Molecular, Pressure, and Thermal Diffusion in Nonideal Multicomponent Mixtures

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A formalism based on powerful concepts of the thermodynamics of irreversible processes is derived for calculating multicomponent diffusion flux both at the critical point and away from the critical point. The derivations are based on the entropy balance expression combined with the phenomenological equations and Onsager reciprocal relations. The formalism results in a clear expression of the thermal contribution in the diffusion flux for nonideal multicomponent mixtures. The diffusion flux analysis at the critical point showed that, unlike isothermal and isobaric conditions where molecular diffusion flux is zero, molecular diffusion flux is finite and nonzero at the critical point. The thermal contribution in the diffusion flux is also finite at the critical point in multicomponent mixtures. At nonisothermal conditions, as well as nonisothermal and nonisobaric conditions, the composition gradient reaches infinity at the critical point; therefore, the mol fraction plot vs. spatial coordinates has an inflection point.

Introduction

Multicomponent diffusion (molecular, pressure, and thermal) is important in a variety of disciplines including oceanography, geology, metallurgy, material science, geophysics, chemical engineering, and hydrocarbon reservoir engineering (Turner, 1973, 1974, 1985; Huppert and Turner, 1981; Wilcox, 1993; Firoozabadi, 1999). The ratio of molecular, pressure, and thermal diffusion to the total diffusion flux depends on the nonideality of the fluid mixture. Our motivation for the study of the subject is to understand the irreversible phenomena in hydrocarbon reservoirs (cavities). An understanding of thermal, pressure, and molecular diffusion is required to determine the distribution of various species of a hydrocarbon fluid mixture in cavities with dimensions of the order of hundreds of meters and more. The fluid mixture contains a number of components, each having a significant amount; it can be at the critical region in certain parts of a large cavity.

There is a vast literature on the subject of multicomponent (more than two components) molecular diffusion and pressure diffusion (sometimes referred to as gravitational effect). The literature on thermal diffusion (often referred to as the Soret effect) is, however, mainly limited to two-component mixtures. To the best of our knowledge, there are no reported measured thermal diffusion factors (which are a measure of thermal diffusion) for ternary or higher mixtures. This may be due to the lack of proper formulation of thermal diffusion flux in multicomponent mixtures.

It has been established that multicomponent molecular diffusion flux is zero at the critical point (throughout the study our focus is the gas−liquid critical point) for both binary and multicomponent mixtures (Haase, 1990; Taylor and Krishna, 1993; Cussler, 1976; Ackerson and Hanely, 1980; Myerson and Senol, 1984). One purpose of this work is to establish the formulation that allows the determination of molecular diffusion flux at the critical point for (1) isothermal and nonisobaric, (2) nonisothermal and isobaric, and (3) nonisothermal and nonisobaric conditions. We are also interested in determining thermal diffusion flux at the critical point for multicomponent nonideal mixtures.

The behavior of the thermal diffusion coefficient for binary mixtures in the critical region has been the subject of several studies in the three last decades (Hohenberg and Halperin, 1977; Sengers and Levelt Sengers, 1986; Anisimov and Kiselev, 1992; Kiselev and Kulikov, 1994; Luettmer-Strathmann and Sengers, 1994, 1996; Anisimov et al., 1995; Kiselev, 1997; Cheng et al., 1997; Sakonidou et al., 1998; Kiselev and Huber, 1998; Giterman and Gorodetskii, 1970; Mistura, 1972, 1975; Haase et al., 1994, 1971; Rutherford and Roof, 1959).

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It has been shown using the mode–mode coupling analysis (Mistura, 1972, 1975) that thermal diffusion coefficients of a binary mixture have a finite value at the critical point. It is of interest to examine the finiteness of thermal diffusion at the critical point for multicomponent mixtures. In this work we show, by simple analysis of the diffusion flux for nonideal binary mixtures, that the compositional gradient becomes infinity at the critical point. We extend our analysis to multicomponent nonideal mixtures and show, for the first time, that the composition gradient of all the components undergo an inflexion point.

The cross effects characterize molecular diffusion and to a larger extent thermal diffusion in multicomponent mixtures. When those effects are significant, concentration gradients may change radically. To be specific, consider binary mixtures of methane (C_1)/ethane (C_2), methane (C_1)/propane (C_3), and methane (C_1)/*n*-butane (nC_4), where experimental thermal diffusion data are available (Sakonidou et al., 1998; Haase et al., 1971; Rutherford and Roof, 1959). In all those methane binaries of C_1/C_2, C_1/C_3, and C_1/nC_4, methane segregates to the hot side at isobaric conditions. On the other hand, in a ternary mixture of $C_1/C_2/nC_4$, methane may segregate to the cold side (Ghorayeb and Firoozabadi, 1999). The segregation of methane in binary mixtures to the hot side and in a ternary mixture to the cold side implies that one cannot use effective binary thermal diffusion factors to study thermal diffusion in ternary and higher mixtures in a nonisothermal process.

Cross-molecular diffusion coefficients have also been shown to be important in some ternary and higher mixtures. Larre et al. (1997) investigated the stability of a horizontal layer heated from below filled with a water–isopropanol–ethanol mixture. The authors neglected the cross-molecular diffusion coefficients and assumed that the thermal diffusion factor of a given component could be expressed as the sum of the thermal diffusion factors of the binaries consisting of this component and the two others, respectively. The model results do not, however, agree with the experimental data. A similar conclusion has been reported by Krupiczka and Rotkegel (1997), who investigated mass transfer in ternary mixtures of isopropanol–water–air and isopropanol–water–helium. Many discrepancies between experimental data and theoretical predictions were observed when cross-diffusion terms were neglected.

The main goal of this work is to present a consistent and clear formulation of diffusion flux expression for multicomponent mixtures. We include diffusion processes due to (1) concentration, (2) pressure, and (3) temperature gradients for complex near-critical mixtures. The derivations are based on the concepts of irreversible thermodynamics. Parts of our derivations are somewhat similar to those of de Groot and Mazur (1984) and Haase (1990). However, these authors have not attempted to present a complete formulation of multicomponent diffusion. We will repeat some aspects of the work of these authors for completeness in advancing concepts.

Phenomenological Equations

In a mixture consisting of n components ($n \geq 2$), where there is no heat generation, viscous dissipation, or chemical reaction, and where the only external force $\vec{F}$ is gravity, the entropy production strength σ (entropy production per unit time and volume) can be written as (de Groot and Mazur, 1984)

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

where $\vec{J}_q$ is the heat flux; T is the temperature; and M_k, μ_k, $\vec{J}_k$ are the molecular weight, the chemical potential, and the molar diffusion flux relative to the molar average velocity of component k, respectively. A different form of the entropy production can be obtained by using

$$T\vec{\nabla}\frac{\mu_k}{T} = \vec{\nabla}\mu_k - \frac{\mu_k}{T}\vec{\nabla}T \tag{2}$$

$$= \vec{\nabla}_T\mu_k - \left(\mu_k - T\frac{\partial\mu_k}{\partial T}\bigg|_{n,P}\right)\frac{\vec{\nabla}T}{T}, \tag{3}$$

where $n \equiv (n_1, n_2, \ldots, n_k, \ldots, n_n)$; n_k is the number of moles of component k; and P is the pressure. The subscript T implies that the gradient is calculated at constant temperature. One can readily show that

$$\overline{H}_k = \mu_k - T\frac{\partial\mu_k}{\partial T}\bigg|_{n,P}, \qquad k = 1, \ldots, n. \tag{4}$$

Here $\overline{H}_k$ is the partial molar enthalpy of component k. Equations 1, 3, and 4 imply that

$$\sigma = -\frac{1}{T^2}\left(\vec{J}_q - \sum_{k=1}^{n}\frac{\overline{H}_k}{M_k}\vec{J}_k\right)\cdot\vec{\nabla}T - \frac{1}{T}\sum_{k=1}^{n}\vec{J}_k\cdot\left(\vec{\nabla}_T\frac{\mu_k}{M_k} - \vec{F}\right), \tag{5}$$

where $\sum_{k=1}^{n}(\overline{H}_k/M_k)\vec{J}_k$ is the transfer of heat due to diffusion. By introducing a new heat-flux expression, defined as

$$\vec{J}'_q = \vec{J}_q - \sum_{k=1}^{n}\frac{\overline{H}_k}{M_k}\vec{J}_k, \tag{6}$$

and using $\sum_{k=1}^{n}\vec{J}_k = 0$, one can write the entropy production strength as a function of the diffusion flux of only $n-1$ components. Equation 1 then reads

$$\sigma = -\frac{1}{T^2}\vec{J}'_q\cdot\vec{\nabla}T - \frac{1}{T}\sum_{k=1}^{n-1}\vec{J}_k\cdot\vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right). \tag{7}$$

The phenomenological equations for heat flux and diffusion flux are therefore (de Groot and Mazur, 1984)

$$\vec{J}'_q = L'_{qq}\frac{\vec{\nabla}T}{T^2} - \frac{1}{T}\sum_{k=1}^{n-1}L'_{qk}\vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right), \tag{8}$$

$$\vec{J}_i = -L'_{iq}\frac{\vec{\nabla}T}{T^2} - \frac{1}{T}\sum_{k=1}^{n-1}L_{ik}\vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right), \quad i = 1, \ldots, n-1, \tag{9}$$

respectively. In Eqs. 8 and 9, L'_{qq}, L_{qk}, L'_{iq}, and L_{ik} are the phenomenological coefficients (see Onsager, 1931a,b). The fact that the entropy production strength σ is ≥ 0 puts conditions on the sign of some, and provides relations between some other phenomenological coefficients. The main theme of this study is the diffusion flux, and therefore we will focus on $\vec{J}_i$.

Diffusion Flux Expression

Let M, N, and x_j denote the total molecular weight ($M = m/N$, where m is the total mass), the total number of moles ($N = \sum_{k=1}^{n} n_k$), and the mol fraction of component j ($x_j = n_j/N$), respectively. The Gibbs-Duhem expression can be written as (see Firoozabadi, 1999)

$$\vec{\nabla}_T \mu_n = \frac{1}{x_n}\left(\frac{1}{c}\vec{\nabla}P - \sum_{j=1}^{n-1} x_j \vec{\nabla}_T \mu_j\right), \qquad (10)$$

where c is the total molar density. Let x_j and x denote

$$x_j \equiv (x_1, \ldots, x_{j-1}, x_{j+1}, \ldots, x_{n-1})$$

and

$$x \equiv (x_1, \ldots, x_{n-1}),$$

respectively. Then $\vec{\nabla}_T \mu_k$ can be written as

$$\vec{\nabla}_T \mu_k = \sum_{j=1}^{n-1} \left.\frac{\partial \mu_k}{\partial x_j}\right|_{x_j, T, P} \vec{\nabla} x_j + \left.\frac{\partial \mu_k}{\partial P}\right|_{x, T} \vec{\nabla} P \quad k = 1, \ldots, n. \quad (11)$$

$\vec{\nabla}_T$ $(\mu_k/M_k - \mu_n/M_n)$, which appears in Eq. 9, can be expressed as (using Eqs. 10 and 11)

$$\vec{\nabla}_T\left(\frac{\mu_k}{M_k} - \frac{\mu_n}{M_n}\right) = \sum_{j=1}^{n-1}\left(\frac{x_j}{M_n x_n} + \frac{\delta_{jk}}{M_j}\right)\sum_{l=1}^{n-1}\left.\frac{\partial \mu_j}{\partial x_l}\right|_{x_l, T, P}\vec{\nabla} x_l$$
$$+ \left[\sum_{j=1}^{n-1}\frac{x_j}{M_n x_n}\left.\frac{\partial \mu_j}{\partial P}\right|_{x, T} + \frac{1}{M_k}\left.\frac{\partial \mu_k}{\partial P}\right|_{x, T} - \frac{1}{c M_n x_n}\right]\vec{\nabla}P$$
$$k = 1, \ldots, n-1, \qquad (12)$$

where δ_{jk} denotes the Kronecker delta. By combining Eqs. 9 and 12, the diffusion flux expression takes the form

$$\vec{J}_i = -L'_{iq}\frac{\vec{\nabla}T}{T^2}$$
$$-\frac{1}{T}\sum_{k=1}^{n-1} L_{ik}\sum_{j=1}^{n-1}\left(\frac{x_j}{M_n x_n} + \frac{\delta_{jk}}{M_j}\right)\sum_{l=1}^{n-1}\left.\frac{\partial \mu_j}{\partial x_l}\right|_{x_l, T, P}\vec{\nabla} x_l$$
$$-\frac{1}{T}\sum_{k=1}^{n-1} L_{ik}\left[\frac{1}{M_k}\left.\frac{\partial \mu_k}{\partial P}\right|_{x, T} + \sum_{j=1}^{n-1}\frac{x_j}{M_n x_n}\left.\frac{\partial \mu_j}{\partial P}\right|_{x, T}\right.$$
$$\left. - \frac{1}{c M_n x_n}\right]\vec{\nabla}P \quad i + 1, \ldots, n-1. \qquad (13)$$

Terms $(\partial \mu_i/\partial x_j)_{x_j, T, P}$ and $(\partial \mu_i/\partial P)_{x_j, T}$ can be written as (see Firoozabadi, 1999)

$$\left.\frac{\partial \mu_i}{\partial x_j}\right|_{x_j, T, P} = RT\left.\frac{\partial \ln f_i}{\partial x_j}\right|_{x_j, T, P} \qquad i = 1, \ldots, n, \quad j = 1, \ldots, n-1$$
$$(14)$$

$$\left.\frac{\partial \mu_i}{\partial P}\right|_{x, T} = \left.\frac{\partial V}{\partial n_i}\right|_{n_i, T, P} = \bar{V}_i \qquad i = 1, \ldots, n, \qquad (15)$$

where R, V, f_i, and $\bar{V}_i$ are the gas constant, the total volume, the fugacity of component i, and the partial molar volume of component i, respectively; $n_i \equiv (n_1, \ldots, n_{i-1}, n_{i+1}, \ldots, n_n)$. By using an equation of state $\bar{V}_i$ and f_i can be obtained. (Firoozabadi, 1999). The new form of Eq. 13 after using Eqs. 14 and 15 is

$$\vec{J}_i = -\frac{RL_{ii}}{M_i x_i M_n x_n}\left\{\frac{M_i x_i M_n x_n L'_{iq}}{RL_{ii}}\frac{\vec{\nabla}T}{T^2}\right.$$
$$+ \frac{M_i x_i}{L_{ii}}\sum_{k=1}^{n-1} L_{ik}\sum_{j=1}^{n-1}\frac{M_j x_j + M_n x_n \delta_{jk}}{M_j}\sum_{l=1}^{n-1}\left.\frac{\partial \ln f_j}{\partial x_l}\right|_{x_l, T, P}\vec{\nabla} x_l$$
$$\left. + \frac{M_i x_i}{RT L_{ii}}\sum_{k=1}^{n-1} L_{ik}\left[\sum_{j=1}^{n-1} x_j \bar{V}_j + \frac{M_n x_n}{M_k}\bar{V}_k - \frac{1}{c}\right]\vec{\nabla}P\right\}$$
$$i = 1, \ldots, n-1. \qquad (16)$$

Let

$$a_{in} = \frac{M_i M_n}{M^2}, \qquad i = 1, \ldots, n-1, \quad (17)$$

$$D_{in} = \frac{M^2 RL_{ii}}{c M_i^2 M_n^2 x_i x_n}, \qquad i = 1, \ldots, n-1, \quad (18)$$

$$k_{Ti} = \frac{M_i x_i M_n x_n L'_{iq}}{MRT L_{ii}} = \alpha_{T_i} x_i x_n, \quad i = 1, \ldots, n-1, \quad (19)$$

where k_{Ti} and α_{Ti} denote the thermal diffusion ratio and the thermal diffusion factor of component i, respectively. An important result of this work is the simple expression for thermal diffusion factors of a multicomponent mixture given by Eq. 19 (that is, $k_{Ti} = \alpha_{Ti} x_i x_n$). For a binary mixture, $k_{T1} = \alpha_{T1} x_1 (1 - x_1)$. The expression $k_{Ti} = \alpha_{Ti} x_i (1 - x_i)$, which is a generalization of binary to multicomponent mixtures, is incorrect but has been used to represent the thermal diffusion ratio in multicomponent mixtures (Kempers, 1989; Van Vaerenbergh and Legros, 1996). For an ideal binary mixture, the molecular diffusion coefficient reduces to $a_{12} D_{12}$; the nonideality could, however, be incorporated into $a_{12} D_{12}$ by multiplication with $(\partial \ln f_1/\partial \ln x_1)_{T, P}$; that is, the molecular diffusion coefficient is equal to $a_{12} D_{12} (\partial \ln f_1/\partial \ln x_1)_{T, P}$.

From Eqs. 16 to 19,

$$\vec{J}_i = -c a_{in} D_{in} \left\{ M k_{Ti} \frac{\vec{\nabla} T}{T} + \frac{M_i x_i}{L_{ii}} \sum_{l=1}^{n-1} \sum_{k=1}^{n-1} L_{ik} \sum_{j=1}^{n-1} \frac{M_j x_j + M_n x_n \delta_{jk}}{M_j} \left. \frac{\partial \ln f_i}{\partial x_l} \right|_{x_l, T, P} \vec{\nabla} x_l + \frac{M_i x_i}{RT L_{ii}} \sum_{k=1}^{n-1} L_{ik} \left[\sum_{j=1}^{n-1} x_j \bar{V}_j + \frac{M_n x_n}{M_k} \bar{V}_k - \frac{1}{c} \right] \vec{\nabla} P \right\} \qquad i = 1, \ldots, n-1. \quad (20)$$

We define the following column vectors and matrices

$$J \equiv [J_i] \equiv \vec{J}_i \qquad i = 1, \ldots, n-1,$$

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

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

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

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

$$F \equiv [F_{ij}] \equiv \left. \frac{\partial \ln f_i}{\partial x_j} \right|_{x_j, T, P} \qquad i, j = 1, \ldots, n-1,$$

$$\nabla \mathbf{x} \equiv [\nabla x_i] \equiv \vec{\nabla} x_i \qquad i = 1, \ldots, n-1,$$

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

$$V \equiv [V_i] \equiv \frac{1}{RT} \left[\sum_{j=1}^{n-1} x_j \bar{V}_j + \frac{M_n x_n}{M_i} \bar{V}_i - \frac{1}{c} \right] \qquad i = 1, \ldots, n-1,$$

to write the expression for diffusion flux in the vector form

$$J = -c \left(D \cdot M \cdot L \cdot W \cdot F \cdot \nabla x + D \cdot K_T \vec{\nabla} T + D \cdot M \cdot L \cdot V \vec{\nabla} P \right). \quad (21)$$

Let

$$D^M = D \cdot M \cdot L \cdot W \cdot F, \quad (22)$$

$$D^T = D \cdot K_T, \quad (23)$$

and

$$D^P = D \cdot M \cdot L \cdot V; \quad (24)$$

then the expression for diffusion flux in a compact vector form is

$$J = -c \left(D^M \cdot \nabla x + D^T \vec{\nabla} T + D^P \vec{\nabla} P \right). \quad (25)$$

On the right side, the first, second, and third terms represent molecular diffusion, thermal diffusion, and pressure diffusion, respectively. The elements D_{il}^M, D_i^T, and D_i^P are given by

$$D_{il}^M = a_{in} D_{in} \frac{M_i x_i}{L_{ii}} \sum_{k=1}^{n-1} L_{ik} \sum_{j=1}^{n-1} \frac{M_j x_j + M_n x_n \delta_{jk}}{M_j} \left. \frac{\partial \ln f_j}{\partial x_l} \right|_{x_1, T, P}, \qquad i, l = 1, \ldots, n-1, \quad (26)$$

$$D_i^T = a_{in} D_{in} M \frac{k_{Ti}}{T}, \qquad i = 1, \ldots, n-1. \quad (27)$$

$$D_i^P = a_{in} D_{in} \frac{M_i x_i}{RT L_{ii}} \sum_{k=1}^{n-1} L_{ik} \left[\sum_{j=1}^{n-1} x_j \bar{V}_j + \frac{M_n x_n}{M_k} \bar{V}_k - \frac{1}{c} \right] \qquad i = 1, \ldots, n-1. \quad (28)$$

The preceding equations reconfirm the well-known fact that the diffusion flux of component i, $i = 1, \ldots, n-1$, in a mixture of n components is a function of the mol fraction gradients of $n-1$ components and of temperature and pressure gradients as well. The molecular diffusion coefficients D_{il}^M, $i, l = 1, \ldots, n-1$ (including D_{ii}^M) are functions of the phenomenological coefficients L_{ik}, $k = 1, \ldots, n-1$ and of the quantities $(\partial \ln f_j / \partial x_l)_{x_1, T, P}$, $l = 1, \ldots, n-1$, as well as the mol fractions. The molecular diffusion coefficient D_{ii}^M cannot be generally assumed to be the binary molecular diffusion coefficient measured in binary mixtures of components i and n. Likewise, the thermal diffusion ratio for component i, k_{Ti}, is not the same in binary and ternary mixtures, even at the same pressure, temperature, and mol fraction of component i.

From Eq. 22 one can deduce the relation between the phenomenological coefficients and the molecular diffusion coefficients, which reads

$$L = (D \cdot M)^{-1} \cdot D^M \cdot (W \cdot F)^{-1}. \quad (29)$$

Using the relation $(A \cdot B)^T = B^T \cdot A^T$ (A^T is the transpose of A) and the fact that L is symmetric (the Onsager reciprocal relations) and that $D \cdot M$ is a diagonal matrix ($(D \cdot M)^T = D \cdot M$; D and M are both diagonal matrices), one obtains the following relationship between D^M and D^{M^T}

$$D^{M^T} = (W \cdot F)^T \cdot D^M \cdot (W \cdot F)^{-1}. \quad (30)$$

Equations 29 and 30 are valid provided $\det(W \cdot F) \neq 0$, which implies that $\det(W) \neq 0$ and $\det(F) \neq 0$ [$\det(W \cdot F) = \det(W) \cdot \det(F)$]. From Eqs. 29 and 30,

$$L \cdot W \cdot F = D^{-1} \cdot M^{-1} \cdot D^M \quad (31)$$

and

$$D^{M^T} \cdot W \cdot F = (W \cdot F)^T \cdot D^M, \quad (32)$$

respectively. One thus obtains the equations relating the phenomenological coefficients to the molecular diffusion coefficients (from Eqs. 17, 18 and 31)

$$\sum_{l=1}^{n-1}\sum_{k=1}^{n-1}\frac{M_k x_k + M_n x_n \delta_{lk}}{M_k}\left.\frac{\partial \ln f_k}{\partial x_j}\right|_{x_j,T,P} L_{li} = \frac{cM_n x_n}{R} D_{ij}^M, \qquad i,j=1,\ldots,n-1, \quad (33)$$

and those relating the diffusion coefficients to each other (from Eq. 32)

$$\sum_{l=1}^{n-1}\sum_{k=1}^{n-1}\frac{M_k x_k + M_n x_n \delta_{lk}}{M_k}\left.\frac{\partial \ln f_k}{\partial x_j}\right|_{x_j,T,P} D_{li}^M = \sum_{l=1}^{n-1}\sum_{k=1}^{n-1}\frac{M_k x_k + M_n x_n \delta_{lk}}{M_k}\left.\frac{\partial \ln f_k}{\partial x_i}\right|_{x_i,T,P} D_{lj}^M, \qquad i,j=1,\ldots,n-1. \quad (34)$$

The $(n-1)^2$ relations appearing in Eq. 34 are not all independent. For $i=j$ the two sides of the equality are identical; therefore, the number of independent relations reduces to $(n-1)^2-(n-1)$. Furthermore, by replacing i with j and j with i in Eq. 34, one obtains the same equations. Thus, the number of independent equations relating the molecular diffusion coefficients reduces to $[(n-1)^2-(n-1)]/2$, and then the number of independent molecular diffusion coefficients reduces to $(n-1)^2-[(n-1)^2-(n-1)]/2 = n(n-1)/2$. Various authors have established the preceding relations among molecular diffusion coefficients.

In a binary mixtures, Eq. 25 reduces to (after substitution $a_{12}=M_1M_2/M^2$, $c=\rho/M$)

$$\vec{J}_1 = -\rho D_{12}\frac{M_1M_2}{M_2}\left[\left.\frac{\partial \ln f_1}{\partial \ln x_1}\right|_{P,T}\vec{\nabla}x_1 + \frac{x_1}{RT}\left(\bar{V}_1 - \frac{M_1}{\rho}\right)\vec{\nabla}P + \frac{k_{T1}}{T}\vec{\nabla}T\right], \quad (35)$$

where ρ is the total mass density. This equation appears in Bird et al. (1960). Now let us consider diffusion flux expression in a ternary mixture.

Diffusion in ternary mixtures

We focus now on a ternary mixture; multicomponent mixtures with more than three components are logical extensions of a ternary mixture, differing primarily in algebraic complexity. Let

$$c_1 = \frac{M_1x_1+M_3x_3}{M_1}f_{12} + x_2 f_{22}, \quad (36)$$

$$c_2 = x_1 f_{12} + \frac{M_2x_2+M_3x_3}{M_2}f_{22}, \quad (37)$$

$$c_3 = \frac{M_1x_1+M_3x_3}{M_1}f_{11} + x_3 f_{21}, \quad (38)$$

$$c_4 = x_1 f_{11} + \frac{M_2x_2+M_3x_3}{M_2}f_{21}, \quad (39)$$

where $f_{ij} \equiv (\partial \ln f_i/\partial x_j)_{x_j,T,P}$. For ternary mixtures, Eqs. 26–28 then read [$L_{ii}>0$; this results from the fact that the entropy production $\sigma \geq 0$; see de Groot and Mazur (1984)]

$$D_{11}^M = a_{13}D_{13}M_1x_1\left(c_3 + c_4\frac{L_{12}}{L_{11}}\right), \quad (40)$$

$$D_{12}^M = a_{13}D_{13}M_1x_1\left(c_1 + c_2\frac{L_{12}}{L_{11}}\right), \quad (41)$$

$$D_{21}^M = a_{23}D_{23}M_2x_2\left(c_4 + c_3\frac{L_{21}}{L_{22}}\right), \quad (42)$$

$$D_{22}^M = a_{23}D_{23}M_2x_2\left(c_2 + c_1\frac{L_{21}}{L_{22}}\right), \quad (43)$$

$$D_1^T = a_{13}D_{13}M\frac{k_{T1}}{T}, \quad (44)$$

$$D_2^T = a_{23}D_{23}M\frac{k_{T2}}{T}, \quad (45)$$

$$D_1^P = a_{13}D_{13}\frac{M_1x_1}{RT}\left[\frac{M_1x_1+M_3x_3}{M_1}\bar{V}_1 + x_2\bar{V}_2 - \frac{1}{c} + \left(\frac{M_2x_2+M_3x_3}{M_2}\bar{V}_2 + x_1\bar{V}_1 - \frac{1}{c}\right)\frac{L_{12}}{L_{11}}\right], \quad (46)$$

$$D_2^P = a_{23}D_{23}\frac{M_2x_2}{RT}\left[\frac{M_2x_2+M_3x_3}{M_2}\bar{V}_2 + x_1\bar{V}_1 - \frac{1}{c} + \left(\frac{M_1x_1+M_3x_3}{M_1}\bar{V}_1 + x_2\bar{V}_2 - \frac{1}{c}\right)\frac{L_{21}}{L_{22}}\right]. \quad (47)$$

Equations 33 and 34 imply

$$\left(\frac{M_1x_1+M_3x_3}{M_1}f_{1j} + x_2 f_{2j}\right)L_{1i} + \left(x_1 f_{1j} + \frac{M_2x_2+M_3x_3}{M_2}f_{2j}\right) \times L_{2i} = \frac{cM_nx_n}{R}D_{ij}, \quad i,j=1,2, \quad (48)$$

and

$$\left(\frac{M_1x_1+M_3x_3}{M_1}f_{1j} + x_2 f_{2j}\right)D_{1i}^M + \left(x_1 f_{1j} + \frac{M_2x_2+M_3x_3}{M_2}f_{2j}\right) \times D_{2i}^M = \left(\frac{M_1x_1+M_3x_3}{M_1}f_{1j} + x_2 f_{2i}\right)D_{1j}^M + \left(x_1 f_{1i} + \frac{M_2x_2+M_3x_3}{M_2}f_{2i}\right)D_{2j}^M, \qquad i,j=1,2, \quad (49)$$

respectively. From Eq. 48,

$$c_3L_{11} + c_4L_{21} = \frac{cM_3x_3}{R}D_{11}^M, \quad (50)$$

$$c_1L_{11} + c_2L_{21} = \frac{cM_3x_3}{R}D_{12}^M, \quad (51)$$

$$c_3 L_{12} + c_4 L_{22} = \frac{cM_3 x_3}{R} D^M_{21}, \tag{52}$$

$$c_1 L_{12} + c_2 L_{22} = \frac{cM_3 x_3}{R} D^M_{22}. \tag{53}$$

Provided that det $(W) \neq 0$ and det $(F) \neq 0$, one obtains

$$L_{11} = \frac{cM_3 x_3}{R(c_2 c_3 - c_1 c_4)} \left(c_2 D^M_{11} - c_4 D^M_{12} \right), \tag{54}$$

$$L_{21} = \frac{-\,cM_3 x_3}{R(c_2 c_3 - c_1 c_4)} \left(c_1 D^M_{11} - c_3 D^M_{12} \right), \tag{55}$$

$$L_{12} = \frac{cM_3 x_3}{R(c_2 c_3 - c_1 c_4)} \left(c_2 D^M_{21} - c_4 D^M_{22} \right), \tag{56}$$

$$L_{22} = \frac{-\,cM_3 x_3}{R(c_2 c_3 - c_1 c_4)} \left(c_1 D^M_{21} - c_3 D^M_{22} \right), \tag{57}$$

$[c_2 c_3 - c_1 c_4 = \det(W) \det(F)]$. For $i = j$ the two members of Eq. 49 are identical. Furthermore, by replacing i by j and j by i in Eq. 49, one obtains two identical equations. Equation 49 thus reads

$$c_1 D^M_{11} + c_2 D^M_{21} = c_3 D^M_{12} + c_4 D^M_{22}. \tag{58}$$

Similar relations between the molecular diffusion coefficients have been reported by de Groot and Mazur (1984) and Haase (1990). Equations 55, 56 and 58 are not independent. By combining Eqs. 55 and 58, one obtains Eq. 56 (that is, $L_{12} = L_{21}$).

Critical Point

Some hydrocarbon reservoirs contain near-critical fluid mixtures. Therefore, multicomponent diffusion and species spatial distribution at the critical point are of special interest. Let us start by presenting the problem in the general case of n components. Then, we discuss in more detail the case of binary mixtures. At the critical point det $(F) = 0$ (Firoozabadi, 1999; Taylor and Krishna, 1993), which implies

$$\det(D^M) = 0. \tag{59}$$

Equation 59 provides the well-known result that at the critical point of a binary mixture, the molecular diffusion coefficient D^M_{11} vanishes, and in a multicomponent mixture, the diffusion coefficient determinant vanishes at the critical point. From Eq. 59

$$\operatorname{rank}(D^M) \leq n-2. \tag{60}$$

Let us discuss the case of equality in Eq. 60 (the same reasoning applies in the general case): at isothermal and isobaric conditions, one has only $n-2$ independent diffusion fluxes: $\vec{J}_i$, $i = 1, \ldots, n-2$; $\vec{J}_{n-1}$ and $\vec{J}_n$ are linear combinations of the $n-2$ remaining independent diffusion fluxes. This implies that there exist constants $\alpha_1, \ldots, \alpha_{n-2}$ such that

$$D^M_{(n-1)i} = \sum_{j=1}^{n-2} \alpha_j D^M_{ji}, \qquad i = 1, \ldots, n-1. \tag{61}$$

Therefore, at isothermal and isobaric conditions

$$\begin{aligned} \vec{J}_{n-1} &= \sum_{i=1}^{n-1} D^M_{(n-1)i} \vec{\nabla} x_i \\ &= \sum_{i=1}^{n-1} \sum_{j=1}^{n-2} \alpha_j D^M_{ji} \vec{\nabla} x_i \\ &= \sum_{j=1}^{n-2} \alpha_j \vec{J}_j. \end{aligned} \tag{62}$$

Let $D_i = (D^M_{i1}, \ldots, D^M_{i(n-2)})$, $i = 1, \ldots, n-2$, and $A = (\alpha_1, \ldots, \alpha_{n-2})$. Equation 61 reads

$$D^M_{(n-1)i} = A \cdot D_i \qquad i = 1, \ldots, n-1. \tag{63}$$

Let $D_{n-\mathbf{1}} = (D^M_{(n-1)1}, \ldots, D^M_{(n-1)(n-2)})$, and $D^M_{\mathbf{1}} = [D^M_{ij}]$, $i, j = 1, \ldots, n-2$, then det $(D^M_{\mathbf{1}}) \neq 0$ since rank $(D^M_{\mathbf{1}}) = n-2$. One thus obtains

$$A = \left(D^M_{\mathbf{1}} \right)^{-1} \cdot D_{n-\mathbf{1}}, \tag{64}$$

which allows the determination of A knowing the molecular diffusion coefficients. For $i = n-1$, Eq. 63 reads

$$D^M_{(n-1)(n-1)} = A \cdot D_{n-1} \tag{65}$$

Equations 64 and 65 imply that

$$D^M_{(n-1)(n-1)} = \left[\left(D^M_{\mathbf{1}} \right)^{-1} \cdot D_{n-\mathbf{1}} \right] \cdot D_{n-\mathbf{1}} \tag{66}$$

at the critical point; in addition to the results from the reciprocal relations in Eq. 34, there exists one more relationship between the diffusion coefficients. This means that for a ternary mixture, for example, two molecular diffusion coefficients, say the mutual diffusion coefficients, describe molecular diffusion flux. For ternary mixtures, $(D^M_{21} D^M_{22} - D^M_{12} D^M_{21})$ vanishes at the critical point. Experimental support can be drawn from the work of Vitagliano et al. (1978) for water–chloroform–acetic acid ternary mixture. Analysis of diffusion in ternary mixtures at the critical point has been made by Taylor and Krishna (1993). The authors show that the criticality condition establishes a relation between the molecular diffusion coefficients. The combination of the criticality and the Onsager reciprocal relation implies that, for a ternary mixture at the critical point, only two diffusion coefficients are independent.

If we consider a multicomponent mixture at isothermal conditions and neglect the pressure gradient, at the steady state one obtains $D^M \cdot \nabla x = \mathbf{0}$, which implies $\boldsymbol{\nabla} \boldsymbol{x} = \mathbf{0}$ unless det $(D^M) = 0$. This means that at isothermal and isobaric conditions at the critical point, the steady state may be reached with compositional gradients in the system. However, away from the critical point the mixture is, in principle, homogeneous. At isothermal and nonisobaric conditions at steady state, Eq. 25 reduces to

$$D^M \cdot \nabla x + D^P \vec{\nabla} P = 0. \tag{67}$$

The solution of this equation can be written as

$$\vec{\nabla} x_i = -\vec{\nabla} P \frac{\det(B_i)}{\det(D^M)}, \tag{68}$$

where B_i, $i = 1, \ldots, n-1$ is the matrix D^M with column i replaced by column vector D^P. $D^P \vec{\nabla} P$ is, in principle, different from zero at the critical point; so is $\det(B_i)$. From Eqs. 59 and 68, one may deduce that ∇x reaches infinity at the critical point. The mol fraction plot vs. the vertical coordinate for each component has an inflection point at critical conditions. The same reasoning applies when $\vec{\nabla} P$ and $\vec{\nabla} T$ are both different from zero. This is discussed in more detail for binary mixtures in the following subsection.

Binary mixtures

At the critical point of a binary mixture $(\partial \ln f_1 / \partial \ln x_1)_{T,P} = 0$. The coefficient D_{12} has generally a finite value at the critical point (Myerson and Senol, 1984). The molecular diffusion coefficient $D_{11}^M = a_{12} D_{12} \, (\partial \ln f_1 / \partial \ln x_1)_{T,P}$ thus vanishes at the critical point, which has been established by various authors; it decreases asymptotically when one approaches the critical state (see, for example, Haase, 1990; Taylor and Krishna, 1993; Ackerson and Hanley, 1980; Kiselev and Kulikov, 1994; Luettmer-Strathmann and Sengers, 1996; Cheng et al., 1997; Sakonidou et al., 1998). With regard to the thermal diffusion coefficient, it is well established, using the mode–mode coupling theory that this coefficient has a finite value at the critical point (Mistura, 1972, 1975; Anisimov et al., 1995). In the following, we discuss the behavior of diffusion in a binary mixture at the critical point for (1) isothermal and nonisobaric, and (2) nonisothermal and isobaric conditions.

For a binary mixture at isothermal and isobaric conditions, Eq. 35 at the steady state reduces to

$$\left. \frac{\partial \ln f_1}{\partial \ln x_1} \right|_{P,T} \vec{\nabla} x_1 = 0, \tag{69}$$

which is valid for any value of the composition gradient $\vec{\nabla} x_1$.

Let us now consider a binary mixture at isothermal and nonisobaric conditions. It should be mentioned that the contribution of the pressure gradient in the diffusion flux has often been neglected in the studies treating diffusion in multicomponent systems. At steady state, Eq. 35 reduces to

$$\left. \frac{\partial \ln f_1}{\partial \ln x_1} \right|_{P,T} \vec{\nabla} x_1 + \frac{x_1}{RT} \left(\bar{V}_1 - \frac{M_1}{\rho} \right) \vec{\nabla} P = 0. \tag{70}$$

Since $\vec{\nabla} P \neq 0$ (say from gravity), and since $(\bar{V}_1 - M_1/\rho)$ has generally a finite value different from zero, $(\partial \ln f_1 / \partial \ln x_1)_{T,P} \vec{\nabla} x_1$ must have a finite value. The fact that $(\partial \ln f_1 / \partial \ln x_1)_{T,P}$ vanishes at the critical point, implies that $\vec{\nabla} x_1$ should be infinity at this point. Figure 1 sketches the compositional variation in the critical region in a one-dimensional vertical medium with a critical point at height z^0. Although $(\partial \ln f_1 / \partial \ln x_1)_{T,P} \to 0$ and $\vec{\nabla} x_1 \to \infty$ when one approaches the critical point, their product has a finite value.

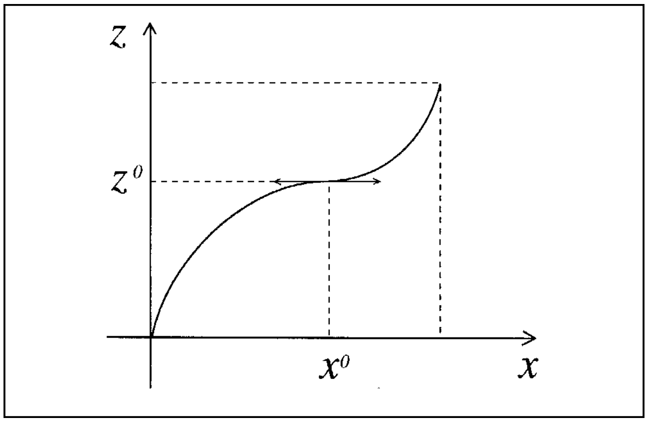

Figure 1. Composition/height plot for a binary mixture in an isothermal nonisobaric process in the critical region.

The same reasoning can be applied at nonisothermal and isobaric conditions. In that case, at the steady state Eq. 35 reduces to

$$\left. \frac{\partial \ln f_1}{\partial \ln x_1} \right|_{P,T} \vec{\nabla} x_1 + \frac{k_{T1}}{T} \vec{\nabla} T = 0. \tag{71}$$

The product $(\partial \ln f_1 / \partial \ln x_1)_{T,P} \nabla x_1$ can be finite and nonzero at the critical point where $(\partial \ln f_1 / \partial \ln x_1)_{T,P} = 0$; this may occur when $\vec{\nabla} x_1 \to \infty$. Therefore, at the critical point for a finite temperature gradient, k_{T1} may also have a finite value. Note that our analysis is provided based on very simple terms. Next, we discuss in more detail the finiteness of the thermal diffusion ratio k_{T1} in view of some results presented in the literature (Hohenberg and Halperin, 1977; Sengers and Levelt Sengers, 1986; Anisimov and Kiselev, 1992; Kiselev and Kulikov, 1994; Luettmer-Strathmann and Sengers, 1994, 1996; Anisimov et al., 1995; Kiselev, 1997; Cheng et al., 1997; Sakonidou et al., 1998; Kiselev and Huber, 1998; Giterman and Gorodetskii, 1970; Mistura, 1972, 1975; Haase et al., 1994, 1971; Rutherford and Roof, 1959).

Away from the critical point, the transport properties of a mixture vary generally slowly with temperature and composition. However, when the critical point is approached, some transport properties exhibit singular behavior. The diffusion flux for a binary mixture can be written as

$$\vec{J}_1 = \alpha \vec{\nabla} \mu - \beta \vec{\nabla} T, \tag{72}$$

where $\mu = \mu_1/M_1 - \mu_2/M_2$. Equation 72 can be readily obtained from Eq. 9 (for $n = 2$) by replacing L_{11} and L'_{1q} by $-T\alpha$ and $T^2 \, (\beta - \alpha(\partial \mu / \partial T)_{x_1,P})$, respectively. In the critical region, coefficients α and β can be separated into background values and critical enhancements (Mistura, 1972, 1975)

$$\alpha = \alpha_b + \delta\alpha = \alpha_b + \frac{k_B T \rho}{6\pi \tilde{\eta} \xi} \left(\frac{\partial x_1}{\partial \mu} \right)_{P,T}, \tag{73}$$

$$\beta = \beta_b + \delta\beta = \beta_b + \frac{k_B T \rho}{6\pi \tilde{\eta} \xi} \left(\frac{\partial x_1}{\partial T} \right)_{P,\mu}, \tag{74}$$

where k_B, ξ, and $\tilde{\eta}$ are the Boltzmann constant, the correlation length divergent at the critical point (Anisimov et al., 1995), and the shear viscosity, respectively. The subscript b denotes the part of the transport coefficient that is not affected by criticality (the so-called background value); $\delta\alpha$ and $\delta\beta$ are the critical enhancements of α and β, respectively. Away from the critical point, the transport coefficients are described by their background values. The behavior of the transport properties in the region close to the critical point has been investigated by extending the concept of the critical point universality (Anisimov et al., 1995) to binary mixtures (generalized isomorphism approach) (Hohenberg and Halperin, 1977; Anisimov and Kiselev, 1992; Kiselev and Kulikov, 1994; Anisimov et al., 1995; Kiselev, 1997; Cheng et al., 1997). In the intermediate region where the transport properties cannot be described either by their background values or by the generalized isomorphism approach, the transport properties are investigated using a crossover approach (Sengers and Levelt Sengers, 1986; Kiselev and Kulikov, 1994; Luettmer-Strathmann and Sengers, 1994, 1996; Sakonidou et al., 1998). Mode–mode coupling calculations have been performed by Giterman and Gorodetskii (1970) and Mistura (1972, 1975) to investigate the transport properties in the critical region (see the summary in Anisimov et al., 1995). From Eqs. 72, 73 and 74 one obtains

$$\delta\beta = -\left(\frac{\partial\mu}{\partial T}\right)_{P,\mu}\delta\alpha. \tag{75}$$

It is shown (Anisimov et al., 1995; Giterman and Gorodetskii, 1970; Mistura, 1972, 1975) that α and β diverge at the critical point. Furthermore, those coefficients have the same power law when approaching the critical point (Anisimov et al., 1995). Coefficients α and β are not directly measurable. To relate those coefficients to some experimentally accessible properties (the diffusion coefficients), the diffusion flux $\vec{J}_1$ has been expressed in terms of the diffusion coefficients as (Anisimov et al., 1995; Mistura, 1975)

$$\vec{J}_1 = -\rho D_{11}^M\left(\vec{\nabla}x_1 + k_{T1}^*\frac{\vec{\nabla}T}{T}\right), \tag{76}$$

where D_{11}^M is the molecular diffusion coefficient and k_{T1}^* is the thermal diffusion ratio (as defined by some authors: Luettmer-Strathmann and Sengers, 1996; Sakonidou et al., 1998); $D_1^T = D_{11}^M k_{T1}^*$ is the thermal diffusion coefficient. α, β, D_{11}^M, and k_{T1}^* are related by

$$D_{11}^M = \frac{\alpha}{\rho}\left(\frac{\partial\mu}{\partial x_1}\right)_{P,T}, \tag{77}$$

$$k_{T1}^* D_{11}^M = \frac{T}{\rho}\left[\alpha\left(\frac{\partial\mu}{\partial T}\right)_{P,x_1} + \beta\right]. \tag{78}$$

We emphasize that Eq. 76 cannot be extended to multicomponent nonideal mixtures.

Equations 73 and 77 imply that the diffusion coefficient D_{11}^M vanishes at the critical point as ξ^{-1}. The thermal diffusion coefficient, D_1^T, however, has a finite value at the critical point, since the critical enhancements compensate each other according to Eq. 78; the coefficient $k_{T1}^* = D_1^T/D_{11}^M$ therefore diverges as ξ toward the critical point. This has been supported by experimental data by Haase et al. (1994).

From experimental data, Haase et al. (1994) claim that the thermal diffusion factor α_T and the related quantities approach infinity in the critical state for binary mixtures. However, the expression these authors use for the diffusion mass flux is not appropriate for nonideal systems. At steady state, by representing the spatial variations of temperature and mol fraction by ΔT and Δx_1, respectively, Haase et al., provide the following relation, from which they calculate the thermal diffusion factor using the experimental data

$$\Delta x_1 = \alpha_T x_1(1-x_1)\frac{\Delta T}{T}. \tag{79}$$

This expression ignores the thermodynamic factor $(\partial \ln f_1/\partial \ln x_1)_{T,P}$, which approaches zero when one approaches the critical state. Thus, the coefficient α_T used by Haase et al. (1994) is in reality the thermal diffusion factor divided by the thermodynamic factor.

In their investigation of the crossover behavior of the transport properties in the critical region, Luettmer-Strathmann and Sengers (1996) and Sakonidou et al. (1998) used Eq. 76 to express the diffusion flux. Equation 76 also can be written in the following form:

$$\vec{J}_1 = -\rho a_{12} D_{12}\left(\left.\frac{\partial \ln f_1}{\partial \ln x_1}\right|_{P,T}\vec{\nabla}x_1 + \left.\frac{\partial \ln f_1}{\partial \ln x_1}\right|_{P,T} k_{T1}^*\frac{\vec{\nabla}T}{T}\right). \tag{80}$$

From comparison of Eq. 80 and Eq. 35 (for the isobaric condition), one deduces that the appropriate expression for the thermal diffusion ratio is $k_{T1} = (\partial \ln f_1/\partial \ln x_1)_{T,P} k_{T1}^*$. Luettmer-Strathmann and Sengers (1996) and Sakonidou et al. (1998) used the mode–mode coupling analysis to calculate the molecular diffusion and the thermal diffusion coefficient by fitting the crossover equation of the thermal conductivity to thermal conductivity data in the vicinity of the critical point. These authors concluded that $D_{11}^M k_{T1}^*$ reaches a finite value at the critical point (Luettmer-Strathmann and Sengers, 1996; Sakonidou et al., 1998). Since D_{12} generally has finite value at the critical point, the thermal diffusion ratio, k_{T1} should also have a finite value. Luettmer-Strathmann and Sengers (1996) conclude that D_{11}^M vanishes at the critical point and that k_{T1}^*, on the other hand, diverges at the critical point. This conclusion is in agreement with our simple analysis of Eq. 71.

One could summarize then that at the critical point (1) the thermal diffusion ratio reaches a finite value, and (2) the mol fraction gradient reaches infinity with either temperature or pressure gradient or both; that is, the mol fraction has an inflexion point when plotted vs. depth.

Concluding Remarks

A general formalism is provided to describe multicomponent molecular, pressure, and the thermal diffusion flux for nonideal mixtures. The treatment is within the framework of thermodynamics of irreversible processes. The formalism has allowed us to evaluate thermal diffusion factors for ternary and higher mixtures that have not been attempted in the past (Firoozabadi et al., 1999). The general expression also allows the determination of various diffusion processes at the critical point. One main conclusion of this study is that molecular diffusion is finite at the critical point for nonisothermal and for isothermal, nonisobaric conditions.

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