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KINETIC THEORY OF DIFFUSION IN LIQUID AND GAS MIXTURES

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Expressions for evaluating diffusion coefficients in real multicomponent solutions are obtained on the basis of the kinetic theory of dense gases and liquids.

For multicomponent mixtures, molecular mass transport is determined from [1] $\mathbf{j} = -\mathbf{D} \cdot \text{grad}\, \mathbf{y}$, where $\mathbf{D}$ is the diffusion coefficient matrix of multicomponent systems.

Since most mass-exchange processes of separation, mixing, and chemical transformation occur, as a rule, in multicomponent systems, to calculate these processes information is needed on the diffusion coefficient matrix, providing the total pattern of mass transport. There are quantitative and qualitative distinctions between multicomponent and binary diffusion [2, 3]. However, due to the absence of information on $\mathbf{D}$ the available methods of evaluating processes in multicomponent systems operate only with a single coefficient of binary diffusion. This situation restricts the development of mass transfer theory in multicomponent systems and the creation of justified methods of a computational structure.

It must also be noted that experimental data on diffusion coefficients in a wide interval of concentrations and temperatures, necessary for the calculations, are absent even for binary mixtures. Theoretical methods of calculating transport coefficients in liquid mixtures are far from complete. Thus, the more recently developed kinetic theory of multicomponent dense gases and liquids for rigid sphere models [4] with the use of a radial distribution function [3] generally renders the basic transport characteristics in ideal mixtures. For this reason, this theory does not fully include the complexity of molecular interactions, and the agreement between calculated and experimental values of diffusion coefficients in nonideal systems is very poor. Therefore, further development of the kinetic theory must occur in the direction of a refined intermolecular interaction in real solutions.

One of the methods of taking into account the real molecular interaction in liquid mixtures, more precisely the presence of many-particle interactions and real shapes of intermolecular forces, as well as capabilities of formation of associated complexes, is their account in describing collision terms of the kinetic equations, which is still an unresolved problem. Another method, recently developed, consists of using in the solution of the kinetic

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equations reliable information on equilibrium properties of solutions, which automatically include all characteristic features of liquid mixtures.

In the present study the nonideal behavior of the system is accounted for by using in the transformed kinetic equations equations of state of real mixtures, in which appear activation coefficients, being a quantitative measure of the deviation of properties of real solutions from ideal ones [5].

Unlike thermal conductivity and viscosity, diffusion is observed in systems which can exchange a number of particles in an arbitrary fashion. The properties of these systems are described by using independent variables: the volume V, the temperature T, and the chemical potential μ_i. And then, establishing a connection between statistical mechanics and thermodynamics, we obtain an equation of state of equilibrium systems of the form [6]

$$Vdp - SdT - \sum_i N_i \, d\mu_i = 0 \tag{1}$$

or

$$Vdp - SdT - \sum_i kT \, (x_i \, d \ln x_i + x_i d \ln \gamma_i) = 0. \tag{2}$$

In expression (2) the first three terms determine the connection between thermodynamic quantities in ideal media, and the latter provides the energy increment due to nonideality. It must be noted that if in (2) one takes $\gamma_i = 1$, then an expression is obtained similar to that used in the transformed kinetic equations [4, 7].

To describe transport effects in multicomponent systems we use the modified Enskog equation [4]

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \frac{\partial f_i}{\partial \mathbf{r}} + \mathbf{X}_i \frac{\partial f_i}{\partial \mathbf{v}_i} = \sum_j \iint [g_{ij}(\mathbf{r} + 1/2\,\sigma_{ij}\mathbf{k}, \sigma_{ij}) f_i'(\mathbf{r}) \, f_j'(\mathbf{r} + \sigma_{ij}\mathbf{k}) -$$

$$- g_{ij}(\mathbf{r} - 1/2\,\sigma_{ij}\,\mathbf{k}, \ \sigma_{ij}) \, f_i(\mathbf{r}) \, f_j(\mathbf{r} - \sigma_{ij}\mathbf{k})] \sigma_{ij}^2 (\mathbf{w}_{ji} \cdot \mathbf{k}) \, dk d\mathbf{v}_j \quad i, j = 1, 2, \ldots, \nu. \tag{3}$$

The solution of Eq. (3) is carried out in the same manner as in [4, 7].

The time derivatives are eliminated as usual [4, 7], while for fixed gradients and established relations between them we use, unlike the available solutions, the equation of state (2), which prior to that is regrouped with separation of the terms $\frac{1}{n_i}\frac{\partial n_i}{\partial \mathbf{r}}$ and $\frac{1}{x_i}\frac{\partial x_i}{\partial \mathbf{r}}$ [5]. Keeping in mind that since the transformed kinetic equations lead to using the equation of state of a real mixture, in the collision parts of these equations we neglect all terms besides the first, since they provide corrections to the equation of state of an ideal gas, and take into account momentum and energy transport during molecular collisions [7]. Solving (3), then, we obtain kinetic equations for the case of mass transport, which for $dp=0$, $dT=0$, $\mathbf{X}_i = 0$ have the following form:

$$\frac{n}{n_i} \mathbf{d}_i \cdot \mathbf{C}_i = \sum_j \iint f_i^0 \, f_j^0 \, (\Phi_i' + \Phi_j' - \Phi_i - \Phi_j) \sigma_{ij}^2 \, g_{ij}(\sigma_{ij}) \, (\mathbf{w}_{ji} \cdot \mathbf{k}) \, d\mathbf{k} d\mathbf{v}_j \, ; \tag{4}$$

where

$$\mathbf{d}_i = \sum_j n^{-1} \left[\delta_{ij} + \frac{x_i}{\gamma_i} \frac{\partial \gamma_i}{\partial x_j} (1 - \delta_{ij}) \right] \frac{\partial n_j}{\partial \mathbf{r}} \, . \tag{5}$$

Similar expressions for $\mathbf{d}_i$ are obtained in thermodynamics of irreversible processes [1, 7].

We seek a solution of Eq. (4) in the form

$$\Phi_i = n \sum_h \mathbf{C}_i^h \cdot \mathbf{d}_h,$$

with the calculation being performed as in [7]. As a result we obtain expressions for the determination of the expansion coefficients of the function $\mathbf{C}_j^h$:

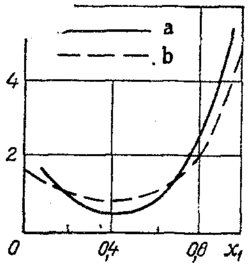

Fig. 1

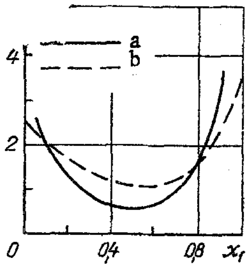

Fig. 2

Fig. 1. Diffusion coefficients $\mathscr{D}_{12}\cdot 10^9$ (m^2/sec) of the acetone–water system as a function of the acetone concentration in the mixture x_1 (molecular weight) at T = 298°K: a) calculated, b) experimental values [11].

Fig. 2. Diffusion coefficients $\mathscr{D}_{12}\cdot 10^9$ (m^2/sec) of the benzene–methanol system as a function of the benzene concentration in the mixture x_1 (molecular weight) at T = 298°K: a) calculated; b) experimental values [10].

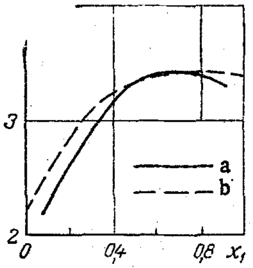

Fig. 3. Diffusion coefficients $\mathscr{D}_{12}\cdot 10^9$ (m^2/sec) of the acetone–chloroform system as a function of the acetone concentration in the mixture x_1 (molecular weight) at T = 298°K: a) calculated; b) experimental values [11].

$$\sum_{j\neq q} F_{ij}\, n_i \left(\frac{m_j\, kT}{2}\right)^{1/2} (C_{j0}^{h} - C_{j0}^{k}) = \delta_{ik} - \delta_{ih} \quad i,\ h = 1,\ 2,\ \ldots,\ \nu, \tag{6}$$

where

$$F_{ij} = \sum_{l} \frac{n_i n_l g_{il} \delta_{ij}}{n n_j \mathscr{D}_{il}^{*}} (m_j \quad m_i)^{-1/2} + \frac{n_i g_{ij}}{n m_j \mathscr{D}_{ij}^{*}} + \sum_{l} \frac{n_i n_l g_{il}}{n n_q \mathscr{D}_{il}^{*}} (m_q \quad m_l)^{-1/2} \left[\left(\frac{m_l}{m_q}\right)^{1/2} (\delta_{iq} - \delta_{lq})\right], \tag{7}$$

$$\mathscr{D}_{il}^{*} = \frac{3}{16} \frac{m_i + m_l}{m_i\, m_l} \frac{kT}{n\Omega_{il}^{(1,1)}}. \tag{8}$$

The diffusion rate is determined as usual [4, 7]. Eliminating the gradient dependence, and using an expansion of the function C_j^h in Sonin–Laguerre polynomials [4, 7], we obtain

$$\overline{\mathbf{C}}_j = -\left(\frac{kT}{2m_j}\right)^{1/2} \left[\sum_{h\neq k} (C_{j0}^{h} - C_{j0}^{k})\, n\, \mathbf{d}_h\right].$$

Using (5) and Eq. (2) for the elimination of the gradient dependence, we have

$$\overline{\mathbf{C}}_j = -\left(\frac{kT}{2m_j}\right)^{1/2} \sum_{l\neq m} \left\{\sum_{h\neq k} (C_{j0}^{h} - C_{j0}^{k}) \left[\left(\delta_{hl} + \frac{x_h}{\gamma_h} \frac{\partial \gamma_h}{\partial x_l} (1 - \delta_{hl})\right) - \right.\right.$$

$$-\frac{\sum\limits_i\left(\delta_{il}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_l}(1-\delta_{il})\right)}{\sum\limits_i\left(\delta_{im}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_m}(1-\delta_{im})\right)}\left(\delta_{hm}+\frac{x_h}{\gamma_h}\frac{\partial\gamma_h}{\partial x_m}(1-\delta_{hm})\right)\Bigr]\Bigr]\Bigr\}\frac{\partial n_l}{\partial \mathbf{r}}. \tag{9}$$

Comparing (9) with

$$\mathbf{j}_j = m_j n_j \overline{\mathbf{C}}_j = -\sum_{l\neq m} D^0_{jl} m_l \frac{\partial n_l}{\partial \mathbf{r}},$$

we obtain expressions for the multicomponent diffusion coefficients

$$D^0_{jl}=\left(\frac{m_j n_j}{m_l}\right)\left(\frac{kT}{2m_j}\right)^{1/2}\sum_{h\neq k}(C^h_{j0}-C^k_{j0})\Biggl[\left(\delta_{hl}+\frac{x_h}{\gamma_h}\frac{\partial\gamma_h}{\partial x_l}(1-\delta_{hl})\right)-$$
$$-\frac{\sum\limits_i\left(\delta_{il}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_l}(1-\delta_{il})\right)}{\sum\limits_i\left(\delta_{im}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_m}(1-\delta_{im})\right)}\left(\delta_{hm}+\frac{x_h}{\gamma_h}\frac{\partial\gamma_h}{\partial x_m}(1-\delta_{hm})\right)\Biggr]. \tag{10}$$

In (10) $(C^h_{j0}-C^k_{j0})$ are determined from Eq. (6).

In writing down Eqs. (6), (7), and (10) the choice of m and q is arbitrary: if $\nu > 2$, it is convenient to take $m = q = \nu$, if $\nu = 2$, then $q = i$.

Multiplying (6) by the expression in the square brackets of (10) and summing over $h \neq k$, with account of (10) we have

$$\sum_{j\neq q}F_{ij}m_l D^0_{jl}=\left(\delta_{im}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_m}(1-\delta_{im})\right)\frac{1+\sum\limits_{k\neq l}\frac{x_k}{\gamma_k}\frac{\partial\gamma_k}{\partial x_l}}{1+\sum\limits_{k\neq m}\frac{x_k}{\gamma_k}\frac{\partial\gamma_k}{\partial x_m}}-\left(\delta_{il}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_l}(1-\delta_{il})\right). \tag{11}$$

It follows from (11) that $\sum\limits_i F_{ij}=0$, and

$$\sum_i\left[\left(\delta_{im}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_m}(1-\delta_{im})\right)\frac{1+\sum\limits_{k\neq l}\frac{x_k}{\gamma_k}\frac{\partial\gamma_k}{\partial x_l}}{1+\sum\limits_{k\neq m}\frac{x_k}{\gamma_k}\frac{\partial\gamma_k}{\partial x_m}}-\left(\delta_{il}+\frac{x_i}{\gamma_i}\frac{\partial\gamma_i}{\partial x_i}(1-\delta_{il})\right)\right]=0.$$

Thus, to calculate the diffusion coefficients it is necessary to be able to calculate the radial distribution function g_{ij} and the derivatives of the activation coefficients with respect to composition $\frac{1}{\gamma_k}\frac{\partial\gamma_k}{\partial x_m}$.

The calculation of g_{ij} was performed by equations available in the literature, and obtained on the basis of equations of state for the rigid sphere model, which gives most accurate results for reduced densities $\zeta \leqslant 0.52$ [3]. It must be noted here that the radial distribution function is not very sensitive to the choice of the molecular interaction potential [8].

The derivatives of the activation coefficients with respect to composition $\frac{1}{\gamma_k}\frac{\partial\gamma_k}{\partial x_m}$ are calculated by the Wilson equation [9], which gives a fair approximation to experimental data on equilibrium between the liquid and the vapor in binary and even in three-component mixtures. According to this equation we have

$$\frac{1}{\gamma_k}\frac{\partial\gamma_k}{\partial x_m}=\frac{\left[\left(\sum\limits_j 2x_j\Lambda_{kj}\right)-x_k\right]-\left[\left(\sum\limits_j x_j\Lambda_{kj}\right)-x_k\right]\Lambda_{km}}{\left(\sum\limits_j x_j\Lambda_{kj}\right)^2}+$$

TABLE 1. Diffusion Coefficients in Three-Component Liquid Mixtures ($D_{ij}\cdot 10^9$ m^2/sec) at T = 298°K

x_1	x_2	D_{11}^c	D_{11}^e	D_{12}^c	D_{12}^e	D_{21}^c	D_{21}^e	D_{22}^c	D_{22}^e
Acetone (1)–Benzene (2)–Methanol (3)									
0,766	0,114	4,6	4,4	−0,9	0,9	−0,6	−0,83	3,2	2,7
0,15	0,30	3,4	3,0	−0,25	0,15	−1,0	−0,3	1,6	2,2
0,1	0,80	3,3	3,5	0,5	1,2	−1,5	−1,4	0,8	1,1
0,4	0,5	4,3	4,4	0,7	1,8	−1,2	−0,8	2,1	1,7
0,35	0,3	3,6	3,8	−0,3	0,4	−1,1	−0,6	1,6	2,1
Acetone (1)–Benzene (2)–Carbon tetrachloride (3)									
0,3	0,35	1,9	1,9	−0,2	−0,24	−0,06	−0,047	2,1	2,2
			1,88		−0,213		−0,037		2,25
0,15	0,15	1,4	1,6	−0,07	−0,06	−0,06	−0,08	1,5	1,7

$$+\frac{x_i\Lambda_{ik}(\Lambda_{im}-\Lambda_{ik})}{\left(\sum_j x_j\Lambda_{ij}\right)^2}+\frac{[(x_k+x_m)\Lambda_{mk}+x_i\Lambda_{mi}]\Lambda_{mk}}{\left(\sum_j x_j\Lambda_{mj}\right)^2},$$

$$i\neq k,\ m;\ k\neq m;\ k,\ m,\ j=1,\ 2,\ 3.$$

The parameters Λ_{kj} are given in the literature; besides, they can be calculated easily.

The diffusion coefficients in liquid mixtures were measured in a mean-bulk reference system. Therefore the values of the diffusion coefficients, calculated from Eq. (10) and written in the center of mass system, must be recalculated (in coefficients obtained in the mean-bulk reference system) [1]:

$$D_{ij}=D_{ij}^0-\rho_i\left[\sum_{k=1}^{\nu-1}D_{kj}^0\,(v_k-v_\nu)\right].$$

The diffusion coefficients of a number of ideal and nonideal binary and multicomponent liquid mixtures were calculated by the given method. According to (10) the expression for the diffusion coefficient in binary liquid and gas mixtures in the center-of-mass system is

$$\mathscr{D}_{12}^0=\frac{n\mathscr{D}_{12}^*}{g_{12}}\left[\frac{\left(1+\frac{x_1}{\gamma_1}\frac{\partial\gamma_1}{\partial x_2}\right)-\left(\frac{x_1}{\gamma_1}\frac{\partial\gamma_1}{\partial x_2}\right)\left(1+\frac{x_2}{\gamma_2}\frac{\partial\gamma_2}{\partial x_1}\right)}{n_1\left(1+\frac{x_2}{\gamma_2}\frac{\partial\gamma_2}{\partial x_1}\right)+n_2\left(1+\frac{x_1}{\gamma_1}\frac{\partial\gamma_1}{\partial x_2}\right)}\right],$$

where $\mathscr{D}_{12}^*$ is the diffusion coefficient of a binary mixture, calculated by Eq. (8), and $\mathscr{D}_{12}^*/g_{12}$ corresponds to the diffusion coefficient obtained by Thorne for a binary dense mixture [4].

The diffusion coefficients were calculated for the binary ideal mixture benzene–carbon tetrachloride and for the nonideal solutions acetone–water, acetone–methanol, acetone–chloroform, benzene–methanol, acetone–carbon tetrachloride, acetone–benzene, and ethanol–water. For all mixtures the integrals $\Omega_{ie}^{1,1}$ were calculated for the rigid sphere model.

The results of the calculations are shown in Figs. 1-3. Also provided are the experimental values of the diffusion coefficients $\mathscr{D}_{12}^e$. It is seen from the comparison that the calculated values of the diffusion coefficients $\mathscr{D}_{12}^c$ are in fair agreement with the experimental ones, with the mean deviation not exceeding 35%. The existing disagreement is explained by the inaccuracy in calculating the radial distribution function. Thus, most of the deviation corresponds to cases in which $\zeta > 0.52$. At the same time, with increasing deviation of ζ from the limiting value of 0.52 the error in calculating $\mathscr{D}_{12}^c$ also increases. Some error in the calculation is also due to the calculation of v_i, defined as the inverse of the density of a pure liquid, which is valid only for ideal solutions.

Also calculated were the diffusion coefficients D_{ij}^c of the three-component systems acetone–benzene–methanol, acetone–benzene–carbon tetrachloride. The results of the calculations are given in Table 1. Also given are the experimental values of the diffusion coefficients D^e_{ij} [10]. As seen from the comparison, here also there is satisfactory agreement between the calculated and experimental values of the diffusion coefficients of all matrix elements. In the case of three-component mixtures the errors occurring in calculating the diffusion coefficients of binary systems also increase due to the inaccuracy in calculating the quantity $\frac{1}{\gamma_k}\frac{\partial \gamma_k}{\partial x_m}$, to which the nondiagonal matrix elements are largely sensitive, particularly due to their small values in comparison with the diagonal values. Thus, a small change in Λ_{ij} improves the convergence of the nondiagonal elements to the experimental values. It must be noted that a measurement of the nondiagonal matrix is carried out with a small error, which also increases in the region of small of D_{ij} values, and can reach 100% and more.

By this method were also calculated the diffusion coefficients in the vapor phase of the benzene–methanol system. In changing the liquid phase concentration from 0.05 to 0.8 the boiling temperature of the mixture remains almost constant, being $T = 329°K$. The diffusion coefficients of benzene vapors in methanol remained in this case also almost constant, being $\mathscr{D}^c_{12} = 0.95 \cdot 10^{-4}$ m^2/sec, despite the fact that the composition of the vapor phase varied substantially.

Thus, the method suggested of calculating the diffusion coefficients can be used to calculate mass-transport coefficients in mixtures. An improved agreement between calculated and experimental values should be expected with the extension of the validity limits of equations of state for the solid sphere model, inside which one can obtain reliable values of the radial distribution function, as well as with the refined description of equilibrium data, particularly for three-component systems.

NOTATION

grad y, a $(\nu - 1)$-dimensional vector; y_i, a quantity characterizing the mixture composition; S, entropy; x_i, molar fraction of the i-th component in the mixture; γ_i, activity coefficient of the i-th component; f_i, f_i°, nonequilibrium and equilibrium distribution functions; v_i, linear velocity of the i-th molecule; Φ, perturbation function; X_j, external force acting on the j-th molecule; $g_{ij}(r + 1/2\,\sigma_{ij}k, \sigma_{ij})$, equilibrium radial distribution function calculated at the collison point of two molecules; σ_{ij}, interaction parameter of molecules i and j; k, a vector directed from the center of molecule j to the i-th molecule; w_{ji}, relative velocity of molecules j and i; n_i, number of particles of the i-th molecule per unit volume; v_0, mean molecular mass velocity; ρ_i, mass concentration of the i-th component in the mixture, and v_i, partial specific volume of the i-th component.

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