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]

\[ \rho_k (v_k - v) = -\rho \sum_{i=1}^{M-1} D_{ki} \nabla c_i - \rho D_k \nabla \ln T. \]  

(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 \( \alpha \):

\[ \rho_1 (v_1 - v) = -\rho D [\alpha c_1 + \alpha c_1 (1 - c_1) \nabla \ln T]. \]  

(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:

\[ \nabla c_1 = -\alpha c_1 (1 - c_1) \nabla \ln T. \]  

(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:

\[ \alpha_{k} = \alpha_k - \alpha_i, \]  

(4)

where the \( \alpha_k \) have the following simple relation to the steady-state concentration and temperature gradients measured:

\[ \nabla \ln c_k = -\alpha_k \nabla \ln T. \]  

(5)

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

\[ \sum_{i=1}^{M} c_i \alpha_i = 0. \]  

(6)

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

\[ D^T_h = \sum_{i=1}^{M-1} D_{hi} c_i. \]  

(10)

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

\[ D^T_h = \sum_{i=1}^{M-1} D_{hi} \sum_{j=1}^{M} c_i c_{ij}. \]  

(11)

We substitute (11) into (1) to get

\[ \rho_h (v_h - \nu) = -\rho \sum_{i=1}^{M-1} D_{hi} \left[ \nu c_i + c_i \sum_{j=1}^{M} c_{ij} \psi \ln T \right]. \]  

(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,

\[ \rho_h (v_h - \nu) = -\rho D \left[ \nu c_h + c_h \sum_{j=1}^{M} c_{ij} \psi \ln T \right], \]  

(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

\[ c_M = 1 - \sum_{j=1}^{M-1} c_j. \]  

(14)

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

\[ \rho_h (v_h - \nu) = -\rho \sum_{i=1}^{M-1} D_{hi} \left[ \nu c_i + c_i \left( c_{iM} - \sum_{j=1}^{M-1} c_{ij} \right) \psi \ln T \right]. \]  

(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 \( \alpha_{ki} \) 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 molecule-center system). In that case, the concentrations are expressed as molar fractions \( x_k \), which are clearly related to the mass values

\[ c_k = \frac{m_k}{m} x_k, \]  

(16)

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