

TRANSPORT EQUATIONS FOR A COMPLEX MIXTURE
IN A THERMAL-DIFFUSION COLUMN

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Transport equations are derived for a thermal-diffusion column containing a multicomponent molecular mixture.

The existing theory of thermal-diffusion columns [1] is restricted to binary mixtures; a generalization to multicomponent mixtures [2] relates only to the particular case of isotope mixtures. It is an open question whether the theory is applicable to any liquid or gaseous mixture containing an arbitrary number of components.

Here we employ general phenomenological arguments in a reasonably rigorous discussion of thermal diffusion in any mixture; transport equations are derived for a thermal-diffusion column and application to particular separations are discussed.

1. Diffusion Fluxes in the Presence of Thermal Diffusion in a Multicomponent System. Reasonably general arguments provide an expression for the diffusion flux of the k-th component in a system containing M components as [3]

$$\rho_k (\mathbf{v}_k - \mathbf{v}) = -\rho \sum_{i=1}^{M-1} D_{ki} \nabla c_i - \rho D_k^T \nabla \ln T. \quad (1)$$

However, this equation is not by any means convenient for practical purposes. The diffusion flux is usually written in a rather different form for a binary system, namely in terms of the thermal-diffusion constant α :

$$\rho_1 (\mathbf{v}_1 - \mathbf{v}) = -\rho D [\nabla c_1 + \alpha c_1 (1 - c_1) \nabla \ln T]. \quad (2)$$

The advantages of this are firstly that it is possible to define the concentration dependence of the thermal-diffusion term in (2) (this dependence can be neglected in certain instances). Secondly, this constant is to be preferred as a means of describing thermal diffusion, since it has a simple physical meaning and can readily be derived from steady-state measurements on the concentration and temperature gradients. The following equation applies for this state:

$$\nabla c_1 = -\alpha c_1 (1 - c_1) \nabla \ln T. \quad (3)$$

Equation (2) is readily generalized to any number of components; we define the thermal-diffusion constants for a multicomponent system as the following quantities:

$$\alpha_{ki} = a_k - a_i, \quad (4)$$

where the a_k have the following simple relation to the steady-state concentration and temperature gradients measured:

$$\nabla \ln c_k = -a_k \nabla \ln T. \quad (5)$$

Equations (4) and (5) become (3) for a binary system. Also, (5) implies

$$\sum_{i=1}^M c_i a_i = 0. \quad (6)$$

We see from (4) and (6) that only $M = 1$ is independent out of all the α_{ki} , and we therefore note the following obvious features:

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$$\alpha_{ki} = -\alpha_{ik}, \quad (7)$$

$$\alpha_{kj} + \alpha_{ji} = \alpha_{ki}, \quad (8)$$

$$\alpha_{ki} + \alpha_{jn} = \alpha_{kn} + \alpha_{ji}. \quad (9)$$

In the steady state, there are no diffusion fluxes, and therefore the right side in (1) can be equated to zero. This produces the following result with (5):

$$D_k^T = \sum_{i=1}^{M-1} D_{ki} c_i a_i. \quad (10)$$

Then (4) and (6) transform the latter to

$$D_k^T = \sum_{i=1}^{M-1} D_{ki} \sum_{j=1}^M c_j \alpha_{ij}. \quad (11)$$

We substitute (11) into (1) to get

$$\rho_k (\mathbf{v}_k - \mathbf{v}) = -\rho \sum_{i=1}^{M-1} D_{ki} \left(\nabla c_i + c_i \sum_{j=1}^M c_j \alpha_{ij} \nabla \ln T \right). \quad (12)$$

This is a generalization of (2) to any number of components; this can sometimes be simplified. A particular case of (12) is, for example,

$$\rho_k (\mathbf{v}_k - \mathbf{v}) = -\rho D \left(\nabla c_k + c_k \sum_{j=1}^M c_j \alpha_{kj} \nabla \ln T \right), \quad (13)$$

which Jones derived for an isotope mixture [4]. Jones derived this from Hellund's kinetic theory for gas mixtures [5, 6]. As we have derived (12) purely phenomenologically, one concludes that it applies in general for any liquid or gaseous mixture.

An obvious relation is

$$c_M = 1 - \sum_{j=1}^{M-1} c_j, \quad (14)$$

and this with (7) and (8) allows us to represent (12) as

$$\rho_k (\mathbf{v}_k - \mathbf{v}) = -\rho \sum_{i=1}^{M-1} D_{ki} \left[\nabla c_i + c_i \left(\alpha_{iM} - \sum_{j=1}^{M-1} \alpha_{ij} c_j \right) \nabla \ln T \right]. \quad (15)$$

The diffusion-flux representations of (12) and (15) are the most convenient when the thermal-diffusion constants are independent of the concentrations; the molecular theory of mixtures implies that this is so if the radial distributions are independent of concentration [7]. This applies particularly to isotopic mixtures, and also to regular molecular solutions, since it is found [8] that the radial functions of a regular solution are independent of concentration. Clearly, this condition is met if the parameters of the molecules do not differ too substantially. If the thermal-diffusion constant for the component pair k and i is independent of concentration, it is then also independent of the other components in the mixture and is actually equal to the thermal-diffusion constant for a binary mixture of molecular species k and i . However, (12) and (15) are more convenient than (1) even when the α_{ki} cannot be taken as independent of concentration, since the thermal-diffusion constants can be derived directly by experiment, in contrast to the thermal-diffusion coefficients.

2. Diffusion Fluxes in Different Frames of Reference. The fluxes given by (12) are defined in a frame of reference linked to the center of mass; the concentration has the meaning of a mass fraction. A different definition of the diffusion fluxes has sometimes been used (in the mole-center system). In that case, the concentrations are expressed as molar fractions x_k , which are clearly related to the mass values

$$c_k = \frac{m_k}{m} x_k, \quad (16)$$

where m is the mean molar mass of the mixture, i.e.,

$$m = \sum_{i=1}^M m_i x_i. \quad (17)$$

One therefore has to examine how the transport coefficients alter on going from one system to another. It is readily seen from (4), (5), and (16) that the thermal-diffusion constants are unaltered on going from mass concentrations to molar ones, which is an advantage of these constants over the thermal-diffusion coefficients. The corresponding transformation of the diffusion coefficients may be examined by reference to the pure diffusion terms in the fluxes:

$$\rho_k (\mathbf{v}_k - \mathbf{v}) = -\rho \sum_{i=1}^{M-1} D_{ki} \nabla c_i, \quad (18)$$

$$n_k (\mathbf{v}_k - \mathbf{u}) = -n \sum_{i=1}^{M-1} D'_{ki} \nabla x_i, \quad (19)$$

where \mathbf{u} is the velocity relative to the center of moles, i.e.,

$$\mathbf{u} = \sum_{i=1}^M x_i \mathbf{v}_i. \quad (20)$$

Appropriate steps with (16)-(20) give the following relationship between the diffusion coefficients in the two frames of reference:

$$D'_{ki} = m_i \left[\frac{1}{m_k} D_{ki} - x_k \sum_{j=1}^{M-1} \left(\frac{1}{m_j} - \frac{1}{m_M} \right) D_{ji} \right] - \frac{m_i - m_M}{m} \sum_{l=1}^{M-1} m_l x_l \left[\frac{1}{m_k} D_{kl} - x_k \sum_{j=1}^{M-1} \left(\frac{1}{m_j} - \frac{1}{m_M} \right) D_{jl} \right]. \quad (21)$$

We see that in general the diffusion coefficients in the two systems have a very complex relation; in certain particular cases, these coefficients are invariant under change in the frame of reference, which applies particularly for arbitrary systems, where a single diffusion coefficient applies. This follows from (21) for $M = 2$. The diffusion coefficients for multicomponent isotope mixtures are also invariant.

The only nontrivial case of invariance in the diffusion coefficients for a multicomponent molecular mixture is an infinitely dilute solution of several substances in a solvent; a solution can be taken as infinitely dilute if the concentrations x_k are much less than 1. In that case, one can neglect the concentration dependence of the diffusion coefficients, and therefore the D_{ki} and D'_{ki} matrices are diagonal and equal. In other cases the diffusion coefficients are dependent on the choice of frame of reference, and therefore one has to state not only the magnitudes of the diffusion coefficients but also the frame of reference for which these are defined for any molecular mixture containing more than two components. In particular, the equations for the diffusion fluxes in the presence of thermal diffusion take the following form in the mole-center system:

$$n_k (\mathbf{v}_k - \mathbf{u}) = -n \sum_{i=1}^{M-1} D'_{ki} \left(\nabla x_i + x_i \sum_{j=1}^M x_j \alpha_{ij} \nabla \ln T \right), \quad (22)$$

where the relation between D'_{ki} and D_{ki} is given by (21).

3. Transport Equations for a Thermal-Diffusion Column. Jones and Furry used (2) to derive the transport equations for a binary mixture in a thermal-diffusion column [1]. A detailed derivation of this equation is given also in [9]. The arguments used in that derivation can be extended to any number of components, but it is then necessary to start from the diffusion-flux equations of (12). We then get the following transport equations:

$$\tau_k = \sigma c_k + c_k \sum_{i=1}^M H_{ki} c_i - \sum_{i=1}^{M-1} K_{ki} \frac{\partial c_i}{\partial z}, \quad (23)$$

where

$$H_{ki} = H_0 \alpha_{ki}; \quad (24)$$

$$H_0 = \frac{g\beta\rho^2\delta^3(\Delta T)^2 B}{6!\eta\bar{T}}; \quad (25)$$

$$K_{hi} = K_{hi}^{(c)} + K_{hi}^{(d)}; \quad (26)$$

$$K_{hi}^{(c)} = \frac{g^2\beta^2\rho^3\delta^7(\Delta T)^2 B}{9!\eta^2} (D^{-1})_{hi}; \quad (27)$$

$$K_{hi}^{(d)} = B\delta\rho D_{hi}. \quad (28)$$

Here $(D^{-1})_{ki}$ indicates the element in the k -th row and i -th column after inversion of the diffusion-coefficient matrix for the center-of-mass system.

From (7), (8), (14), and (24) we rewrite (23) as

$$\tau_k = \sigma c_k + H_0 c_k \left(\alpha_{kM} - \sum_{i=1}^{M-1} \alpha_{iM} c_i \right) - \sum_{i=1}^{M-1} K_{ki} \frac{\partial c_i}{\partial z}. \quad (29)$$

Unfortunately, the structure of the K_{ki} matrix is unknown in the general case, since the structure of the diffusion-coefficient matrix is also unknown. It is therefore impossible to obtain a general solution by means of (23) and (29) if no additional assumptions are made about the diffusion coefficients.

Equations (23) and (29) have been written for the mass concentrations, and therefore τ_k has the meaning of the mass flux of the k -th component through the column cross section, while σ is the mass flux of the entire mixture through the cross section, i.e.,

$$\sigma = \sum_{i=1}^M \tau_i. \quad (30)$$

In some instances it is convenient to convert to the molar concentrations in the transport equations, for this enables one, for example, to linearize these equations for dilute solutions. It is best to replace τ_k by τ'_k on going to the molar concentrations, and this is the flux in moles of the k -th component through the cross section. Clearly, the following relationship applies:

$$\tau'_k = \frac{\tau_k}{m_k}. \quad (31)$$

Correspondingly,

$$\sigma' = \sum_{i=1}^M \tau'_i \quad (32)$$

is the number of moles of the entire mixture passing through the section of the column in unit time. Then (16) and (30)-(32) allow us to relate this quantity as follows to the mass characteristics:

$$\sigma' = \frac{\sigma}{m} + \sum_{i=1}^{M-1} \left(\frac{1}{m_i} - \frac{1}{m_M} \right) (\tau_i - \sigma c_i). \quad (33)$$

In the nonstationary case, σ and σ' may be dependent on z , since then the mass and molar concentrations in general vary with time; however, the quantities of practical value are $\sigma(z)$ and $\sigma'(z')$, namely at the end of the column ($z = L$, at the sampling point). An obvious boundary condition is

$$(\tau_i - \sigma c_i)_{z=L} = 0, \quad (34)$$

and from (33) we get

$$\sigma'(L) = \frac{\sigma(L)}{m(L)}. \quad (35)$$

Then $\sigma(L)$ and $\sigma'(L)$ are simply the mass and molar amounts tapped off.

Then (4), (6), (14), (16), (24), (31), and (33) allow us to convert to molar characteristics in (23), and the transport equations become

$$\tau'_k = \sigma' x_k + x_k \sum_{i=1}^M H'_{ki} x_i - \sum_{i=1}^{M-1} K'_{ki} \frac{\partial x_i}{\partial z}, \quad (36)$$

where

$$H'_{ki} = H'_0 \alpha_{ki}; \quad (37)$$

$$H'_0 = \frac{H_0}{m}, \quad (38)$$

and the K'_{ki} are related to the K_{ki} as follows:

$$K'_{ki} = \frac{m_i}{m} \left[\frac{1}{m_k} K_{ki} - x_k \sum_{j=1}^{M-1} \left(\frac{1}{m_j} - \frac{1}{m_M} \right) K_{ji} \right] - \frac{m_i - m_M}{m^2} \sum_{l=1}^{M-1} m_l x_l \left[\frac{1}{m_k} K_{kl} - x_k \sum_{j=1}^{M-1} \left(\frac{1}{m_j} - \frac{1}{m_M} \right) K_{jl} \right]. \quad (39)$$

This relationship takes the simplest form for a binary mixture:

$$K' = \frac{K}{m}. \quad (40)$$

Then (7), (8), (14), (16), (17), and (37) converts (36) to

$$\tau'_k = \sigma' x_k + H'_0 x_k \left(\alpha_{kM} - \sum_{i=1}^{M-1} \alpha_{iM} x_i \right) - \sum_{i=1}^{M-1} K'_{ki} \frac{\partial x_i}{\partial z}. \quad (41)$$

If the diffusion-coefficient matrix is known, we can use (29) and (41) directly to examine steady-state processes in the column, but these equations must be supplemented with appropriate equations of continuity for transient states, and these take the following forms for the mass and molar concentrations respectively:

$$\rho B \delta \frac{\partial c_k}{\partial t} + \frac{\partial \tau_k}{\partial z} = 0, \quad (42)$$

$$n B \delta \frac{\partial x_k}{\partial t} + \frac{\partial \tau'_k}{\partial z} = 0. \quad (43)$$

The following is an important point relating to the linearization of (29) and (41) for small values of c_k and x_k ; let the main component (solvent) be M, while the concentrations of the other components are low enough for us to take only the linear terms in the equations. In that case, the diffusion-coefficient matrix may be taken as diagonal, and

$$D_{ki} = D'_{ki} = D_k^{(M)} \delta_{ki}, \quad (44)$$

and therefore (17), (26)-(28), (39) give us that

$$K_{ki} = m K'_{ki} = K_k^{(M)} \delta_{ki}, \quad (45)$$

where

$$K_k^{(M)} = \frac{g^2 \beta^2 \rho^3 \delta^2 (\Delta T)^2 B}{9 \eta^2 D_k^{(M)}} + B \delta \rho D_k^{(M)}. \quad (46)$$

Then (29) and (41) become

$$\tau_k = \sigma c_k + H_0 \alpha_{kM} c_k - K_k^{(M)} \frac{\partial c_k}{\partial z}, \quad (47)$$

$$\tau'_k = \sigma' x_k + H'_0 \alpha_{kM} x_k - \frac{1}{m} K_k^{(M)} \frac{\partial x_k}{\partial z}. \quad (48)$$

An important point is that (47) and (48) are not always equivalent, because the conditions of smallness for c_k and x_k are themselves not always equivalent.

NOTATION

B	is the width of slot;
c_k	is the mass concentration of component k ;
D_{ki}	are the diffusion coefficients in the center-of-mass system;
D_{ki}^I	are the diffusion coefficients in the mole-center system;
D_k^T	is the thermal-diffusion coefficient for component k in the center-of-mass system;
D	is the diffusion coefficient for a binary mixture;
$D_k^{(M)}$	is the diffusion coefficient of the k -th component in solvent M at infinite dilution;
g	is the acceleration due to gravity;
M	is the number of components;
m_k	is the molar mass of component k ;
m	is the mean molar mass of mixture;
n_k	is the molar concentration of mixture;
T	is the absolute temperature,
\bar{T}	is the mean temperature in annulus;
ΔT	is the temperature difference across annulus;
u	is the mean molar velocity of mixture;
v_k	is the hydrodynamic velocity of component k ;
v	is the mean mass flow rate of mixture;
x_k	is the molarity of component k ,
z	is the height coordinate;
α_{ki}	is the thermal-diffusion constant for pair k and i ;
α	is the thermal diffusion constant for binary mixture;
β	is the volume expansion coefficient of mixture;
δ	is the width of annulus;
δ_{ki}	is the Kronecker symbol;
η	is the viscosity;
ρ_k	is the mass concentration of k -th component in mixture;
ρ	is the density of mixture;
σ	is the mass flow rate;
σ'	is the molar flow rate;
τ_k	is the mass flow rate of component k through column;
τ_k^I	is the molar flow rate of component k .

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