Comment on "A Multicomponent Boundary Layer Chemically Coupled to an Ablating Surface"

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IN Ref. 1 there is presented inter alia an approximation which pertains to the binary diffusion coefficients $\mathfrak{D}_{ij}$, which is claimed to lead to convenience in the numerical treatment of multicomponent diffusive flows and which was apparently proposed first by Bird in a relatively inaccessible publication.[2] The approximation involves writing

$$\mathfrak{D}_{ij} \simeq \bar{D}(T,p)/F_iF_j \tag{1}$$

where F_i and F_j are at most weak functions of the temperature T. The accuracy of the approximation has been assessed in both Refs. 1 and 2 by comparing calculations based thereon with exact values of $\mathfrak{D}_{ij}$ for a variety of chemical systems and for those systems shown to lead to errors of less than roughly 17%. The apparent convenience achieved by the approximation is that there results an explicit relation for the mass flux of species i in terms of the gradient of concentration of species i and of a sum over gradients of all species.

It is the purpose of this comment to make two observations about the approximation of Eq. (1); the first concerns the absence of any fundamental basis for it. Note that according to the rigid sphere model (the treatment of F_i and F_j as constants appears analogous to the use of such a model)

$$\mathfrak{D}_{ij} \sim \frac{T^{3/2}}{p}\left[\left(\frac{m_i+m_j}{m_im_j}\right)^{1/2}\frac{1}{(\sigma_i+\sigma_j)^2}\right] \tag{2}$$

where m_i and σ_i denote the molecular weight and diameter of species i, respectively. Now comparison with Eq. (1) permits $\bar{D}$ to be identified and we can ask when may the [ ] quantity be approximated by a product F_iF_j. Clearly, if either $m_j \ll m_i$ and if $\sigma_j \ll \sigma_j$, or if the opposite inequalities apply, the approximation holds in the limit; it also holds if $m_j \simeq m_i$, $\sigma_i \simeq \sigma_j$ again in the limit but in general the answer must be that it does not hold! The strictly empirical nature of Eq. (1) is not made clear in Ref. 1 except by implication that the agreement with exact calculations is "surprisingly good."

The second observation pertains to the need for the approximation when detailed calculations of boundary-layer flows involving multicomponent diffusion are being performed. In these cases extensive numerical analysis is called for; depending on the method used it is convenient to have an explicit relation either for the gradient of concentration of species i in terms of the diffusive fluxes of all species and of the temperature gradient if thermal diffusion is included or for the diffusive flux of species i in terms of the gradients of concentration and of temperature. However either of these can be obtained numerically by multiplication of the general matrix system relating the diffusional fluxes, the gradients of concentration, and the temperature gradient by an appropriate inverse matrix which may be obtained for any order of interest from a standard subroutine. It is thus not evident to us that someone embarking on a large-scale computation of boundary layers with complex composition will wish to employ Eq. (1) which may introduce unnecessary empiricism.

References

[1] Kendall, R. M., Rindal, R. A., and Bartlett, E. P., "A Multicomponent Boundary Layer Chemically Coupled to an Ablating Surface," *AIAA Journal*, Vol. 5, No. 6, June 1967, pp. 1063–1071.

[2] Bird, R. B., "Diffusion in Multicomponent Gas Mixtures," presented at the 25th Anniversary Congress of the Society of Chemical Engineers (Japan), November 6–14, 1961; published in abbreviated form in *Kagaku Kogaku*, Vol. 26, 1962, pp. 718–721.

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Reply by Authors to P. A. Libby

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IN his comment, Professor Libby has advanced two observations, both relating to the approximation for binary diffusion coefficients proposed by Professor Bird‡ and later by ourselves. The first observation has to do with whether the approximation has a "fundamental basis"; the second pertains to the "need for the approximation." These two items will be discussed in that order.

Whether a fundamental basis exists depends primarily on the definition of "fundamental." Professor Libby seems to imply by this word the existence of a physical and associated mathematical model. Certainly no such model was advanced in our paper nor has one been developed subsequently to rationalize the success of the approximation. The fact that this approximation is not mathematically consistent with the rigid sphere model, or any other physical model for that matter, does not seem to be germane. It is, as we hoped we had clarified in the paper, a correlation equation. It permits the inexact replacement of sets of binary diffusion coefficients, whether measured or calculated, by smaller sets of parameters (the diffusion factors). Thus, the physical models upon which the original data are based are retained in the approximation, granted with some error. One cannot prove that such a correlation will always be successful. It is significant, therefore, that correlations have been performed for a variety of systems and have consistently resulted in little loss of accuracy[1] (as illustrated in Table 1 of our paper, errors are typically from 1 to 5% and seldom exceed 10%). It is also significant that all errors in $\mathfrak{D}_{ij}$ are known, and, furthermore, are known in advance. Thus, the approximation does not have to be employed in the event that some errors are unacceptably large.

In his comment, Professor Libby has related the proposed correlation expression with the rigid sphere model [his Eq. (2)]. We would like to state for the record that we see no significant analogy between "the treatment of F_i and F_j as constants" and "the use of such a (rigid sphere) model" as stated parenthetically in the comment. Furthermore, the arguments associated with Eq. (2) of the comment are ambiguous and demand some clarification. It has been well established that bifurcation can be accomplished exactly for any binary or ternary system and therefore his Eq. (2) and the associated arguments can only be viewed from the standpoint of a multicomponent system. Certainly if all $\mathfrak{M}_i$ and σ_i are equal, the bifurcation of the bracketed term will be precise. However, the large inequality postulate presented is insufficient to describe a multicomponent system, and, furthermore, *no* system including such an inequality permits an exact bifurcation of the bracketed term. It

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‡ Professor Bird's paper cited in our original paper is now available in English as NASA TT F-10, 925.