LETTERS TO THE EDITOR

TO THE EDITOR: SELF-DIFFUSION IN LIQUIDS

In the recent papers of Dullien (1972) and Vadovic and Colver (1972) on the self-diffusion coefficient in liquids, the group $(D\mu V/T)$ is correlated with either V_c, critical volume (cm^3/mole) [Equation (26) of Dullien], or with V_m, molal volume at melting point (cm^3/mole) [Equation (10) of Vadovic and Colver], to estimate the value of the self-diffusion coefficient. Both of their correlations could reproduce the experimental data satisfactorily, and Vadovic and Colver concluded that the choice of V_c or V_m depends entirely on the availability of the critical or melting point data.

Tyn and Calus (1974) have shown that for most of the liquids V_c can be related to V_b, molal volume at normal boiling point (cm^3/mole), as

$$V_b = 0.285\, V_c^{1.048} \qquad (1)$$

By combining Equation (1) with Dullien's equation, the following expression can be obtained:

$$\frac{D\mu V}{T} = 0.229 \times 10^{-8}\, V_b^{0.636} \qquad (2)$$

where D is in cm^2/s, μ in centipoise, T in °K and V in cm^3/mole at T.

Equation (2) represents the self-diffusion data in Figure 1 (taken from Dullien) with an average accuracy of 4.8% which is comparable to the quoted accuracy of 4% by Dullien's equation.

Therefore, the self-diffusion coefficient of a liquid may be estimated to the same degree of accuracy by either the equations of Dullien, or Vadovic and Colver, or the equation presented here, depending on the availability of data for the terms V_c, V_m, or V_b.

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LETTER TO THE EDITOR

In a Letter to the Editor, Tsang and Luus (1972) commented on a paper by Jaspan and Coull (1972), anticipating the publication by Rao and Luus (1972).

Rao and Luus promised a "systematic approach to determine the stepping parameter ϵ" which we are in no position to argue with at the present time. However, they misquoted us in stating that "the initially guessed policies as given by Fine and Bankoff (1967) and by Lee (1968) are the *only* two initial control policies that will give convergence to the optimum when CVI (Control Vector Iteration) method is applied." We, in fact, said that no success *has been reported* using any other initial guess.

We challenge Rao and Luus as to how they can state that their method "is thus more efficient when compared to the BCI, GBCI and Horns method" of Jaspan and Coull. Since the computation was done on different machines, the IBM 370/165 being possibly ten times faster than the IBM 7090, this is a rash claim. In fact, the authors stand by their recommendation for the use of Horns method and feel that, if applicable, this must be the fastest method in unconstrained problems. It is also significant to note that Rao and Luus do not specify their starting value of K nor their convergence criteria.

The authors thus feel that the letter of Tsang and Luus (1972) is far from being a scientific appraisal of our paper. We recommend that they try Horn's method.

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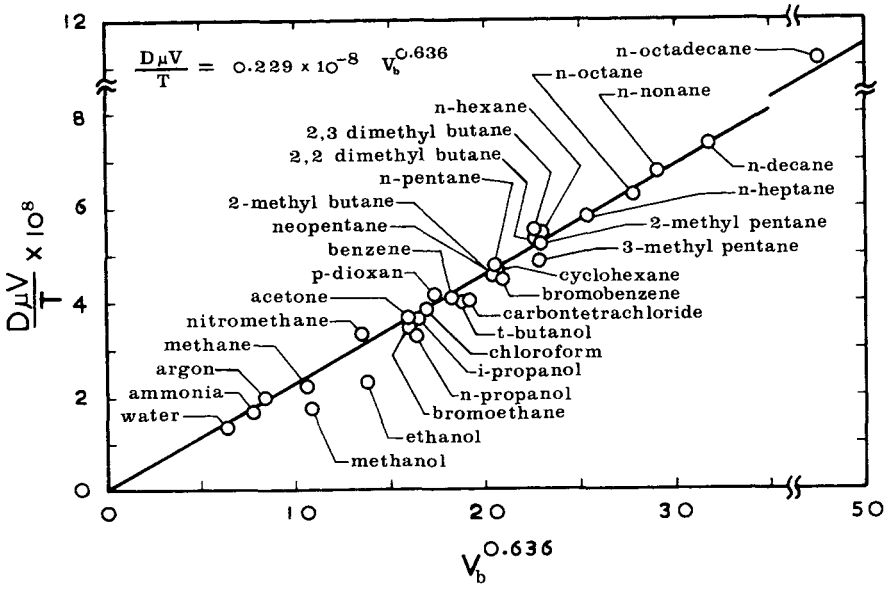

Fig. 1. Correlation of self-diffusion coefficient for pure liquids.

TO THE EDITOR: BCI VS. CVI

To answer the comments of Jaspan and Coull (1974), four different methods were programmed in Fortran IV to solve the reactor optimization problem considered by Jaspan and Coull (1971, 1972). For integration, a standard subroutine based on Runge-Kutta method was used and the integration step size was 0.1 min. An IBM 370/165 computer was used, and all computations were performed in double precision.

Since the objective was to compare the boundary condition iteration (BCI) methods to the control vector iteration (CVI) methods, a preliminary run was made to establish equivalent convergence criteria. It was found that $e < 0.001$ for BCI corresponds to $x_2(t_f) > 0.6792$ for CVI and that $e < 0.0001$ corresponds to $x_2(t_f) > 0.6800$. The notations of Jaspan and Coull (1971) and of Rao and Luus (1972) are used throughout this letter. The problem corresponds to $t_f = 10.0$ with $x_{10} = 0.95$ and $x_{20} = 0.05$ for which the optimum value of $x_2(t_f)$ is 0.68015.

Jaspan and Coull (1971) were unable to get convergence by using the method of Denn and Aris (1965) because of their misinterpretation of the latter method. For purposes of comparison of BCI to CVI, both BCI methods were run and the results are given in Tables 1 and 2. The initial value used for the stepping parameter ϵ for the BCI method of Jaspan and Coull was 0.02 and for the BCI method of Denn and Aris was 0.10. These were the largest values that could be used without instability and were determined from several preliminary runs. During the course of iteration when overstepping occurred, as determined by the error e, the stepping parameter ϵ was halved.

The CVI method of Rao and Luus (1972) does not require any preliminary runs since the stepping parameter is determined from

$$\epsilon = \frac{P}{2|Q|} \tag{1}$$

and if overstepping occurs, a new value of ϵ is chosen from

$$\epsilon_{new} = \frac{\epsilon}{2[1 + \delta I/(\epsilon P)]} \tag{2}$$

where the parameters are defined by Rao and Luus (1972). Although the CVI method of Rao and Luus requires the evaluation of several auxiliary functions, there are only 2 state equations and 2 adjoint equations to be integrated vs. 5 equations for the BCI method of Denn and Aris. Furthermore, since in the CVI method the control (temperature) is kept constant over an integration time step, the rate constants k_1 and k_2 can be evaluated outside the integration subroutine and do not have to be re-evaluated for backward integration. Therefore, in spite of the extra functions that must be evaluated, the computation time per iteration for the CVI method is about the same as for the BCI method. For direct comparison purposes, both the number of iterations

Table 1. Computational Requirements for Convergence to $e < 0.001$

$x_1(t_f)^{(0)}$	$x_2(t_f)^{(0)}$	Number of iterations: BCI method of Jaspan and Coull	BCI method of Denn and Aris
0.15	0.75	337	81
0.15	0.74	317	78
0.15	0.73	291	74
0.15	0.72	255	36
0.15	0.71	191	61
0.15	0.70	9	50
0.15	0.69	401	18
0.15	0.68	515	37
0.15	0.67	584	56
0.15	0.66	N*	65
Total Cpu time, min.		4.23	0.66
Cpu time/iteration, min.		0.00108	0.00119

* N denotes nonconvergence after 1000 iterations.

Table 2. Computational Requirements for Convergence to $e < 0.0001$

$x_1(t_f)^{(0)}$	$x_2(t_f)^{(0)}$	Number of iterations: BCI method of Jaspan and Coull	BCI method of Denn and Aris
0.15	0.75	537	126
0.15	0.74	517	123
0.15	0.73	491	119
0.15	0.72	455	58
0.15	0.71	391	106
0.15	0.70	178	94
0.15	0.69	801	63
0.15	0.68	916	82
0.15	0.67	985	101
0.15	0.66	N*	110
Cpu time, min.		6.77	1.18
Cpu time/iteration, min.		0.00108	0.00120

* N denotes nonconvergence after 1000 iterations.

Table 3. Number of Iterations Required for Convergence to $x_2(t_f) > 0.6792$ (Corresponding to $e < 0.001$)

K	Method of Rao and Luus	Horn's method proposed by Jaspan and Coull	Proposed Horn's method
335	5	49	4
340	4	43	4
345	4	37	4
350	5	30	1
355	6	21	3
360	7	8	3
365	8	7	2
370	9	14	4
375	10	17	7
380	12	18	9
Total Cpu time, min.	0.08	0.21	0.05
Cpu time/iteration, min.	0.00114	0.00086	0.00122

Table 4. Number of Iterations Required for Convergence to $x_2(t_f) > 0.6800$ (Corresponding to $e < 0.0001$)

K	Method of Rao and Luus	Horn's method proposed by Jaspan and Coull	Proposed Horn's method
335	7	58	4
340	4	52	5
345	7	45	4
350	7	38	3
355	8	30	4
360	9	17	3
365	10	15	3
370	11	22	5
375	12	24	7
380	15	26	9
Total Cpu time, min.	0.10	0.29	0.05
Cpu time/iteration, min.	0.00111	0.00089	0.00106

and the computation time are given in each table.

When the initial value of $x_2(t_f)$ was held at 0.70 and ten initial values of $x_1(t_f)$ were taken from 0.15 to 0.06, the BCI method of Denn and Aris required 0.61 min. of computation time to reach $e < 0.001$ and 1.09 min. to reach $e < 0.0001$. With the BCI method of Jaspan and Coull, only 5 cases were run corresponding to $x_1(t_f) = 0.15, 0.14, 0.13, 0.12$, and 0.11. The computation times were 2.67 min. to obtain $e < 0.001$ and 3.89 min to obtain $e < 0.0001$. For the initial value of $x_1(t_f) = 0.11$ and $x_2(t_f) = 0.70$, convergence, however, was not obtained within 1000 iterations.

In Tables 3 and 4 the computational results of the CVI method based on the method of Rao and Luus (1972) are given. Also, Horn's method as proposed by Jaspan and Coull (1971) was run for comparison. As can be seen, the CVI method is considerably faster. It should be noted also that for the CVI method isothermal initial trajectories were used

$$u^{(0)}(t) = K \quad 0 \leq t < 10 \qquad (3)$$

whereas for Horn's method

$$u^{(0)}(0) = K \qquad (4)$$

so that the CVI method is placed at a disadvantage.

A modification is proposed for the Horn's method. Instead of using $\epsilon = 0.05$ initially, it is proposed to use $\epsilon = 1.0$ and then to halve ϵ whenever overstepping occurs. This modification greatly improves the method to make it comparable to CVI method for convergence to $x_2(t_f) > 0.6792$ and better for convergence to $x_2(t_f) > 0.6800$.

It is, however, important to note that even with the presently proposed modification to Horn's method, the CVI method is still faster with the choice of $K = 340$ and $x_2(t_f) > 0.6800$. This refutes the statement of Jaspan and Coull (1974) that Horn's method must be the fastest method in unconstrained problems.

The letter of Tsang and Luus (1972) and the present letter have not been intended to appraise the work of Jaspan and Coull but to defend the position of CVI methods in the face of unjustified claims of Jaspan and Coull. Although Tables 1 to 4 do not give a complete picture, it is nevertheless clear that we should not be too hasty in dispatching the CVI methods.

The tables also show that the claim of Tsang and Luus (1972) that the CVI method is superior to the BCI, GBCI, and Horn's method (as formulated by Jaspan and Coull) for this particular example is not rash at all. In fact, the CVI method is about 10 times faster than the BCI method and about 3 times faster than the latter method, not to mention the extra effort required for the procedures of Jaspan and Coull to obtain the initial values for ϵ and the initial range for $x_1(t_f)$ and $x_2(t_f)$ to ensure stability. It should also be noted that Horn's method is not a boundary condition iteration method.

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BOOKS *(continued from page 1037)*

The book is illustrated with good line drawings and with photographs. A few of the photographs are not of the first quality. Bibliographic listings are somewhat skimpy, possibly because the author leaned heavily on instrument manufacturer's literature for much of his basic information. A convenient summary of all the on-line analyzers described in the book is presented in a table preceding the index. The table contains these items: (1) manufacture, (2) quantitative capability, (3) power supply requirements, (4) physical dimensions, (5) weight, and (6) electrical safety classification. A list of the addresses of selected instrument manufacturers in the United States, the United Kingdom, and Europe is also included.

Any reader familiar with a particular kind of analyzer will doubtlessly find some gaps in the coverage provided by Clevett. This is inevitable in a field which is developing at so fast a rate. Nonetheless, this book is the best presentation of the current state of the art on instruments for process stream analysis.

The readership to which this work is directed includes practicing chemical engineers involved in plant design or operation, laboratory analysts, and instrument engineers in almost any field of food, chemical, or petroleum manufacture. Advanced undergraduates or professional engineers in these fields will find this handbook a valuable source of information.

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New Developments in Gas Chromatography, Howard Purnell, (Ed.), John Wiley, New York (1973). 408 pages. $9.95.

This book is Vol. 11 in the *Advances in Analytical Chemistry and Instrumentation* series edited by C. N. Reilley and R. W. Murray and contains seven articles describing developments in the forensic applications of gas chromatography, applications of digital computers to GC; applications of gas chromatography to production-scale separations, and GC studies of reaction kinetics, solvent phase changes, chemical complex formation, and the structure of polymers.

The articles are well written and noteworthy in that, unlike too many other *Advances* compendia, the articles have sufficient breadth and background to make their material accessible to research workers who are not specialists in each field. In addition, the articles present overviews of fields of application rather than a catalog of the contents of the long bibliographies that are an essential part of this type of book.

The review of chemical reactor applications of GC is particularly timely, as is the section on forensic applications of GC. The section on production scale gas chromatography presents suggested criteria for choosing GC over more conventional industrial separation techniques but lacks any discussion of gas chromatography processes such as hypersorption, and others which have reached commercial scale. The article also fails to note that a major commercial source of production-scale GC columns, referred to frequently, is no longer available.

The book is recommended strongly as a useful reference.

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