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Diffusion Transport Vector for Multicomponent Gas Separation in Ultracentrifuge

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Diffusion Transport Vector for Multicomponent Gas Separation in Ultracentrifuge

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ABSTRACT

Simplified diffusion transport vector expressions for multicomponent gas mixture mass transfer analysis have been derived. Approximate relations for the general diffusion coefficients for multicomponent gas separation in an ultracentrifuge for both isotope and nonisotope mixtures are developed. Taking into account that diffusion coefficients matrices are diagonally dominant, a simple relationship for diffusion transport vectors for the case of isotope separation is derived. It is shown that the relative inaccuracies in separative power and separation factors calculation are less than 1–2%. Analogous relationships for diffusion coefficients for the separation of a nonisotope mixture containing small admixtures in the main gas are suggested. These relationships can be used when the total mole fraction of the admixtures is less then 5%.

Key Words. Diffusion transport vector; Multicomponent gas separation; Ultracentifuge; Diffusion coefficient

I. INTRODUCTION

Interest in the analysis of multicomponent gas mixture mass transfer has resulted from the development of nuclear, aerospace, chemical, and other modern technologies. Of particular interest is the separation of mul-

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ticomponent mixtures caused by pressure diffusion in a gas that is rotating at high speed. Gases are subjected to very strong centrifugal forces in ultracentrifuges, which are being widely used in ^{235}U production (1, 2). At present there is some interest in using ultracentrifuges to separate multicomponent isotopes of elements other then uranium (3) and in separation of nonisotope gas mixtures. Previous theoretical work on the analysis of ultracentrifuge separation dealt with either comparatively simple cases of ternary isotope mixture separation (4) or with simplified formulations of the mass transfer equations (5).

One of the difficulties is the complex structure of the diffusion transport vector, which depends on the mole fraction and the molecular weight of each component of a multicomponent gas mixture. This paper includes a theoretical analysis of common expressions for the transport vector and general multicomponent diffusion coefficient (GMDC), and some practical recommendations for the calculation of the diffusion transport vector as applied to an ultracentrifuge.

Section II considers the set of equations for GMDC determination. Based on the theorem of phenomenological coefficients (6), it is shown that the GMDC matrix may be transformed to a matrix having not less than n zero elements (n is the number of gas mixture components).

Section III contains simple expressions for GMDC calculations. Expressions have been obtained for two special cases that are used frequently in gas ultracentrifugal separation processes. In one case the gas mixture contains one component having a large mole fraction and the other components have small mole fractions. The other case is for an isotope gas mixture with small relative differences in component molecular weights. In both cases it is shown that the GMDC matrices are diagonally dominant.

Section IV contains three examples for calculating GMDC in the rotor of a gas ultracentrifuge. The first considers a gas mixture which contains mainly SF_6 gas along with O_2, N_2, and CO_2 as admixtures. The second considers a multicomponent sulfur isotope mixture in the form of SF_6 gas. The third considers a ^{16}O, ^{17}O, ^{12}C, and ^{13}C isotope mixture in the form of CO_2 gas. The last example corresponds to a mixture whose relative differences in molecular weights are not small. It illustrates correction of the GMDC matrix elements. Finally, two useful expressions for the diffusion transport vector are formulated.

II. DIFFUSION TRANSPORT VECTOR AND GENERAL MULTICOMPONENT DIFFUSION COEFFICIENTS

The mole fractions C_i distribution in a multicomponent gas mixture is determined by the set of equations (7)

$$\frac{\partial}{\partial t}\left(\rho\frac{m_i}{\overline{m}}C_i\right)+\nabla\cdot\left(\rho\mathbf{V}\frac{m_i}{\overline{m}}C_i+\mathbf{J}_i\right)=0,\qquad i=1,2,\ldots,n-1 \tag{1a}$$

$$C_n=1-\sum_{j=1}^{n-1}C_j \tag{1b}$$

where **V** is the average velocity vector, ρ is the mass density, m_i is the molecular weight of the ith component, $\overline{m}$ is the average molecular weight:

$$\overline{m}=\sum_{i=1}^{n}m_iC_i \tag{2}$$

and $\mathbf{J}_i$ is the diffusion transport vector (8):

$$\mathbf{J}_i=-\rho\frac{m_i}{\overline{m}}C_i\left(\sum_{j=1}^{n}D_{ij}\mathbf{d}_j+D_i^T\nabla\ln T\right),\qquad i=1,2,\ldots,n-1 \tag{3a}$$

$$\mathbf{J}_n=-\sum_{j=1}^{n-1}\mathbf{J}_j \tag{3b}$$

Here D_{ij} are the general multicomponent diffusion coefficients (GMDC), D_i^T are the thermodiffusion coefficients, and T is the temperature. The vector $\mathbf{d}_j$ can be written as (7)

$$\mathbf{d}_j=\nabla C_j+C_j\left(1-\frac{m_j}{\overline{m}}\right)\nabla\ln P-\frac{m_j}{\overline{m}}\frac{C_j}{P}\left(\rho\mathbf{F}_j-\sum_{k=1}^{n}\rho_k\mathbf{F}_k\right) \tag{4}$$

where P is the pressure. If a gas mixture is rotated in an ultracentrifuge, the thermodiffusion phenomenon in Eq. (3) can be neglected. The external space forces $\mathbf{F}_k=\omega^2\mathbf{r}$ (ω is the angular gas velocity, **r** is the radius vector) are not dependent on molecular weight, and the last term in Eq. (4) is equal to zero.

The GMDC is determined by (8)

$$\sum_{k=1}^{n}\frac{C_iC_k}{\mathcal{D}_{ik}}(D_{ij}-D_{kj})=\delta_{ij}-\frac{m_i}{\overline{m}}C_i,\qquad j=1,2,\ldots,n \tag{5a}$$

$$\sum_{i=1}^{n}m_iC_iD_{ij}=0 \tag{5b}$$

δ_{ij} is the Kronecker delta and $\mathcal{D}_{ik}$ is the binary diffusion coefficients (7)

$$\mathcal{D}_{ik} = 1.8583 \times 10^{-7} \frac{T^{3/2} \sqrt{(m_i + m_k)/(2m_i m_k)}}{P\sigma_{ik}^2 \Omega_{ik}^{(1,1)*}} \tag{6}$$

σ_{ik}^2 (10^{-20} m^2) is the molecular interaction diameter; $\Omega_{ik}^{(1,1)*}$ is the integral of interaction for molecular mass transfer; m_i, m_k (mole) are the molecular weights of the ith and the kth components; T (K) is the temperature; and p (atm) is the pressure. The $\mathcal{D}_{ij}$ (m^2/s) coefficients are not dependent on mole fractions and can be calculated or measured. The coefficients D_{ij} from Eqs. (5a) and (5b) are symmetrical, $D_{ij} = D_{ji}$, in agreement with reciprocity relations (6).

The coefficients D_{ij}, obtained from Eqs. (5a) and (5b), are not the only ones which satisfy Eq. (3). It is possible to demonstrate the following theorem:

> The composition of coefficients D^*_{ij}, derived from solution of Eqs. (5a) and (5b), D_{ij}, by adding the arbitrary constant D^{**}_i to any ith row of the $[D_{ij}]$ matrix, satisfies Eq. (3).

Therefore, any transformation such as

$$D^*_{ij} = D_{ij} + D^{**}_i \tag{7}$$

gives new values of the diffusion coefficients. If the new values are substituted into Eq. (3), the diffusion transport vectors are unchanged. The demonstration of this theorem is given from an evident equality:

$$\sum_{j=1}^{n} D^{**}_i \mathbf{d}_j = D^{**}_i \sum_{j=1}^{n} \mathbf{d}_j = \mathbf{0} \tag{8}$$

Coefficients D^*_{ij} are not symmetrical. This is at variance with the Onsager reciprocity relations (6) which were used (8) to obtain Eqs. (3), (5a), and (5b). According to the theorem demonstrated by De Groot and Mazur (6), it is easy to eliminate this variance. This theorem shows that if there is a linear relationship between forces and transport vectors, then the phenomenological coefficients are not binding, but it is possible to select coefficients which satisfy those relations.

Using Eq. (7), a new matrix of D^*_{ij} coefficients, which may contain not less than n zero elements, can be found. In this case it is possible to calculate each diffusion transport vector, $\mathbf{J}_i$, using not more than $(n - 1)$ vectors $\mathbf{d}_j$. In particular, under the condition $n = 2$: $D^*_{ii} = 0$, $D^*_{12} = -m_2\mathcal{D}_{12}/(m_1C_1)$, $D^*_{21} = -m_1\mathcal{D}_{12}/(m_2C_2)$.

In Sections III and IV it will be shown that in some special cases it is possible to eliminate all nondiagonal elements from the $[D_{ij}]$ matrix and to considerably simplify the diffusion transport vector and the calculations of the mole fraction distribution.

III. GMDC OF MIXTURES WITH SMALL ADMIXTURES AND ISOTOPE MIXTURES

Two special cases in which the GMDC calculations do not require the complete solution of the set of linear equations (5a) and (5b) are considered.

A. Small Admixtures in the Main Gas

Assume that the mole fractions in the multicomponent mixture are $C_i \ll C_n, i = 1, \ldots, n-1$. In most mixtures the binary diffusion coefficients are of the same order of magnitude (7). Neglecting terms containing products of the mole fractions of the less dense components and using Eq. (7), the solution of Eqs. (5a) and (5b) can be written in the following form:

$$C_i D^g_{ij} = \frac{\mathcal{D}_{in}}{C_n}\left(\delta_{ij} - \frac{m_i}{\bar{m}} C_i + C_n C_i \frac{D^g_{nj}}{\mathcal{D}_{in}}\right), \qquad i = 1, 2, \ldots, n-1 \tag{9a}$$

where

$$C_n D^g_{nj} = \sum_{k=1}^{n} C_k \frac{m_k^2}{\bar{m}^2}\mathcal{D}_{kn} - \frac{m_j}{\bar{m}}\mathcal{D}_{jn} \tag{9b}$$

The matrix $[C_i D^g_{ij}]$ is diagonally dominant. The diagonal elements can simply be evaluated as

$$C_i D^g_{ii} \approx \frac{\mathcal{D}_{in}}{C_n} \tag{10}$$

B. Isotope Mixture

Let the mole fractions, C_i, have arbitrary values and small relative differences between the component molecular weights:

$$y = \frac{|m_j - m_i|}{m_i} \ll 1 \tag{11}$$

Assuming that for all molecules the values σ_{ij} and $\Omega_{ij}^{(1,1)*}$ in Eq. (6) are the same, the following approximate relations can be written:

$$\mathcal{D}_{ij}^{-1} \approx a \cdot m_i^{-1/2}(3m_i + m_j), \qquad a = \text{constant} \tag{12a}$$

when $(m_j - m_i) > 0$, and

$$\mathcal{D}_{ij}^{-1} \approx b\cdot m_i^{-1/2}(5m_i - m_j), \qquad b = \text{constant} \tag{12b}$$

when $(m_j - m_i) < 0$. Substituting Eqs. (12a) and (12b) into Eqs. (5a) and (5b), it is easy to show that

$$C_iD_{ij}^{is} = f_{ij} - \frac{3}{2}\frac{m_iC_i}{\overline{m}(3m_i + \overline{m})}\sum_{k=1}^{n} f_{kj}(3m_k + \overline{m}) \tag{13a}$$

when $(m_j - m_i) > 0$, and

$$C_iD_{ij}^{is} = f_{ij} - \frac{5}{6}\frac{m_iC_i}{\overline{m}(5m_i - \overline{m})}\sum_{k=1}^{n} f_{kj}(5m_k - \overline{m}) \tag{13b}$$

when $(m_j - m_i) < 0$, where

$$f_{ij} = \left(\delta_{ij} - \frac{m_iC_i}{\overline{m}}\right)\left(\sum_{k=1}^{n} \frac{C_k}{\mathcal{D}_{ik}}\right)^{-1} \tag{13c}$$

To better understanding Eqs. (13a), (13b), and (13c), one can consider the sufficiently exact approximation to Eqs. (12a) and (12b):

$$\mathcal{D}_{ij} \approx \overline{\mathcal{D}}_i = \text{constant} \tag{14}$$

In the case of an isotope mixture, approximating Eq. (5b) as $\sum_{i=1}^{n} C_im_jD_{ij} \approx 0$, then $\sum_{i=1}^{n} C_iD_{ij} \approx 0$, Eq. (5a) yields the relationship

$$C_iD_{ij}^{is} = \overline{\mathcal{D}}_i\left(\delta_{ij} - \frac{m_iC_i}{\overline{m}}\right) \tag{15}$$

Equation (15) shows that the GMDC matrix $[C_iD_{ij}^{is}]$ is diagonally dominant and that the nondiagonal elements of the ith row are of the same order of magnitude.

The solutions (9a), (9b) and (13a), (13b) can be simplified using the GMDC matrix transformation (7). However, the complete form of these solutions may be useful in some cases because they satisfy the condition (5b) in the form

$$\sum_{j=1}^{n} C_jm_jD_{ij} = 0 \tag{16}$$

The transformed elements of the GMDC matrix for Case B, Eqs. (13a) and (13b), can be approximately written as diagonal matrix

$$C_iD_{ij}^{is*} \approx \overline{\mathcal{D}}_i\delta_{ij} \tag{17a}$$

where

$$\overline{\mathcal{D}}_i = \left(\sum_{k=1}^{n} \frac{C_k}{\mathcal{D}_{ik}}\right)^{-1} \tag{17b}$$

The transformed elements of the GMDC matrix for Case A, Eqs. (9a) and (9b), are

$$C_i D^{g*}_{ij} = \frac{\mathcal{D}_{in}}{C_n}\left(\delta_{ij} + C_i C_n \frac{D^{g*}_{nj}}{\mathcal{D}_{in}}\right), \qquad i = 1, 2, \ldots, n - 1 \tag{18a}$$

where

$$C_n D^{g*}_{nj} = \frac{m_j}{m}\,\mathcal{D}_{jn}(\delta_{jn} - 1) \tag{18b}$$

IV. APPLICATION TO GAS MIXTURE SEPARATION IN ULTRACENTRIFUGE

Before discussing several applications, errors in the calculation of ultracentrifuge separation properties which can appear with inaccuracies in GMDC values will be estimated. These inaccuracies result when the diagonal form of the GMDC matrix is used.

The separative power and the separations factors (4) are the main characteristics in the theory of ultracentrifuge separation. Let F be the feed flow to an ultracentrifuge, P and W the product and the waste flows, respectively, and C_i^F, C_i^P, C_i^W the mole fractions of the components in the flows. For simplicity, assume that $P = W = F/2$. The separative power for the ith and jth components can be written as

$$\delta U_{ij} = \frac{F}{2}\left[V(C_i^P, C_j^P) + V(C_i^W, C_j^W) - V(C_i^F, C_j^F)\right] \tag{19a}$$

where the value function is

$$V(C_i, C_j) = (C_i - C_j)\ln\left(\frac{C_i}{C_j}\right) \tag{19b}$$

The separation factors can be written

$$\alpha_{ij} = \frac{C_i^P}{C_j^P}\bigg/\frac{C_i^F}{C_j^F}, \qquad \beta_{ij} = \frac{C_i^F}{C_j^F}\bigg/\frac{C_i^W}{C_j^W} \tag{20}$$

The separative power δU can be used to calculate the ultracentrifuge efficiency. Highly accurate values of α and β are needed to calculate the cascade characteristics.

If D_{ij}^0 represents the exact GMDC values, obtained from Eqs. (5a), (5b), and transformation (7); $\mathbf{J}_i^0$ represents the exact values of the diffusion transport vector; and C_i^0 represents the component mole fractions, corresponding to the D_{ij}^0 coefficients, then the inexact values can be written as

$$\hat{D}_{ij} = D_{ij}^0 + \delta_i D_{ij}^0 \tag{21}$$

where $|\delta_i| \ll 1$. Since, in the first approximation, there is a linear relationship between the diffusion transport vector and the driving forces through the GMDC, the following relations can be used:

$$\hat{\mathbf{J}}_i = (\delta_i + 1)\mathbf{J}_i^0 \tag{22a}$$

$$\hat{C}_i = (\delta_i + 1)C_i^0 \tag{22b}$$

Using Eq. (22b), it can be shown that

$$\delta\hat{U}_{ij} - \delta U_{ij}^0 = (\delta_i + \delta_j)\delta U_{ij}^0 + \varphi_{ij} \tag{23a}$$

$$\hat{\alpha}_{ij} - \alpha_{ij}^0 = (\delta_i - \delta_j)\alpha_{ij}^0 \tag{23b}$$

$$\hat{\beta}_{ij} - \beta_{ij}^0 = (\delta_i - \delta_j)\beta_{ij}^0 \tag{23c}$$

where

$$\begin{aligned}\varphi_{ij} = \frac{F}{2}\Big[&2(C_i^F - C_j^F)(\delta_i - \delta_j) - 2(C_j^F\delta_i - C_i^F\delta_j)\ln\beta_{ij}^0 \\ &+ (C_i^F + C_j^F)(\delta_i - \delta_j)\ln\frac{C_i^F}{C_j^F} + 2C_i^F\frac{\beta_{ij}^0 - 1}{\alpha_{ij}^0\beta_{ij}^0 - 1}(\delta_i - \delta_j\alpha_{ij}^0)\Big]\end{aligned} \tag{24}$$

From Eqs. (23a), (23b), (23c), and (24), if the inaccuracies δ_i and δ_j have the same sign and the same order, then the errors in δU_{ij}, α_{ij}, and β_{ij} are small. The $\ln(C_i^F/C_j^F)$ term in Eq. (24) indicates that the mole fraction ratio is significant only when the mole fractions differ by several orders of magnitude.

Table 1 presents an example of GMDC calculations for a multicomponent, nonisotope gas mixture with large differences between the molecular weights of the components. Tables 2 and 3 present examples for two isotope mixtures with different average molecular weights. Calculations were performed using Eqs. (5a), (5b), (18a), (18b), and (10) for the nonisotope mixture, and using Eqs. (13a), (13b), (7), and (17a) for the isotope mixtures. The results were obtained for gas mixtures rotating as a rigid body in an ultracentrifuge. The gas rotation characteristics are: the gas compression degree $A^2 = \omega^2 r_0^2\overline{m}(r_0)/(2RT) = 12.0$ (R is the gas constant,

TABLE I
Diffusion Coefficients for O_2–N_2–CO_2–SF_6 Gas Mixture

i	1	2	3
$\mathcal{D}_{in}/C_n$	1.0360	0.9520	0.8243

	$i\backslash j$	1	2	3	4
			$r/r_0 = 1.0$		
C_j		5.0×10^{-4}	5.0×10^{-4}	5.0×10^{-4}	0.9985
$C_iD_{ij}^*$	1	1.03710	1.4×10^{-4}	1.3×10^{-4}	0.0
	2	1.2×10^{-4}	0.95276	1.1×10^{-4}	0.0
	3	1.4×10^{-4}	1.4×10^{-4}	0.82502	0.0
$C_iD_{ij}^{g^*}$	1	1.03770	-9.1×10^{-5}	-1.2×10^{-4}	0.0
	2	-1.1×10^{-4}	0.95333	-1.2×10^{-4}	0.0
	3	-1.1×10^{-4}	-9.2×10^{-4}	0.82544	0.0
			$r/r_0 = 0.8$		
C_j		1.41×10^{-2}	1.59×10^{-2}	9.87×10^{-3}	0.961013
$C_iD_{ij}^*$	1	1.06060	4.1×10^{-3}	3.9×10^{-3}	0.0
	2	3.9×10^{-3}	0.97625	3.8×10^{-3}	0.0
	3	3.0×10^{-3}	3.0×10^{-3}	0.84282	0.0
$C_iD_{ij}^{g^*}$	1	1.07590	-2.7×10^{-3}	-3.6×10^{-3}	0.0
	2	-3.8×10^{-3}	0.98844	-4.1×10^{-3}	0.0
	3	-2.3×10^{-3}	-1.9×10^{-3}	0.85593	0.0
			$r/r_0 = 0.6$		
C_j		1.299×10^{-1}	1.6036×10^{-1}	6.905×10^{-2}	0.64069
$C_iD_{ij}^*$	1	1.31670	6.2×10^{-2}	5.7×10^{-2}	0.0
	2	6.4×10^{-2}	1.24280	6.2×10^{-2}	0.0
	3	3.2×10^{-2}	3.4×10^{-2}	1.02560	0.0
$C_iD_{ij}^{g^*}$	1	1.57130	-3.7×10^{-2}	-5.0×10^{-2}	0.0
	2	-5.7×10^{-2}	1.44010	-6.2×10^{-2}	0.0
	3	-2.5×10^{-2}	-2.0×10^{-2}	1.25980	0.0

ω is the angular velocity of the ultracentrifuge rotor, r_0 is the rotor radius) with $T = 300$ K and the pressure at the rotor side wall $P_w = 13{,}300$ Pa. The isotope binary diffusion coefficients were calculated from Eq. (6). The parameter σ corresponds to the Lenard–Jones potential intermolecular interaction (7). The integrals $\Omega^{(1,1)*}$ were calculated from the following expression (9):

$$\Omega^{(1,1)*} = a\cdot T^{*-B} + c\cdot \exp(-dT^*) + e\cdot \exp(-fT^*) + g\cdot \exp(hT^*) \tag{25}$$

TABLE 2
Diffusion Coefficients for $^{36}SF_6$–$^{34}SF_6$–$^{33}SF_6$–$^{32}SF_6$ Gas Mixture

			$r/r_0 = 1.0$			
	$i\backslash j$	1	2	3	4	
C_j		2.9×10^{-4}	5.46×10^{-2}	8.48×10^{-3}	0.9366	$\overline{\mathcal{D}}_i$
$C_iD^*_{ij}$	1	0.34577	-1.0×10^{-6}	-3.5×10^{-7}	0.0	0.34577
	2	-3.9×10^{-4}	0.34676	-6.5×10^{-5}	0.0	0.34689
	3	-6.0×10^{-5}	-3.0×10^{-5}	0.34695	0.0	0.34696
$C_iD^{g*}_{ij}$	1	0.34577	-9.0×10^{-7}	-4.0×10^{-7}	0.0	
	2	-1.4×10^{-6}	0.34671	-9.3×10^{-5}	0.0	
	3	-2.2×10^{-6}	-2.2×10^{-6}	0.34694	0.0	
			$r/r_0 = 0.1$			
C_i		1.7×10^{-4}	4.23×10^{-2}	7.51×10^{-3}	0.95032	$\overline{\mathcal{D}}_i$
$C_iD^*_{ij}$	1	0.34579	-6.0×10^{-7}	-2.0×10^{-7}	0.0	0.34579
	2	-3.0×10^{-4}	0.34681	-5.0×10^{-5}	0.0	0.34692
	3	-5.4×10^{-5}	-2.7×10^{-5}	0.34696	0.0	0.34697
$C_iD^*_{ij}$	1	0.34579	-5.0×10^{-7}	-2.0×10^{-7}	0.0	
	2	-6.8×10^{-6}	0.34678	-7.3×10^{-5}	0.0	
	3	-1.2×10^{-6}	-1.2×10^{-6}	0.34696	0.0	

where $T^* = kT/\epsilon$. The definition and values of ϵ/k were found in Ref. 7. For the nonisotope mixture the binary diffusion coefficients were calculated by the following empirical formulation (10):

$$\mathcal{D}_{ij} = \mathcal{D}_{0ij}(T/273)^{\gamma_{ij}} \cdot \exp(-S_{ij}/T) \tag{26}$$

All binary diffusion coefficients were represented in cm^2/s. The diffusion coefficients at radius r were given by means of the transformation

$$\overline{\mathcal{D}}_{ij}(r) = \mathcal{D}_{ij}(r) \cdot P(r)/P_w = \mathcal{D}_{ij}(r_0) \tag{27}$$

which follows from Eq. (6).

The results in Tables 1–3 show that after using transformation (7), which gives zero elements in the nth column of the GMDC matrices, the transformed matrices are diagonally dominant.

For the isotope mixtures, differences between diagonal and nondiagonal elements are not less than two orders of magnitude for $y \approx 10^{-1}$ (see Table 3) and much more for $y \leq 3 \times 10^{-2}$ (see Table 2). These differences appear over a wide range of radial position and mole fraction values. Equation (17b) is a good approximation for calculating the diagonal elements. All nondiagonal elements in the GMDC matrix have the same sign

TABLE 3

Diffusion Coefficients for $^{13}C^{18}O_2$–$^{12}C^{18}O_2$–$^{13}C^{16}O_2$–$^{12}C^{16}O_2$ Gas Mixture

A. Small Mole Fraction Values

$r/r_0 = 1.0$

	$i\backslash j$	1	2	3	4	
C_j		8.0×10^{-5}	1.43×10^{-2}	5.9×10^{-3}	0.97971	$\overline{\mathcal{D}}_i$
$C_iD_{ij}^*$	1	0.11048	-2.0×10^{-7}	-6.0×10^{-7}	0.0	0.11048
	2	-1.4×10^{-4}	0.11293	-1.1×10^{-4}	0.0	0.11296
	3	-5.3×10^{-5}	-7.7×10^{-6}	0.11164	0.0	0.11171
$C_iD_{ij}^{is^*}$	1	0.11048	-2.0×10^{-7}	-5.0×10^{-7}	0.0	
	2	-1.8×10^{-6}	0.11129	-2.0×10^{-6}	0.0	
	3	-4×10^{-7}	-1.2×10^{-5}	0.11164	0.0	

$r/r_0 = 0.1$

C_j		2.0×10^{-5}	1.1×10^{-2}	2.0×10^{-3}	0.98698	$\overline{\mathcal{D}}_i$
$C_iD_{ij}^*$	1	0.11049	-1.0×10^{-8}	-1.0×10^{-7}	0.0	0.11049
	2	-1.1×10^{-4}	0.11294	-8.7×10^{-5}	0.0	0.11297
	3	-1.8×10^{-5}	-2.0×10^{-6}	0.11169	0.0	0.11170
$C_iD_{ij}^{is^*}$	1	0.11049	-3.0×10^{-8}	-1.0×10^{-7}	0.0	
	2	-4×10^{-7}	0.11294	-4.0×10^{-7}	0.0	
	3	-1.0×10^{-8}	-4.0×10^{-6}	0.11168	0.0	

B. Middle Mole Fraction Values

$r/r_0 = 1.0$

	$i\backslash j$	1	2	3	4	
C_j		3.0×10^{-2}	2.0×10^{-1}	2.3×10^{-1}	5.4×10^{-1}	$\overline{\mathcal{D}}_i$
$C_iD_{ij}^*$	1	0.10960	7.0×10^{-5}	-2.2×10^{-4}	0.0	0.10980
	2	-2.0×10^{-3}	0.11180	-1.5×10^{-3}	0.0	0.11138
	3	-2.0×10^{-3}	-3.0×10^{-4}	0.10910	0.0	0.11366
$C_iD_{ij}^{is^*}$	1	0.10970	-4.0×10^{-5}	1.6×10^{-4}	0.0	
	2	-6.0×10^{-4}	0.11180	-6.0×10^{-4}	0.0	
	3	-7.0×10^{-4}	-3.0×10^{-4}	0.10930	0.0	

$r/r_0 = 0.1$

C_j		1.0×10^{-2}	2.0×10^{-1}	1.0×10^{-1}	0.690	$\overline{\mathcal{D}}_i$
$C_iD_{ij}^*$	1	0.11013	-2.0×10^{-5}	-7.0×10^{-5}	0.0	0.11023
	2	-2.0×10^{-3}	0.11210	-1.5×10^{-3}	0.0	0.11248
	3	-9.0×10^{-4}	-2.0×10^{-4}	0.11040	0.0	0.11109
$C_iD_{ij}^{is^*}$	1	0.11010	-2.0×10^{-5}	-6.0×10^{-5}	0.0	
	2	-2.0×10^{-4}	0.11210	-2.0×10^{-4}	0.0	
	3	-1.0×10^{-4}	-2.0×10^{-4}	0.11040	0.0	

and may be neglected. With these approximations, the relative errors in δU_{ij} and α_{ij}, β_{ij} using Eq. (17a) are still less than 1–2%. This accuracy is sufficient for estimating the separative power and cascade characteristics.

For nonisotope mixtures the result is less definitive. Since the values of $\Delta m/\overline{m}$ for nonisotope mixtures as a rule are not small, there may be appreciable mole fraction changes with rotor radial position. As a result, the GMDC depends on radius. The GMDC matrix is still diagonally dominant; however, the differences between diagonal and nondiagonal elements may not be as large as in the isotope mixture case. For example, from Table 1 for $r/r_0 \leq 0.8$, is impossible to eliminate nondiagonal elements. For allowable inaccuracies in δU_{ij} and α_{ij}, β_{ij} not greater then 5%, the analytical solutions (9a), (9b) or (18a), (18b) are in good agreement with exact values of GMDC only when the total mole fraction of admixtures in the gas mixture is less than 5%.

One should note that the well-known Wilke (11) formulation for multicomponent diffusion coefficients, which can be written in the form

$$C_i D_{ij} = (1 - C_i)\left(\sum_{s \neq i}^{n} \frac{C_s}{\mathcal{D}_{is}}\right)^{-1} \tag{28}$$

is in good agreement with Eq. (17a) for $C_i \ll 1$ ($i = 1, 2, \ldots, n - 1$). However, for separation of nonisotope mixtures, Eq. (28) is not exact since in the derivation of Eq. (28) the pressure diffusion phenomenon was not taken into account.

Finally, we can formulate expressions for the diffusion transport vector calculation. If Eq. (7) is applied as

$$D_{ij}^{*} = D_{ij} - D_{ik}, \qquad k \neq i$$

then using Eq. (16), Eq. (3) can be rewritten as

$$\mathbf{J}_i = -\rho \frac{m_i}{m} C_i[D_{ii}^{*}(\nabla C_i + C_i \nabla \ln P) + D_{ik} \nabla \ln P$$

$$+ \sum_{j \neq i,k}^{n} D_{ij}^{*}(\nabla C_j + C_j \nabla \ln P)]$$

For the case of isotope separation, when the diagonal form GMDC matrix (17a) may be used, Eq. (30) can be written as

$$\mathbf{J}_i = -\rho \frac{m_i}{m} [\mathcal{D}_i(\nabla C_i + C_i \nabla \ln P) + C_i D_{ik} \nabla \ln P]$$

where

$$|D_{ik}| = \max\{|D_{ij}|, j \neq i\}$$

The term containing D_{ik} in Eq. (31a) may be used to increase the accuracy of the calculation.

V. CONCLUSIONS

Simplified diffusion transport vector expressions have been developed for multicomponent gas mixture transfer analysis. The simplification is based on an equivalent GMDC matrix transformation (7), which reduces this matrix to a new form having not less than n zero elements. When the transformed GMDC matrix is diagonally dominant, the diffusion transport vectors may be expressed by Eq. (30). Numerical mass transfer calculations using Eq. (30) are substantially simpler because all nondiagonal elements are grouped into two individual terms. For isotope separation in an ultracentrifuge, either the simple expressions (13a) and (13b) or (17a) and (17b) can be used to calculate the GMDC matrix. In particular, when the diagonal form of the GMDC matrix, Eq. (17a), is used, the diffusion transport vectors have the simple form (31a). Using the simplified expressions, the relative errors in the separative power and the separation factors are less than 2% for the isotope separation cases considered. For nonisotope gas mixture separation, the analogous expressions (9a) and (9b) or (18a) and (18b) for the GMDC can be used only when the total mole fractions of admixtures in the main gas in all regions of the gas flow in an ultracentrifuge are much less then unity. The diagonal form of the GMDC matrix and the expression for the diffusion transport vectors (31a) cannot be used unless the total mole fraction of admixtures has been verified to be sufficiently small. Such verification requires the use of special analytical or digital models for solving the mass transfer equations (1). Such models must take into account the full and diagonal forms of the GMDC matrix.

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