}{v_1}}{x_1 \dfrac{\partial \mu_1}{\partial x_1}}, \tag{2}$$

where v_i, h_i, μ_i are, respectively, the molar volume, molar enthalpy, and chemical potential of component i. The above expression was validated with experimental data of three mixtures in our 1989 paper. The qualitative observations of Kramers and Broeder[3] (i.e., in a mixture of hydrocarbons, the sequence from the hot to the cold region is: light normal paraffins, heavy normal paraffins, branched paraffins, naphtenes, monocyclic aromatics, bicyclic aromatics) are all

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[a] Deceased March 15, 2001.

predicted by our theory. Our theory was also confirmed by the qualitative measurements of Costesèque and Rivière.[4] Faissal and Montel[5] considered the theory for the calculation of the variation of oil composition with depth in underground reservoirs, in which the compositional variation is caused by gravity and the temperature gradient in the earth's crust. Faissat *et al.*[6] made some fundamental observations regarding our theory. Recently, Shapiro and Stenby[7] presented a first attempt to generalize our thermodynamic approach.

To our knowledge there are three other models/expressions in the literature for the thermal diffusion factor, apart from kinetic gas theory. All of these models are limited to binary mixtures. There is the expression of Haase,[18] which is based on thermodynamics and is equal to Eq. (2) but (a) with the molar volumes replaced by molar masses and (b) with an extra term for the so-called kinetic contribution. We will discuss the validity of Haase's expression in this paper [see end of Sec. II and expression (17)]. The second model is the kinetic model of Dougherty and Drickamer,[9] which connects the heat of transport with the activation energy. The model has a low predictive power because it contains a fitting parameter.[2] The third model was developed recently by Shukla and Firoozabadi[10] along the kinetic approach of Dougherty and Drickamer. Their model contains a proportionality factor τ with a physical meaning. It can be shown that their expression for the thermal diffusion factor differs a factor τ from expression (2): $\alpha_T^{SF}=\alpha_T^K/\tau$. Despite their calculation of a value of 4 for τ, they use τ as a matching parameter in the range 1–4, hence the predictive power is low. In this paper we will not consider models with a matching parameter.

Despite its success in comparing measurements in various mixtures, there are still four shortcomings in our purely thermodynamic theory and expression (1):

(1) The theory quantifies the thermodynamic contribution to the Soret effect (which is due to selective attraction/repulsion between the components) but ignores the kinetic contribution (which is due to selective collision interaction between the components) to the Soret effect. As a result, the above expression cannot be used for dilute gases, in which the kinetic contribution dominates the thermodynamic contribution. Therefore expression (2) is valid only for very nonideal mixtures, such as dense gases and near-critical mixtures, as was shown in the previous paper by comparison to measured data.

(2) The *total* molar enthalpy is required as input, while generally no more than the deviation of the enthalpy from a reference state is available. (The reference state is normally taken as the ideal gas state of the pure component.)

(3) In the derivation of the theory the assumption of mechanical equilibrium is needed.

(4) Haase's expression compares generally better to the measured data of the near-critical mixture of methane and *n*-butane than expression (1), probably due to a special measurement procedure, as was shown recently by Høier.[11]

Another shortcoming lies in the available test data that are used for validation of expression (1) and of other models:

(5) The calculated thermal diffusion factor for the available test data is very sensitive to input data from the equation-of-state while the accuracy of these data is insufficient.

There is thus a need for a comprehensive theory that (1) takes the kinetic contribution into account, (2) does not need input of the *total* molar enthalpy, (3) combines Haase's expression and our previous theory in one, and (4) is based on a single assumption. In Sec. II of this paper, we will present such a comprehensive approach, which is a subtle variation of the old theory. Several special cases of the comprehensive theory are given in Sec. III. The new theory is tested against experimental data in Sec. IV. Finally, in Sec. V we discuss sensitivity to input data calculated with the equation-of-state, proper selection of test data, and extension of the comprehensive theory to other cross-effects.

II. A COMPREHENSIVE THERMODYNAMIC THEORY

Equation (1) from the theory of irreversible thermodynamics is based on a linear relationship between fluxes and thermodynamic forces. This relationship originates from the hypothesis of local equilibrium and applies to systems close to equilibrium, hence systems with small differences in the intensive variables such as temperature and composition. In our theory, however, there is no restriction to small differences and hence to a linear relationship. We use Eq. (1) only for the purpose of the definition of the thermal diffusion factor α_{Ti}. Because *explicit* expressions for the thermal diffusion factor can be derived only for systems with small differences, however, most final results of the theory presented in this paper are applicable to systems with small composition and temperature differences.

As stated in Sec. I, the Soret effect consists of two contributions, a kinetic and a thermodynamic, which are both included in the new, comprehensive theory. The kinetic contribution is caused by selective collision interaction: the magnitude of the interaction in molecular collisions is generally different for each pair of mixture components. For dilute gases this contribution is quantified by kinetic gas theory.[12] This theory predicts a nonzero Soret effect for an ideal gas. We use the kinetic contribution of the ideal gas state, denoted by the thermal diffusion factor of the ideal gas state α_{Ti}^0, as input to our thermodynamic theory.

The thermodynamic contribution to the Soret effect is caused by selective attraction/repulsion between the components. In mixtures in which a nonuniform temperature is maintained, it is thermodynamically advantageous for some components to concentrate in the region where the temperature is high and for other components to concentrate in the region where the temperature is low. This contribution, which is zero for an ideal gas, is modeled here.

For calculation of the magnitude of the Soret effect we consider the following setup. Two bulbs, *A* and *B*, with equal and constant volume *V*, are joined by an insulated rigid tube of small diameter and filled with an *N*-component mixture

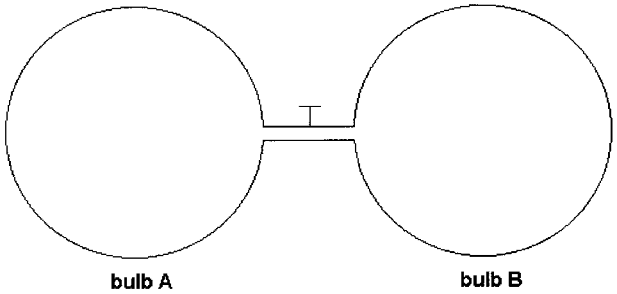

FIG. 1. Setup with two bulbs connected by a tube with valve. The setup contains a mixture with two or more components. In bulb A and B a different temperature is maintained.

$(N \geqslant 2)$. The diameter of the tube is small enough to eliminate convection currents and the volume of the tube is negligible in comparison with the volume of the bulbs. The two-bulb system is in no way intended as a restriction; it helps to simplify the mathematics. The thermodynamic contribution to the Soret effect comes from the two bulbs and the kinetic contribution from the connecting tube.

We consider the following imaginary experiment (see Fig. 1). In the *initial* state, the whole setup is kept at a uniform and constant temperature and the composition of the mixture is uniform everywhere. After closing the valve in the tube, the temperature T of bulb A is increased by an amount $\Delta T/2$ to T^A and the temperature of bulb B is lowered by the same amount to T^B. After this *intermediate state*, the valve is reopened. Measures have been taken such that T^A and T^B remain constant. Because the bulbs are in communication after the valve is opened, there is some interchange of mass between the bulbs by thermal expansion and diffusion. After some time a *final, stationary state* is reached, in which there is still a constant flux of heat from bulb A to bulb B but the mass flux of each component has vanished; in each of the bulbs the thermodynamic properties such as the mole fractions x_i^A and $x_i^B (i=1,...,N)$ are uniform and constant. Due to the Soret effect there is a difference in mole fraction $\Delta x_i (i=1,...,N)$ between the bulbs.

To calculate the magnitude of the concentration differences Δx_i in the final, steady state due to the Soret effect, we make use of a common principle from statistical thermodynamics: the assumption is that the steady state is the macroscopic state accomplished by a maximum number of microstates. If we make use of the canonical partition function Z of the two-bulb system, the steady state can be calculated from the maximum of the canonical partition function. The tube is ignored in the statistical mechanics in view of its small volume. So far, everything resembles the approach presented in our previous paper.[2]

The motivation for the new element in the theory comes from the following facts: (1) the thermodynamic contribution is localized in the two bulbs, while the connecting tube can be ignored in view of its small volume; (2) each bulb is in thermodynamic equilibrium; (3) the kinetic contribution is by definition localized in the connecting tube; (4) the tube is not in equilibrium and produces entropy; and (5) if the mixture in the system was an ideal gas, the thermodynamic contribution would be zero by definition. To be able to apply the methods of equilibrium thermodynamics to a system that is essentially not in equilibrium, the kinetic contribution in the ideal gas state needs to be separated from the statistical thermodynamic description. To model the thermodynamic contribution, we therefore determine the maximum number of microstates *with respect* to the ideal gas state, so we use the *deviation* of the canonical partition function Z from the partition function Z^0 in the ideal gas state. In this way we separate the Soret effect in the ideal gas state (quantified by kinetic gas theory) from the thermodynamic contribution; we do not model the Soret effect in the ideal gas state but consider it as input. Hence, instead of determining maximum $\{Z\}$ as in our previous paper, we determine:

$$\text{maximum}\left\{\frac{Z}{Z^0}\right\}. \tag{3}$$

For calculation of the canonical partition function of the system, only the two bulbs are considered because the volume of the connecting tube is assumed to be negligible. The canonical partition function Z^A of bulb (or subsystem) A is a function of the variables T^A, $V^A(=V)$, $n_i^A,\ldots,n_N^A$. Similarly, the partition function Z^B of bulb B is a function of the variables T^B, $V^B(=V)$, $n_i^B,\ldots,n_N^B$. The canonical partition function Z^{A^0} of bulb A in the ideal gas state is a function of the variables T^A, V, $n_i^{A^0},\ldots,n_N^{A^0}$. Finally, the canonical partition function Z^{B^0} of bulb B in the ideal gas state is a function of the variables T^B, V, $n_i^{B^0},\ldots,n_N^{B^0}$. 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. The partition function $Z(Z^A,Z^B)$ of the total system is then equal to the product of the partition functions of the bulbs:

$$Z(Z^A,Z^B)=Z^A\times Z^B. \tag{4}$$

The value of $\Delta n_i=n_i^A-n_i^B$ in the steady state can be calculated from the maximum statement Eq. (3) with the following constraints. The first constraint is material conservation of the components, expressed by

$$n_i^A+n_i^B=n_i^t \quad (i=1,...,N), \tag{5}$$

where n_i^+ are given constants. The second constraint is material conservation of the components in the ideal gas state:

$$n_i^{A^0}+n_i^{B^0}=n_i^A+n_i^B \quad (i=1,...,N). \tag{6}$$

The third constraint deals with the reference frame in which the diffusion process takes place. In a system without convection currents, the fluid motion is one-dimensional and the movement of the fluid parcels is constrained by the walls of the system. The system of Fig. 1 is attached to the laboratory. Since the interchange of mass between the bulbs, which occurs after the valve has been reopened, causes usually a translation of the center of mass of the fluid mixture, an external force must be exerted on the two-bulb system to keep it attached to the laboratory. The result of this force is that the center-of-volume of the fluid mixture does not translate. Because of the absence of convection, the zero translation of the center of volume applies to every fluid parcel in the system. Since, initially, the volume of the fluid inside bulb *A* is equal to the volume of the fluid inside bulb *B*, the zero translation of the center of volume means that these volumes remain equal:

$$\sum_{i=1}^{N} n_i^A v_i^A = \sum_{i=1}^{N} n_i^B v_i^B . \tag{7}$$

Note that the constraint of mechanical equilibrium is not applied in contrast with our previous derivation.[2] Instead, the constraint of zero translation of the center of volume, Eq. (7), is applied. We consider this last constraint as more obvious than the constraint of mechanical equilibrium. In fact, mechanical equilibrium, which is expressed by $p^A = p^B$, is a consequence of the constraint of zero translation of the center-of-volume: if we apply $p^A = p^B$ as a fourth constraint, the result appears to be the same. This can be shown using the next relation and following the rest of the mathematical procedure:

$$\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial p}{\partial V}\right)_{T,n_j} \Big/ \left(\frac{\partial n_i}{\partial V}\right)_{T,p,n_{j\neq i}} = \left(\frac{\partial p}{\partial V}\right)_{T,n_j} v_i .$$

By substituting in Eq. (3), Eq. (4) and the thermodynamic relationship $Z = \exp(-F/kT)$, where $F(T,V,n_1,\ldots,n_N)$ is the Helmholtz free energy, and including constraints (5)–(7) into the extremum determination, the mathematical problem is to find n_i^A and $n_i^B (i=1,...,N)$ from

$$\min\left\{ \frac{F^A - F^{A^0}}{T^A} + \frac{F^B - F^{B^0}}{T^B} - \sum_{i=1}^{N} [\lambda_i (n_i^A + n_i^B) \right.$$
$$\left. + \kappa_i (n_i^{A^0} + n_i^{B^0} - n_i^A - n_i^B)] - \upsilon \sum_{i=1}^{N} (n_i^A v_i^A - n_i^B v_i^B) \right\}, \tag{8}$$

where $\lambda_l,\ldots,\lambda_N$, $\kappa_i,\ldots,\kappa_N$ and υ are Lagrange multipliers. The mathematical treatment of Eq. (8) is given in the Appendix. The first step in the treatment is differentiation of the expression between brackets in Eq. (8) with respect to the independent variables $n_i^A,\ldots,n_N^A$, $n_i^B,\ldots,n_N^B$, and $n_1^{A^0},\ldots,n_N^{A^0}$, $n_1^{B^0},\ldots,n_N^{B^0}$. This results in $4N$ equations from which the Lagrange multipliers are to be eliminated. The solution is:

$$\frac{\Delta \dfrac{\mu_i - \mu_i^0}{T}}{\Sigma v_i} = \frac{\Delta \dfrac{\mu_N - \mu_N^0}{T}}{\Sigma V_N} \quad (i=1,...,N-1), \tag{9}$$

where Δ stands for the difference between bulb *A* and *B*, and Σ for the addition of bulb *A* and *B*. Another step in the mathematical treatment is the recognition of the term $x_i^{A^0} - x_i^{B^0}$ as the result of the kinetic contribution, which depends on the thermal diffusion factor α_{Ti}^0 of the ideal gas state as in experiment 1. This brings the kinetic contribution back into the equation. For *large* composition and temperature differences one must solve the set of implicit Eqs. (9) for the mole fraction differences Δx_i numerically. The rest of this paper deals with *small* composition and temperature differences. The solution is then the following set of equations in the thermal diffusion factors:

$$\sum_{j=1}^{N-1} \left(\frac{1}{v_i} \frac{\partial \mu_i}{\partial x_j} - \frac{1}{v_N} \frac{\partial \mu_N}{\partial x_j} \right) x_j (1 - x_j) \alpha_{\tau j}$$
$$= \frac{h_N - h_N^0}{v_N} - \frac{h_i - h_1^0}{v_i} + RT \left(\frac{\alpha_{Ti}^0 (1 - x_i)}{v_i} \right.$$
$$\left. - \frac{\alpha_{TN}^0 (1 - x_N)}{v_N} \right) \quad (i=1,...,N-1), \tag{10}$$

where the partial derivatives refer to the variables $T,p,n,x_1,\ldots,x_{N-1}$. To arrive at a numeric prediction for the thermal diffusion factors α_{Ti}, the set of Eqs. (10) can be implemented in a phase behavior computer package, together with:

$$\sum_{j=1}^{N} x_j (1 - x_j) \alpha_{Tj} = 0, \tag{11}$$

which follows from definition (1). It is evident that the derivation of the above set of equations does not suffer from shortcomings (1), (2), and (4) mentioned in Sec. I.

A value for α_T^0, the thermal diffusion factor of the same mixture at the same temperature in the ideal gas state, can be calculated with kinetic gas theory. Hirschfelder, Curtiss, and Bird[12] provide a practical guide for its computation. Calculated values of α_T^0 agree with measurements within 20%. A treatment for binary isotope mixtures is given by Jones and Furry.[13] Experimental values of α_T^0 can also be found in Vargaftik.[14]

Frame of reference

The above equations have been derived with the center-of-volume as the frame of reference. An alternative frame of reference is the center-of-mass. In this frame the center-of-mass does not translate. In that case the constraint Eq. (7) must be replaced by

$$\sum_{i=1}^{N} n_i^A m_i = \sum_{i=1}^{N} n_i^B m_i . \tag{12}$$

With Eq. (12) instead of Eq. (7), the molar volume v_i in the previous mathematical expressions must be replaced by the molar mass m_i. Note that in this frame, mechanical equilibrium does not apply. The question, which frame of reference applies, and hence whether constraint Eq. (7) or constraint Eq. (12) is to be used, has not a straightforward answer in every case. It is evident that in experimental cells that are fixed to the laboratory, and in which the material fluxes are one-dimensional (no convection), the center-of-volume is the frame of reference to be used [and hence constraint Eq. (7)]. Also large-scale convection, such as in a Clausius–Dückel column, is determined by the system walls, and requires the center of volume as a frame of reference. However, if small-scale convection is present, the movement of a fluid parcel is constrained less by the walls of the system. Then the thermal diffusion between adjacently moving fluid parcels is better described with the center-of-mass of the adjacent fluid parcels as a frame of reference, and hence with Eq. (12). An example of such a situation might be the application of thermal diffusion to the compositional variation in underground oil reservoirs in which small-scale convection currents are most likely to be present.

III. SPECIAL CASES

A. Alternative expression for multicomponent mixture (center-of-volume is frame of reference)

The Appendix shows that an alternative expression for Eqs. (10) and (11) is the following equation:[15]

$$\sum_{j=1}^{N-1} \frac{\partial \mu_i}{\partial x_j} x_j(1-x_j)\alpha_{Tj} = \frac{v_i}{v}(h-h^0)-(h_i-h_i^0)+RT(1-x_i)\alpha_{Ti}^0 \quad (i=1,...,N), \tag{13}$$

where h and v are the molar quantities of the mixture. The largest term on the left side of Eq. (13) is usually the one with $j=i$. The sign of α_{Ti} is therefore determined mainly by the term $-(h_i-h_i^0)/v_i$ which is the enthalpy density. If this term is larger than the same term for the mixture, then component i concentrates at the cold side in most cases.

B. Binary mixture (center-of-volume)

Substitution in Eq. (10) of Eq. (11) and the thermodynamic relationship $x_1(\partial\mu_1/\partial x_1)=x_2(\partial\mu_2/\partial x_2)$ yields the following explicit expression for the thermal diffusion factor:

$$\alpha_{T1}=\frac{v_i v_2}{v_1x_1+v_2x_2}\,\frac{\dfrac{h_2-h_2^0}{v_2}-\dfrac{h_1-h_1^0}{v_1}}{x_1\dfrac{\partial\mu_1}{\partial x_1}}+\frac{RT}{x_1\dfrac{\partial\mu_1}{\partial x_1}}\alpha_{T1}^0, \tag{14}$$

where the partial derivatives refer to the variables T,p,n,x_1. An alternative expression follows from Eq. (13):

$$\alpha_{T1}=\frac{\dfrac{v_1}{v}(h-h^0)-(h_1-h_1^0)}{x_1x_2\dfrac{\partial\mu_1}{\partial x_1}}+\frac{RT}{x_1\dfrac{\partial\mu_1}{\partial x_1}}\alpha_{T1}^0, \tag{15}$$

in which $h=h_1x_1+h_2x_2$ and $v=v_1x_1+v_2x_2$. Expression (14) or (15) replaces expression (2) of the old theory. These expressions yield the following qualitative observations. Because the enthalpy is usually negative, the species with the largest negative molar enthalpy per molar volume tends to concentrate in the cold region. Second, the Soret effect increases with increasing nonideal behavior.

C. Multicomponent mixture (center-of-mass is frame of reference)

In some cases, which are discussed at the end of Sec. II, the center-of-mass is a better frame of reference than the center of volume. In such cases constraint Eq. (12) must be used instead of constraint Eq. (7). The set of Eq. (13) has then to be replaced by:

$$\sum_{j=1}^{N-1} \frac{\partial \mu_i}{\partial x_j} x_j(1-x_j)\alpha_{Tj} = \frac{m_i}{m}(h-h^0)-(h_i-h_i^0)+RT(1-x_i) \times\alpha_{T1}^0 \quad (i=1,...,N)^{15}, \tag{16}$$

where m is the molar mass of the mixture.

D. Binary mixture (center-of-mass)

Applying Eq. (16) to a binary mixture yields:

$$\alpha_{T1}=\frac{m_1m_2}{m_1x_1+m_2x_2}\,\frac{\dfrac{h_2-h_2^0}{m_2}-\dfrac{h_1-h_1^0}{m_1}}{x_1\dfrac{\partial\mu_1}{\partial x_1}}+\frac{RT}{x_1\dfrac{\partial\mu_1}{\partial x_1}}\alpha_n^0. \tag{17}$$

This corresponds to Haase's expression,[8] which lacked a derivation but was an educated guess.[2] Hence our methodology provides a basis for his expression. The conditions under which Eq. (17) can be applied are discussed at the end of Sec. II.

E. Binary mixture of which molar volume of a component is small (center-of-volume)

In some near-critical mixtures, the molar volume of one of the components (say component labeled 1) may be very small compared to the molar volume of the other component. In such a case, we have the following approximation for Eq. (13):

$$g a_{T1}=-\frac{h_1h_1^0}{x_1x_2\dfrac{\partial\mu_1}{\partial x_1}}+\frac{RT}{x_1\dfrac{\partial\mu_1}{\partial x_1}}\alpha_{T1}^0. \tag{18}$$

Hence, the magnitude of the Soret effect is determined by the enthalpy of the smaller species, and independent of the specific molar volumes. This result is of interest for near-critical mixtures, such as discussed in Sec. IV.

F. No input from kinetic gas theory available (both frames)

If the value of the thermal diffusion factor of the ideal gas state is not available, one may still calculate a value for the thermal diffusion factor if one measured value for α_T of the same mixture at the same temperature but at another pressure and/or composition is available. The reason is that α_T^0 is independent of pressure and nearly independent of the mole fractions.

G. Dilute gases and dense isotope mixtures: Negligible thermodynamic contribution (both frames)

In the ideal gas limit, we have $h_i=h_i^0$ and $\partial\mu_i/\partial x_j=RT/x_i\delta_{ij}$, hence: $\alpha_{Ti}=\alpha_{Ti}^0$. Among the gases to which this approximation applies are dilute gases and dense isotope mixtures. The present theory covers these cases, but the result is very sensitive to the accuracy of input from kinetic gas theory.

TABLE I. List of mixtures that are used as test cases for expressions (13) and (16).

	Component 1	Component 2	Pressure (bar)	Temperature (K)	Mole fraction comp. 1	#	Reference
1	methane	propane	40–75	346	0.23–0.58	17	Haase *et al.* (Ref. 16)
2	methane	*n*-butane	95–204	319–394	0.40, 0.49	96	Rutherford and Roof (Ref. 17)
3	*n*-hexane	*n*-octane	1	320	0.55	1	Korsching and Wirtz (Ref. 18)
4	cyclo-hexane	benzene	1	313	0.2–0.8	3	Tichachek, Kmak, Drickamer (Ref. 19)
5	*n*-hexane	benzene	1	309	0.1–0.9	5	Korsching (Ref. 20)
6	*n*-heptane	benzene	1	309	0.1–0.9	9	Korsching (Ref. 20)
7	*n*-octane	benzene	1	309	0.1–0.9	9	Korsching (Ref. 20)
8	*n*-hexane	toluene	1	296	0.25–0.75	3	Köhler and Müller (Ref. 21)
9	*n*-heptane	*n*-dodecane	1	296	0.5	5	Trevoy and Drickamer (Ref. 22)
10	*n*-heptane	*n*-tetradecane	1	306–336	0.5	3	Trevoy and Drickamer (Ref. 22)
11	*n*-heptane	*n*-pentadecane	1	306	0.5	1	Trevoy and Drickamar (Ref. 22)
12	*n*-heptane	*n*-hexadecane	1	308	0.10–0.90	8	Shieh (Ref. 23)
13	*n*-heptane	*n*-octadecane	1	306	0.5	1	Trevoy and Drickamer (Ref. 22)
14	methane	carbondioxide	3–81	357	0.48	4	Becker (Ref. 24)
15	methane	nitrogen	4–80	357	0.50	4	Becker (Ref. 24)
16	nitrogen	carbondioxide	3–81	357	0.52	4	Becker (Ref. 24)
17	hydrogen	nitrogen	3–78	357	0.50	4	Becker (Ref. 24)
18	hydrogen	carbondioxide	3–81	223–363	0.24–0.53	12	Becker (Ref. 24), Narayanan and Dickel (Ref. 25)

H. Near-critical mixtures: Negligible kinetic contribution (both frames)

The thermal diffusion factor as a result of the kinetic contribution, α_T^0, is generally smaller than 0.3, while for most nonideal mixtures $\partial\mu_1/\partial x_1$ falls in the range 0.4–1 and α_T is above 3. Hence in highly nonideal liquids and dense gases, the kinetic contribution can be neglected. The thermodynamic contribution is particularly dominant for near-critical mixtures.

IV. COMPARISON WITH EXPERIMENTAL DATA

The new theory has been compared with measured data for both frames of reference: center-of-volume and center-of-mass. The comparison has been done for all measured Soret data, known to us, of mixtures that can be represented by our phase-behavior package (mainly hydrocarbons and simple gases). The equation-of-state (EOS) is a modified version of the Soave EOS; the modification is the inclusion of an interaction parameter in the mixing rule for the *a*-parameter. Interaction parameters are smaller than 0.1 for mixtures with carbondioxide and smaller than 0.02 for all other mixtures. The mixtures are listed in Table I.[16–25]

The α_T values calculated with expression (14) (frame of reference: center-of-volume) and those calculated with expression (17) (frame of reference: center-of-mass) are compared to data in, respectively, Figs. 2 and 3. The α_T values refer to component 2; for all mixtures the measured value is positive. The graphs have logarithmic scales to represent α_T values over four decades. The α_T signs of all calculated data, except a few datapoints of mixtures 4–8, 10, and 11, correspond to measured data. Because of the logarithmic scale, these exceptions are not taken up in Figs. 2 and 3. When the

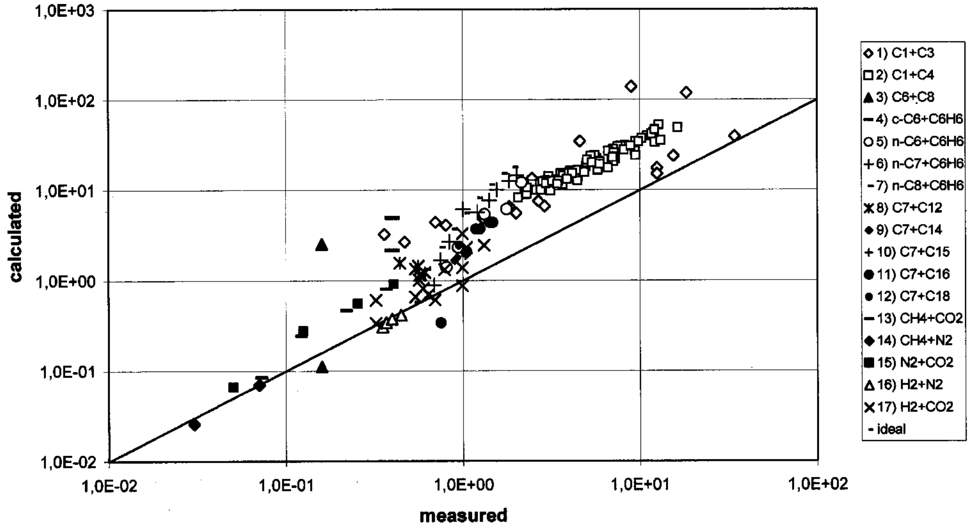

FIG. 2. Comparison to measurements for 18 mixtures if center-of-volume is frame of reference.

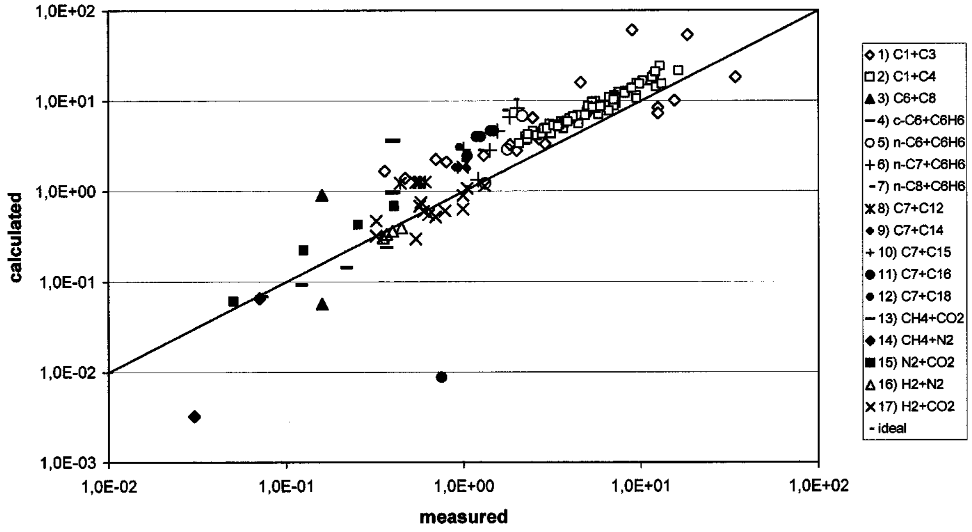

FIG. 3. Comparison to measurements for 18 mixtures if center-of-mass is frame of reference.

Soret data of all mixtures are taken together, both graphs show that there is at least a qualitative agreement between measured and calculated data over four decades. Generally, the agreement is better for the center-of-mass as a frame of reference than for the center-of-volume.

In the case of some mixtures, i.e., gaseous mixtures 14, 16–18, there is good to fair agreement for both frames of reference, and slightly better for the center-of-volume. In the case of the near-critical mixture 2, the agreement is fair for the center-of-mass; for the near-critical mixture 1 the agreement is poor for both frames. In the case of liquid hydrocarbon mixtures 4–13 the agreement varies between fair and poor for both frames.

For most of the 18 mixtures the calculated α_T-value is extremely sensitive to the value of the specific molar volume or the specific molar enthalpy. This means that calibration of the molar volume or molar enthalpy of the mixture to measured density data is not sufficient for an accurately calcu-

TABLE II. List of mixtures with type of agreement to data, some experimental conditions (temperature difference between chambers, presence of large-scale convection) and sensitivity of α_T to specific molar volume and specific molar enthalpy.

	Type mixture	Quantitative agreement for c.o.v., expr. (13)	Quantitative agreement for c.o.m., expr. (17)	ΔT K	Presence convection	Sensitivity ratio sv	Sensitivity ratio sh
1	near-critical	poor[a]	poor	8	stirring	0.6–1.0	0.6–1.0
2	near-critical	poor	fair	10–20	stirring	0.1–2.2	0.1–26[b]
3	liquid at room cond.	poor	poor	40	yes	24	24
4	liquid at room cond.	poor	poor	10	stirring	12–390	12–390
5	liquid at room cond.	poor	fair	not given	no stirring	7–93	7–93
6	liquid at room cond.	poor	poor	not given	no stirring	4–168	4–168
7	liquid at room cond.	poor	poor	not given	no stirring	4–297	4–297
8	liquid at room cond.	poor	fair	not given	no stirring	6–22	6–22
9	liquid at room cond.	poor	poor	5	yes	23–41	3–21
10	liquid at room cond.	fair	fair	5–10	yes	24–32	1–36
11	liquid at room cond.	fair	poor	5	yes	31	197
12	liquid at room cond.	poor	poor	15	stirring	15–70	6–122
13	liquid at room cond.	poor	poor	5	yes	30	17
14	gaseous at high *p*	fair	fair	140	no stirring	1.5–2.1	2.1–2.7
15	gaseous at high *p*	good	poor	140	no stirring	1.4–1.6	0.9–1.9
16	gaseous at high *p*	fair	fair	140	no stirring	0.8–1.0	0.5
17	gaseous at high *p*	good	good	140	no stirring	0.2–0.3	0.2–0.3
18	gaseous at high *p*	fair	good	140, 100	no stirring	0.5–1.3	0.0–1.6

[a] poor: calculated value less than 50% or higher than 200% of measured value; good: calculated value between 80% and 125% of measured value.

[b] of the 96 datapoints 92 have *sh* below 3.

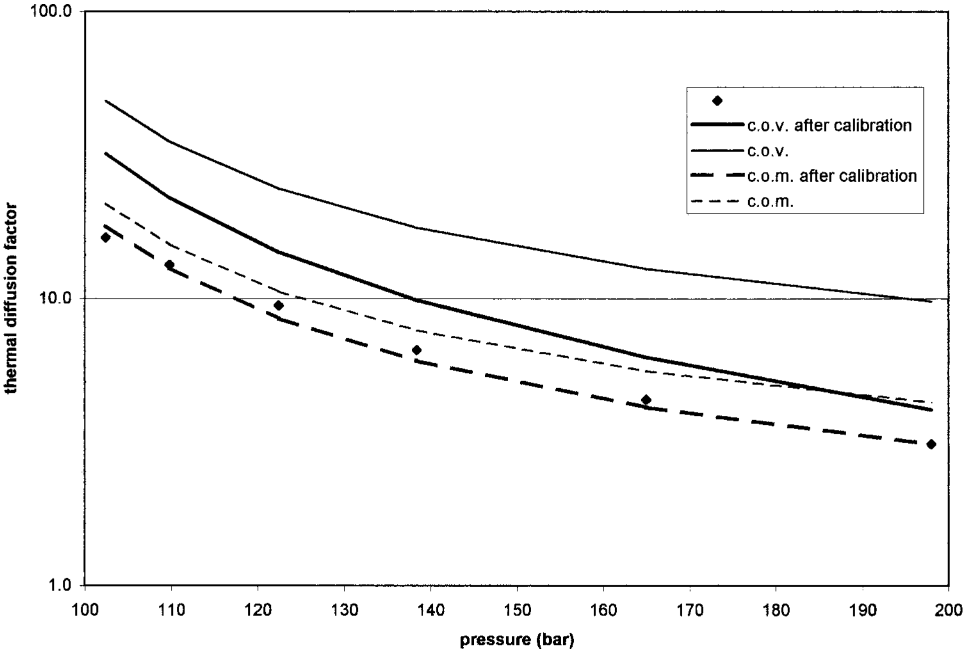

FIG. 4. Comparison to measurements for methane (molefraction 0.40) + *n*-butane at 395 K.

lated value for α_T. To express this sensitivity, the sensitivity ratio sv for the specific molar volume is defined as the ratio between the sensitivity of α_T to the specific molar volume by the sensitivity of the molar volume of the mixture to the specific molar volume:

$$\mathrm{sv}=\max[\mathrm{abs}(sv1),\mathrm{abs}(sv2)]$$

with

$$sv_i=\frac{v_i}{\alpha_T}\frac{\partial\alpha_T}{\partial v_i}\Bigg/\frac{v_i}{v}\frac{\partial v}{\partial v_i}. \tag{19}$$

For example, an sv-value of 5 means that a 10% uncertainty in the mixture volume due to one of the components corresponds to a 50% uncertainty in α_T. A similar ratio *sh* for the specific molar enthalpy is defined. Table II lists the values of these ratios for each mixture.

The table shows that the hydrocarbon mixtures 3–13 are extremely sensitive to specific molar volume and specific molar enthalpy. For some test data of these mixtures, a change in the molar specific enthalpy or molar specific molar volume has a 100 times greater effect on the thermal diffusion factor than on the molar enthalpy or molar volume of the mixture. This means that the uncertainty in α_T of many datapoints is 100% if the uncertainty in enthalpy or volume is 1%.

An alternative test for mixture No. 2 is to use one of the 96 Soret measurements on this mixture as a calibration, e.g., the smallest measured α_T value (2.1) at the lowest temperature, by using the α_T^0 value calculated from this calibration point as input in all other 95 measurements. The result of this exercise is shown for a selection of the 96 datapoints in Fig.

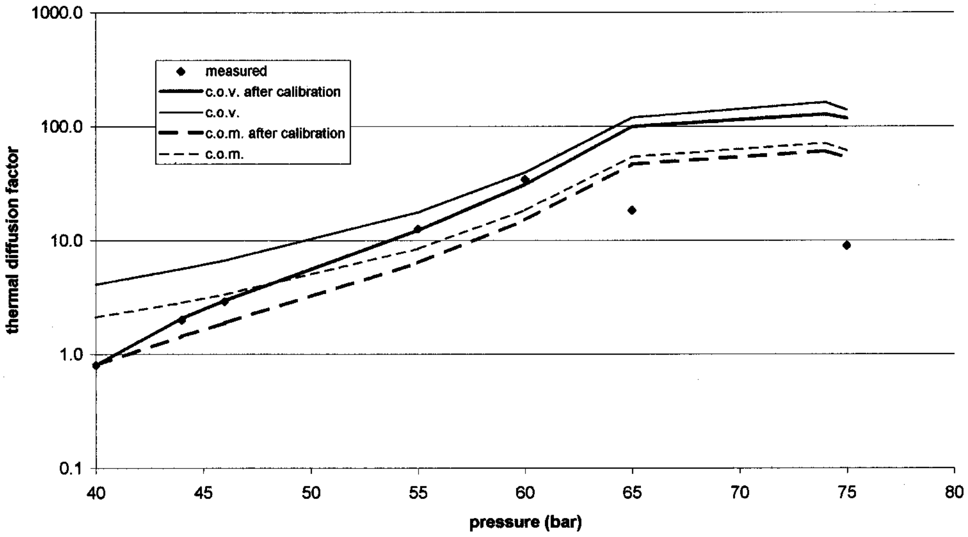

FIG. 5. Comparison to measurements for methane (molefraction 0.34) + *n*-propane at 346 K.

4 for both frames. This figure shows that a better match is obtained for both frames, and that the match for the center-of-mass is best.

The exercise is also done for the 17 datapoints of mixture No. 1 [with the smallest measured α_T-value (0.8) at the lowest pressure as a calibration point]. Figure 5, in which some results of the calibration are shown, shows an improved match for both frames, particularly for the center-of-volume. There is, however, no match near the critical point.

V. DISCUSSION

A. Equation-of-state

In all papers in which our and other's expression for the thermal diffusion factor are compared to measured data,[2,10,11] it is implicitly assumed that the EOS used for the calculation of molar enthalpy and molar volume yields accurate values. This assumption is doubtful. The effect of the EOS on the value of the thermal diffusion factor can be illustrated very well by comparing our calculation of the thermal diffusion factor of the methane/propane mixture in our previous paper to the recent calculation by Shukla and Firoozabadi.[10] Their calculated values for methane/propane at 346 K and 55 bar are 2–3 times larger than the values presented in our previous paper,[2] although the same mathematical expression for the thermal diffusion factor is used.[26]

Another illustration of the insufficient accuracy of EOS is the prediction of the critical pressure of the methane/propane system: 62 bar according to the measurements of Haase and 65.8 bar according to our phase-behavior package. Since the numerator in the expression for α_T becomes zero at the critical point, α_T is very sensitive to the location of the critical point. This explains the absence of a match near the critical point, even after calibration as in Fig. 5. The deviation by an order of magnitude between measurement and theory of α_T in the near-critical regime of the methane/propane mixture must therefore be attributed in the first place to an inadequate EOS. Furthermore, the EOS in the supercritical region is an extrapolation of the EOS 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 EOS of the supercritical liquid region are likely.

The present EOS's are generally not intended for predicting the Soret effect, which depends on the *difference* between component properties. They are calibrated only for predicting quantities that depend on the *addition* of component properties. The prediction of the magnitude of the Soret effect with quantities derived from the EOS is therefore generally more sensitive to an error in a component property (specific molar volume and specific molar enthalpy) than is, for example, the fluid density. But even the density poses a problem. For example, near-critical gas/condensate mixtures are notorious for a bad prediction of density and molar volume; deviations of more than 10% are not uncommon. Although the volume translation method has been developed to match the measured density of the mixture, this method is not intended for the prediction of the molar volume of each component in the mixture. Hence the accuracy of the prediction of the magnitude of the Soret effect, which depends on molar volumes, is mostly worse than 10%. According to Table II, a few extreme examples are the mixtures Nos. 4–7: the sensitivity of the thermal diffusion factor to the molar volume of one of the components is about 10, several hundred times the sensitivity of the mixture density to the molar volume of the same component.

There is thus a need for calibrating the EOS to new demands like the prediction of the Soret effect. Further research in this area is recommended. One may even reverse the problem: measurements of the Soret effect may reveal more about the phase behavior and thermodynamic properties of the components in the mixture.

B. Recipe for improved prediction

With the present EOS accuracy, it seems from Figs. 3 and 4 that an improved prediction of the Soret effect can be obtained by using one measured datapoint as a calibration. The recipe is then:

(1) calculate the thermal diffusion factor with either Eq. (13) or Eq. (16);
(2) determine the sensitivity of a to input data of the EOS with Eq. (19);
(3) in case of high sensitivity, calibrate with measured data.

C. Linearilization

In most tested mixtures the temperature difference between the chambers of the cell was small compared to the average absolute temperature. However, in mixture 3 and gaseous mixtures 13–18 this is not the case (see Table II). For these mixtures α_T values are not symmetric over the temperature range around the average temperature. As a consequence, linearization is not allowed and one must solve the implicit Eq. (9). For comparison to measurements one then needs the composition of each chamber, which is not available from the relevant paper.[24] [For mixture 3 these compositions are available, but the measurement is done in the presence of large-scale convection for which the mathematical description with Eq. (9) is invalid.] Hence only a qualitative comparison to data is possible for these mixtures.

D. Frame of reference

We have shown in Sec. II that the frame of reference is the center-of-volume if the experimental setup is attached to the laboratory and if the fluid motion is one-dimensional. However, the comparison with measurements in Sec. IV, in particular those for mixture 2 of methane and *n*-butane, shows that the center-of-mass compares generally better to data than the center-of-volume. Since the experimental setup is attached to the laboratory, a possible conclusion is that the fluid motion was not one-dimensional in the measurements. Measurements that were designed to eliminate convection might have had convection because of the stirring in the chambers of the experimental cell. Stirring, which promotes a uniform mixture composition in each chamber and helps to attain the steady state quicker, introduces two-or three-dimensional fluid movement. Tichachek *et al.*[19] found a relation between separation and stirring speed.

E. Suitability of measurements to test theory

It appears from Table II that there are no test data available that fulfill the following demands:

- sufficiently reliable EOS, hence small sensitivity to EOS
- small temperature difference or all relevant data available in paper in case of large temperature difference
- no large-scale convection
- no stirring (see also next paragraph)

If one drops the demand of no stirring, then two mixtures remain: those data of mixture 1 and 2 that are far from critical condition. For future measurements it is recommended that all above demands be fulfilled.

Experiments without stirring in a microgravity environment seem to be the most reliable way to eliminate convection. Therefore, the Microgravity Research Center in Bruxelles carries out a project in space[27] for the European Space Agency. It may result in a reliable test of our theory.

F. Application to cross-effect in isothermal diffusion (“Hertz effect”)

The methodology of the theory presented in Sec. II is not restricted to application to the Soret effect. In principle, every cross-effect from irreversible thermodynamics can be modeled with this methodology. An example is the cross-effect between diffusion fluxes in an isothermal mixture of three or more components with a spatial concentration difference. This cross-effect is the cause of diffusion of a component against its own concentration gradient. Gustav Hertz was the first to use this cross-effect for the separation of mixtures. Using the methodology presented in this paper, we have developed for the first time a calculation method for the magnitude of this cross-effect, which we call Hertz effect, without using input of any measured diffusion coefficient.[28]

VI. CONCLUSIONS AND RECOMMENDATIONS

(1) The present comprehensive theory of the Soret effect, which yields a set of Eqs. (13) for a multicomponent mixture and expression (14) for a binary mixture, incorporates both the thermodynamic and the kinetic contribution to the Soret effect.

(2) The new description applies to any multicomponent mixture, gaseous, liquid, or solid. The description is particularly useful for nonideal mixtures, such as concentrated solutes and near-critical mixtures. Applications to solids, polymer solutions, and colloids have not been tested, but are possible in principle.

(3) The theory has been formulated in several frames of reference. The frame of reference for thermal diffusion is normally the center-of-volume. When small-scale convection is present, the frame of reference for the thermal diffusion between moving fluid parcels may be better described by the center-of-mass. The frame of reference determines which mathematical expression for the thermal diffusion factor must be used [Eq. (13) or (16) for a multicomponent mixture and Eq. (14) or (17) for a binary mixture].

(4) The theory can be used also for systems with a large temperature and/or concentration difference. See Eq. (9).

(5) On comparison with nearly 200 measured datapoints of 18 different liquid and gaseous mixtures, the predicted thermal diffusion factor shows agreement within a factor 2 on average over 4 decades (between 0.01 and 100). Closer agreement cannot be expected because of the extreme sensitivity of most datapoints to input from the equation-of-state. The center-of-mass as a frame of reference matches measured data better than the same theory with the center-of-volume as a frame of reference. This can be explained by the presence of two-or three-dimensional fluid movement in the experimental cells. A possible cause for this movement is the stirring during the measurements to reach the steady state quicker.

(6) The present equations-of-state, even those that are calibrated for use in the chemical and petroleum industry, require modification for the calculation of the Soret effect, because of a higher demand in accuracy. Further research to improve the accuracy of the EOS is recommended, particularly for near-critical conditions.

(7) It is recommended to carry out measurements of the Soret effect in which a small temperature difference is applied (or to report the composition of each chamber if a large temperature difference is applied), in which no stirring is applied and convection is absent, and to select mixtures of which the thermal diffusion factor is not very sensitive to input data from the equation-of-state. None of the measurements on the 18 mixtures fulfill these demands.

LIST OF SYMBOLS

c.o.m.	center-of-mass
c.o.v.	center-of-volume
EOS	equation-of-state
F	Helmholtz free energy
g	gravitational acceleration
h	molar enthalpy
k	Boltmann’s constant
m	molar mass
N	number of components in mixture
n	mole number
p	pressure
R	gas constant
T	absolute temperature
V	volume of bulb
v	molar volume
x	mole fraction
Z	canonical partition function of two-bulb system (if with label: single bulb)
α_T	thermal diffusion factor
Δ	operator for the difference between bulb A and bulb B
μ	chemical potential
ρ	density
Σ	operator for the addition of bulb A and bulb B

superscripts:

A, *B*	bulb label
0	ideal gas state

subscripts:

i, *j*, *k*, *N*	component label

APPENDIX: MATHEMATICAL TREATMENT

In this Appendix, the solution of minimum statement Eq. (8) is calculated. From differentiation of the expression between brackets in Eq. (8) with respect to the independent variables $n_i^A, n_i^{A^0}, n_i^B, n_i^{B^0}$ $(i=1,...,N)$, respectively, and using the thermodynamic relationship

$$\left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \mu_i, \tag{A1}$$

where μ_i is the chemical potential of component *i*, it follows that

$$\frac{\mu_i^A}{T^A} - \lambda_i + \kappa_i - \upsilon v_i^A = 0 \quad (i=1,...,N), \tag{A2a}$$

$$\frac{-\mu_i^{A^0}}{T^A} - \kappa_i = 0 \quad (i=1,...,N), \tag{A2b}$$

$$\frac{\mu_i^B}{T^B} - \lambda_i + \kappa_i + \upsilon v_i^B = 0 \quad (i=1,...,N), \tag{A2c}$$

$$\frac{-\mu_i^{B^0}}{T^B} - \kappa_i = 0 \quad (i=1,...,N). \tag{A2d}$$

Adding Eq. (A2b) to Eq. (A2a) and Eq. (A2d) to Eq. (A2c) to eliminate κ_i results in:

$$\frac{\mu_i^A - \mu_i^{A^0}}{T^A} - \lambda_i - \upsilon v_i^A = 0 \quad (i=1,...,N), \tag{A3a}$$

$$\frac{\mu_i^B - \mu_i^{B^0}}{T^B} - \lambda_i + \upsilon v_i^B = 0 \quad (i=1,...,N). \tag{A3b}$$

Subtraction of Eq. (A3b) from Eq. (A3a) to eliminate λ_i gives:

$$\frac{\mu_i^A - \mu_i^{A^0}}{T^A} - \frac{\mu_i^B - \mu_i^{B^0}}{T^B} - \upsilon(v_i^A + v_i^B) = 0 \quad (i=1,...,N), \tag{A4}$$

from which follows Eq. (9). Developing $v_i^A + v_i^B$ in the above equation with a Taylor expansion around the average of bulb *A* and bulb *B*, ignoring the third and higher order derivatives, and using the Δ symbol to denote the difference between bulb *A* and bulb *B* gives:

$$\Delta\left(\frac{\mu_i}{T}\right) - \Delta\left(\frac{\mu_i^0}{T}\right) - 2\upsilon v_i = 0 \quad (i=1,...,N). \tag{A5}$$

Substitution of the equation with $i=N$ to eliminate υ gives an equation without Lagrange multipliers:

$$\frac{\Delta\left(\frac{\mu_i}{T}\right) - \Delta\left(\frac{\mu_i^0}{T}\right)}{v_i} = \frac{\Delta\left(\frac{\mu_N}{T}\right) - \Delta\left(\frac{\mu_N^0}{T}\right)}{v_N} \quad (i=1,...,N-1). \tag{A6}$$

Developing $\Delta(\mu_i/T)$ as a Taylor expansion with independent variables $T,p,n,x_1,\ldots,x_{N-1}$ to make use of $\Delta p = 0$ (which follows from the constraint of zero translation of the center of volume) and of $(\partial\mu_i/T/\partial n)_{T,p,x_j} = 0$ and ignoring second and higher order derivatives gives

$$\Delta\left(\frac{\mu_i}{T}\right) = \left(\frac{\partial\mu_i/T}{\partial T}\right)_{p,n,x_j} \Delta T + \frac{1}{T}\sum_{j=1}^{N-1}\left(\frac{\partial\mu_i}{\partial x_j}\right)_{T,p,n,x_k} \Delta x_j \quad (k\neq j,N). \tag{A7}$$

A thermodynamic relationship for the molar enthalpy of component *i* is:

$$h_i = -T^2\left(\frac{\partial u_i/T}{\partial T}\right)_{p,n,x_j}. \tag{A8}$$

In the ideal gas state the term $T\Delta(\mu_i^0/T)$ is:

$$T\Delta\left(\frac{\mu_i^0}{T}\right) = -h_i^0\frac{\Delta T}{T} + \frac{RT}{x_i}\Delta x_i^0 \quad (i=1,...,N). \tag{A9}$$

Note that the mole fraction differences Δx_i^0 are those of the ideal gas state: relationship (1), when applied to the ideal gas state, yields:

$$\Delta x_i^0 = -x_i(1-x_i)\alpha_{Ti}^0\frac{\Delta T}{T} \quad (i=1,...,N), \tag{A10}$$

where α_{Ti}^0 is the thermal diffusion factor in the ideal gas state and is quantified by kinetic gas theory. Finally, substitution of Eq. (A7)–(A10) and definition (1) in Eq. (A6) gives:

$$\sum_{j=1}^{N-1}\left(\frac{1}{v_i}\frac{\partial\mu_i}{\partial x_j} - \frac{1}{v_N}\frac{\partial\mu_N}{\partial x_j}\right)x_j(1-x_j)\alpha_{Tj} = \frac{h_N - h_N^0}{v_N} - \frac{h_i - h_1^0}{v_i} + RT\left(\frac{(1-x_j)\alpha_{Ti}^0}{v_i} - \frac{(1-x_N)\alpha_{Ti}^0}{v_N}\right) \quad (i=1,...,N-1), \tag{A11}$$

where the partial derivatives refer to the variables $T,p,n,x_1,\ldots,x_{N-1}$. A shorter expression for Eq. (A11) is:[15]

$$\sum_{j=1}^{N-1}\frac{\partial\mu_i}{\partial x_j}x_j(1-x_j)\alpha_{Tj} = \frac{v_i}{v}(h-h^0) - (h_i - h_i^0) + RT(1-x_i)\alpha_{Ti}^0 \quad (i=1,...N), \tag{A12}$$

where *h* and v are the molar quantities of the mixture. This equation can be derived by multiplying Eq. (A11) with $x_i v_i$, summing over $i\,(i=1,...N)$, and substituting Eq. (11) and the Gibbs–Duhem equation:

$$\sum_{i=1}^{N} x_i \Delta \mu_i|_{Tp} = 0, \tag{A13}$$

where the subscripts T and p refer to constant temperature and pressure. The resulting equation must then be substituted back in Eq. (A11) and the result multiplied with v_i.

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