Reference Frames in Diffusion

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It is frequently necessary to convert diffusion equations from one reference frame to another (*1*, *2*). In this note the transformation between two arbitrary reference frames is developed, and a few examples of interest in liquid systems are worked out.

The velocity of species i in an n component mixture is written as

$$v_i = u_i^R + V^R \qquad (1)$$

where the reference velocity is

$$V^R = \frac{\sum_{j=1}^{n} v_j \rho_j Z_j^R}{\sum_{j=1}^{n} \rho_j Z_j^R} = \frac{\sum_{j=1}^{n} n_j Z_j^R}{\sum_{j=1}^{n} \rho_j Z_j^R} \qquad (2)$$

Multiplying Equation (1) by ρ_i one gets the mass fluxes

$$n_i = J_i^R + \rho_i V^R \qquad (3)$$

and multiplying Equation (3) by Z_i^R and summing one gets

$$\sum_{j=1}^{n} J_j^R Z_j^R = 0 \qquad (4)$$

In terms of the second reference velocity $V^{R'}$ Equation (3) becomes

$$n_i = J_i^{R'} + \rho_i V^{R'} \qquad (5)$$

Equating (3) and (5) one gets

$$J_i^R - J_i^{R'} = \rho_i (V^{R'} - V^R) \qquad (6)$$

Multiplying Equation (5) by Z_i^R and summing, using Equation (2), one gets

$$V^{R'} - V^R = -\frac{\sum_{j=1}^{n} J_j^{R'} Z_j^R}{\sum_{j=1}^{n} \rho_j Z_j^R} \qquad (7)$$

and combining with Equation (6)

$$J_i^R = J_i^{R'} - \rho_i \frac{\sum_{j=1}^{n} J_j^{R'} Z_j^R}{\sum_{j=1}^{n} \rho_j Z_j^R} \qquad (8)$$

This is the desired relationship between the fluxes in the two coordinate systems.

The volume average velocity, which is of particular interest in liquid diffusion, is defined by letting $Z_j^{R'} = \bar{v}_j$, the partial mass volume of species j. Equation (2) then defines the volume average velocity.

Measured binary diffusion coefficients are usually defined by

$$J_i^V = -D_i^V \nabla \rho_i \qquad (9)$$

where superscript R' is now written as V, so J_i^V is the flux with respect to the volume average velocity. Assuming constant Z_i^R, and substituting Equation (9) into (8), one gets

$$J_i^R = -D^V (Z_1^R \rho_1 + Z_2^R \rho_2) \nabla \left(\frac{\rho_1}{Z_1^R \rho_1 + Z_2^R \rho_2} \right) \qquad (10)$$

Equation (10) gives the flux with respect to the reference velocity given by Equation (2). For $Z_i^R = 1$ the reference velocity from Equation (2) is the mass average velocity

$$V^m = v_1 w_1 + v_2 w_2 \qquad (11)$$

and the flux is

$$J_i^m = -D^V \rho \nabla w_i \qquad (12)$$

When $Z_i^R = 1/M_i$, the reference velocity is the molar average

$$V^M = v_1 x_1 + v_2 x_2 \qquad (13)$$

and the molar flux with respect to this velocity is

$$\phi_i^M = J_i^M / M_i = -D^V C \nabla x_i \qquad (14)$$

The relationship between Equations (9), (12), and (14) is given by Bird, Stewart and Lightfoot (*1*).

In multicomponent systems Equation (9) may be replaced by (*2*, *3*, *4*)

$$J_i^V = -\sum_{j=1}^{n-1} D^V_{ij} \nabla \rho_j \qquad (15)$$

which, with Equations (8) and (4), leads to

$$J_i^R = -\sum_{l=1}^{n-1} \left[D^V_{il} + \frac{w_i}{\sum_{k=1}^{n} w_k Z_k^R} \sum_{j=1}^{n-1} \left(Z_n^R \frac{\bar{v}_j}{\bar{v}_n} - Z_j^R \right) D^V_{jl} \right] \nabla \rho_l \qquad (16)$$

As before, with $Z_i^R = 1$ one gets the mass flux with respect to the mass average velocity

$$J_i^m = -\sum_{l=1}^{n-1} D^m_{il} \nabla \rho_l \qquad (17)$$

where

$$D^m_{il} = D^V_{il} + w_i \sum_{j=1}^{n-1} \left(\frac{\bar{v}_j}{\bar{v}_n} - 1 \right) D^V_{jl} \qquad (18)$$

and letting $Z_i^R = 1/M_i$ one gets the molar flux with respect to the molar average velocity

$$\phi_i = -\sum_{l=1}^{n-1} D^M_{il} \nabla C_l \qquad (19)$$

where

$$D^M_{il} = \frac{M_l}{M_i} D^V_{il} + x_i \sum_{j=1}^{n-1} \left(\frac{\bar{V}_j}{\bar{V}_n} - 1 \right) \frac{M_l}{M_j} D^V_{jl} \qquad (20)$$

$C_l = \rho_l / M_l$.

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NOTATION

- C = molar density
- u_i^R = velocity of species i with respect to reference velocity
- $\bar{V}$ = partial molal volume
- V^R = some weighted average of the individual velocities
- w = mass fraction
- x = mole fraction
- Z_i^R = weighing property
- ρ = density
- ρ_i = mass of species i per unit volume

LITERATURE CITED

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