

Table 2 (Cont.)

|                          |    |       |        |        |        |
|--------------------------|----|-------|--------|--------|--------|
| Fluorobenzene            | 56 | 71.52 | 29.020 | 0.0962 | 0.0943 |
|                          | 58 | 71.35 | 28.912 | 0.0830 | 0.0813 |
|                          | 59 | 71.69 | 28.705 | 0.0839 | 0.0815 |
|                          | 60 | 71.56 | 28.919 | 0.0825 | 0.0808 |
| <i>n</i> -Butyl chloride | 62 | 73.13 | 29.280 | 0.0907 | 0.0894 |
|                          | 63 | 72.82 | 29.255 | 0.0911 | 0.0898 |
|                          | 64 | 71.56 | 29.434 | 0.0893 | 0.0889 |
| Ethyl bromide            | 65 | 71.39 | 29.316 | 0.1072 | 0.1065 |
|                          | 66 | 71.82 | 28.683 | 0.1082 | 0.1050 |
|                          | 67 | 72.86 | 28.992 | 0.1063 | 0.1038 |

<sup>a</sup> Diffusion coefficient at test conditions.

<sup>b</sup> Diffusion coefficient corrected to 75 F and 1 atm by equation (20).

Table 3 Calculated and measured diffusion coefficient  $D_{AB}$ , sq cm/sec (values corrected to 75 F and 1 atm)

| Material                 | Chapman-Enskog | Wilke-Lee | Slattery-Bird | Chen-Othmer | Average Other Work             | Average Present Work |
|--------------------------|----------------|-----------|---------------|-------------|--------------------------------|----------------------|
| <i>n</i> -Hexane         | 0.0763         | 0.0836    | 0.0799        | 0.0729      | 0.0804 [11, 12]                | 0.0807               |
| <i>n</i> -Heptane        | 0.0675         | 0.0740    | 0.0735        | 0.0658      | 0.0734 [11, 12, 13]            | 0.0692               |
| Benzene                  | 0.0873         | 0.0956    | 0.0905        | 0.0865      | 0.0951 [10, 12, 13, 14, 8, 16] | 0.0938               |
| Carbon tetrachloride     | 0.0749         | 0.0822    | 0.0825        | 0.0783      | 0.0836 [17]                    | 0.0762               |
| Ethyl acetate            | 0.0846         | 0.0927    | 0.0848        | 0.0821      | 0.0848 [8, 10, 15]             | 0.0844               |
| Ethyl iodide             | 0.0868         | 0.0954    | 0.0899        | 0.0828      |                                | 0.0951               |
| Fluorobenzene            | 0.0815         | 0.0893    | 0.0858        | 0.0827      |                                | 0.0812               |
| <i>n</i> -Butyl chloride | 0.0798         | 0.0874    | 0.0843        | 0.0786      |                                | 0.0894               |
| 1,2-Dichloroethane       | 0.0869         | 0.0952    | 0.0905        | 0.0901      |                                | 0.0890               |
| Ethyl bromide            | 0.0967         | 0.1061    | 0.0992        | 0.0925      |                                | 0.1051               |

## DISCUSSION

### J. V. Beck<sup>3</sup>

The authors are commended on their analytical technique for the determination of the Fick diffusion coefficient. Of particular merit is the extensive use of least squares in the analysis.

I would like to suggest a method, however, that utilizes nonlinear least squares in a more direct fashion than the least-squares method of the authors. The availability of nonlinear least-squares subroutines such as Gaussaus [19] alleviates any increased programming complexity over that for linear least squares. The method is basically simple; one minimizes the sum of squares function

$$F(D_{AB}) = \sum_{i,j} (X_{Aij} - X_{Aij}^e)^2 \quad (21)$$

with respect to  $D_{AB}$ . (This can be done using Gaussaus.) The subscripts  $i$  and  $j$  refer to time  $\theta_i$  and position  $Z_j$ .  $X_{Aij}$  is calculated from the mathematical model; it could be found from a finite-difference solution of equation (5) with the boundary and initial conditions. This would be appropriate if the exact solution were not known. In the present case equations (6), (7), and (8) constitute the exact solution. The experimental value of  $X_A$ , designated  $X_A^e$ , is found from equation (9) which is a function of  $S$  which can be calculated from the  $\Delta s$  measurements. The  $\Delta s$  measurements are given times  $\theta_i$  and positions  $Z_j$ .

One of the points made in the paper is that the "technique combines a special relative-time and relative-position data analysis." The method outlined in this discussion can be simply extended to do this also by minimizing  $F$  in equation (21) with respect to some reference position  $K_r$  and some reference time  $\theta_0$  as well as  $D_{AB}$ .

The authors no doubt had good reasons for their procedure but the following are some respects in which it is felt the method just described is superior to the authors' method.

1 Some statistical statements can be made regarding the accuracy.

2 The procedure is a logical extension of linear least squares and as such can be (and has been) applied to various other problems of determining parameters in differential equations [20, 21, 22].<sup>4</sup>

3 The general problem of parameters estimation in differential equations is currently being given a great deal of attention by control and system engineers, chemical engineers, mathematicians, and statisticians. It is usually better to apply techniques that are generally applicable and that have been carefully studied rather than special techniques for each problem.

4 The method extends in a logical manner determining more than one parameter at a time. For example, one might desire  $D_{AB}$  as a linear function of  $T$  or  $X_A$ ; this would introduce more parameters to be found at one time. Note that it is not necessary that the sum of squares function  $F$  be restricted to a single experiment. Another summation over experiments could be introduced.

5 It has been found from some related problems for finding thermal diffusivity that an "optimum" experiment can be performed in terms not only of boundary conditions but of locations and times for measuring  $X_A$  [20]. A key to finding an optimum experiment is the examination of the sensitivity coefficients such as  $D_{AB}\partial X_A/\partial D_{AB}$  and  $K_r\partial X_A/\partial K_r$ . It would be particularly interesting to plot  $D_{AB}\partial X_A/\partial D_{AB}$  versus  $E$  for several values of  $Q$ . It will be found for both  $E = 0$  and  $\infty$  that the sensitivity coefficient is zero and thus a maximum absolute value occurs at some finite  $E$ . It turns out to be about 0.75 for small values of  $Q$ . Measurements taken at  $E$  values when the sensitivity coefficient is large will be more effective in accurate  $D_{AB}$  determination than when the coefficient is small.

It may be that the authors have previously considered such a procedure. It is probably true that the authors' procedure might require less computer time and that it is easier to program if a subroutine such as Gaussaus were not available. Could the

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<sup>4</sup> Numbers in brackets designate Additional References at end of discussion.

authors comment on this method relative to the one given in their paper?

The authors are again congratulated on an excellent contribution.

#### Additional References

20 Beck, J. V., "Analytical Determination of Optimum, Transient Experiments for Measurement of Thermal Properties," *Proceedings of the Third International Heat Transfer Conference*, Vol. IV, 1966, pp. 74-80.

21 Beck, J. V., "Transient Sensitivity Coefficients for the Thermal Contact Conductance," *International Journal of Heat and Mass Transfer*, Vol. 10, 1967, pp. 1615-1617.

22 Pfahl, R. C., Jr., "Nonlinear Least Squares: A Method for Simultaneous Thermal Property Determination in Ablating Polymeric Materials," *Journal of Applied Polymer Sciences*, Vol. 10, 1966, pp. 1111-1119.

#### Authors' Closure

The authors would like to thank Prof. Beck for his detailed interest and comments on the paper. His proposed technique certainly seems to have merit and could probably provide significant information, especially in the areas of items (1) and (4) if the present technique were extended to variable temperatures and pressures as suggested by the authors.

However, it should be noted that the method presented by the authors seems to be the most logical approach based on the objectives of the research project. Accordingly, the linear least squares technique was utilized because the points to be curve fit were on a straight line by theory, as seen in equations (16) and (19). In fact, the requirements for a straight line were used as a significant criteria in judging the accuracy of the test model to simulate the mathematical model. Additionally, the optimization of an experiment for certain values of  $E$  is fine in principle, but the range of  $E$  values measured as a function of  $\theta$  and  $Z$  were generally dictated by factors other than sensitivity coefficients. Some of these factors are the optical properties of the material, the test cell geometry, and the fringe shift measurement equipment. Significantly enough, however, a review of the original test data indicated that interferogram interpretation seemed to be most accurate for values of  $E$  in the range near 0.75, and the values of  $Q$  were small for the materials tested.

Finally, application of Prof. Beck's technique could possibly encounter difficulty in the interpretation of the reference position  $Kr$ , as it is a general point, not a common point for all test runs or for interferograms in the same test run. Once again this is due to the restrictions on the ability to read fringe shifts at the same location for different test materials or test times. Of course, this flexibility on  $Kr$  is one of the principle advantages in the present technique. If this difficulty does not present a problem, Prof. Beck's comments would certainly be valid.