

## Separation of isotopically substituted liquids in the thermal diffusion column

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Isotopic separation of several liquid compounds was studied experimentally in a precisely constructed, 60-cm thermal diffusion column at wall spacings of 0.254 and 0.383 mm. The systems studied were benzene, cyclohexane, carbon disulfide, 1-chloropropane, and bromoethane. The measurements for benzene and cyclohexane included the  $C_6H_6$ - $C_6D_6$  and the  $C_6H_{12}$ - $C_6D_{12}$  pairs. The experiments were done under both static and flowing conditions in order to get experimental values of the initial transport coefficient and the remixing coefficient of the column for each system. The experimentally determined remixing coefficients were found to agree with those predicted from the theory of the thermal diffusion column. Experimental values of the thermal diffusion factor were obtained from the initial transport coefficients. A simple mass-dependent relationship was found to be inadequate to describe the results even for different isotopic substitutions within the same compound. Results for the  $C_6H_6$ - $C_6D_6$  pair were found to agree quite well with recalculated results based on the early work of Korsching.

## I. INTRODUCTION

The separation of mixtures by liquid phase thermal diffusion has been the subject of many investigations.<sup>1,2</sup> For the most part, this work has been confined to nonisotopic mixtures. The separation of isotopes by liquid phase thermal diffusion has received limited attention although the method was applied on a large scale to uranium isotope separation<sup>3</sup> not long after the discovery of the thermogravitational column by Clusius and Dickel in 1938.<sup>4</sup>

In a lengthy review article published in 1960 Alexander<sup>5</sup> summarized previous work on isotopic separation and discussed in some detail the elementary effect, the theory of the column and the characteristics of the ideal separation apparatus. In 1968 Rabinovich<sup>6</sup> attempted to explain the existing data for the isotopic thermal diffusion factor in terms of a simple mass relationship. The data available at that time comprised 11 measurements. Of these, five were direct measurements of the elementary effect in liquid metals and molten salts; the remainder were column measurements on various halogenated compounds,<sup>7,8</sup> benzene,<sup>9</sup> water,<sup>10,11</sup> and  $UF_6$ .<sup>3</sup>

The theory of the thermal diffusion column, developed originally by Furry, Jones, and Onsager<sup>12</sup> for gases, appears to be at least qualitatively correct in predicting the behavior of liquid columns. Good quantitative agreement between theoretical predictions and liquid phase column measurements, however, has apparently not been achieved. There are several possible reasons for this, among which are the following: (1) Precise, reliable single-stage measurements of the thermal diffusion factor are rare. (Most column work has been restricted to the measurement of the equilibrium separation which is directly related

to the thermal diffusion factor; thus, comparison with theory requires the accurate *a priori* knowledge of this quantity.) (2) Most experiments have involved mixtures of components of substantially different properties; therefore, the properties of the fluid in the column were functions of position, both horizontal and vertical. The effect of composition on density, in particular, has acquired some notoriety as the "forgotten" effect; and at one time it was postulated that the direction of the convective circulation of the column could be reversed by the separation of a higher density component toward the hot wall.<sup>13</sup> The recent work of Korchinsky and Emery,<sup>14</sup> Korsching,<sup>15</sup> and Horne and Bearman<sup>16-19</sup> has shown that the importance of this effect had been greatly overestimated; and it appears on the basis of Korchinsky and Emery's work that apparent experimental observations of the reversal of the convective circulation resulted from defects in the experimental apparatus. (3) Practical liquid phase thermal diffusion columns require a spacing between the hot and cold walls on the order of 0.2-0.5 mm.

The behavior of the column is exquisitely sensitive to spacing, and the problem of constructing an apparatus of satisfactorily known geometry is a formidable one. Steep temperature gradients, on the order of 500-5000°C/cm, are associated with the small spacing. Thus heat fluxes are large, and significant local variations in temperature are difficult to avoid.

Horne and Bearman,<sup>19</sup> Beyerlein and Bearman,<sup>20</sup> and Stanford and Beyerlein<sup>21</sup> recently reported some success in the measurement of nonisotopic thermal diffusion factors with the column. These recent results are in quite good agreement with

results obtained by other workers in single-stage experiments. The experiments of Bearman, Beyerlein, and others involved the use of short, high precision columns operated at small temperature differences. These conditions lead to small separations, hence the effects of concentration differences on the physical properties of the fluid are minimized.

In recent papers the author reported the successful use of the thermal diffusion column for accurate determinations of the thermal diffusion factors of nonisotopic<sup>22</sup> and isotopic<sup>23</sup> gas mixtures. These measurements were likewise carried out at small temperature differences in relatively short columns. In addition, the gas phase experiments were designed to yield an independently determined value of the convective remixing coefficient. Comparison of the experimental remixing coefficient with theory served as an important test of the column theory and of the performance of the experimental column.

This paper describes the results of liquid phase thermal diffusion column experiments with isotopic mixtures. The experiments had two basic objectives: (1) evaluation of the validity of existing column theory and (2) development of a reliable experimental technique for determining isotopic thermal diffusion factors of liquids. The use of isotopic mixtures effectively eliminates those ambiguities in column behavior which are related to the effect of composition on properties. Somewhat offsetting this desirable simplification, however, is the fact that more extreme conditions are required to get satisfactorily large separations in isotopic systems. For this reason much of the effort herein described was devoted to deuterated systems with large differences in molecular weight in the expectation that these systems would offer relatively higher separations.

## II. THEORY OF THE THERMAL DIFFUSION COLUMN

The theory of the cylindrical thermal diffusion column was derived by Furry, Jones, and Onsager (FJO) for binary isotopic mixtures.<sup>12</sup> There was no inherent restriction in this treatment to either the liquid or gas state. The integrals appearing in the FJO theory, however, are relatively easy to evaluate for the typical conditions of a liquid column experiment; and the resulting expressions have been widely used for predicting separations of nonisotopic mixtures.

The FJO theory does not take into account the effect of the separation on the properties of the fluid, specifically the density. A number of attempts have been made to include the effect of

the radial separation on the density (the "forgotten effect"). The recent work of Horne and Bearman appears to have solved the problem for the special case of a column at the steady state with no net flow. It seems that the effect on column performance is small, and for isotopic mixtures it is vanishingly small.

In a recent paper<sup>24</sup> the author developed the theory of the thermal diffusion column for non-isotopic gas mixtures; however, the assumptions of that treatment in no way confine the results to dilute gases. The expressions derived from the theory are identical to those of the FJO theory except that the mole fractions appearing in the column transport equation are replaced by mass fractions. Thus the transport of component 1 of a binary mixture is given by

$$\tau_1 = Hw_1w_2 - (K_c + K_d)dw_1/dz + \sigma w_1, \quad (1)$$

where  $\tau_1$  is mass per unit time of component 1 transported in the positive  $z$  direction;  $w_1$  and  $w_2$  are the mass fractions; and  $\sigma$  is the net mass flow rate through the column.

The quantities  $H$ ,  $K_c$ , and  $K_d$  are the initial transport coefficient, the convective remixing coefficient, and the diffusive remixing coefficient, respectively. According to Ref. 24 these are given by the following expressions:

$$H = 2\pi \int_{T_1}^{T_2} [\alpha_T G(T)/T] dT, \quad (2)$$

$$K_c = (2\pi/Q) \int_{T_1}^{T_2} [\lambda G^2(T) D_{12} \rho] dT, \quad (3)$$

$$K_d = (2\pi/Q) \int_{T_1}^{T_2} \lambda D_{12} \rho r^2 dT, \quad (4)$$

where  $T_1$  and  $T_2$  are the temperatures at the cold and hot walls of the column, respectively,  $\alpha_T$  is the thermal diffusion factor,  $2\pi Q$  is the radial heat flow per unit length,  $\lambda$  is the thermal conductivity,  $D_{12}$  is the diffusion coefficient,  $\rho$  is the density, and  $r$  is the radial coordinate.

The quantity  $G(T)$  is related to the mass circulation rate in the column and is given by solution of the fourth order differential equation

$$Q^3 \frac{d}{dT} \frac{1}{r^2 \lambda} \frac{d}{dT} \frac{\eta d}{\lambda dT} \frac{1}{\rho \lambda r^2} \frac{dG}{dT} = -g \frac{d\rho}{dT}, \quad (5)$$

where  $g$  is the acceleration of gravity and the following boundary conditions apply:

$$G = dG/dT = 0 \quad \text{at } T = T_1 \text{ and at } T = T_2. \quad (6)$$

Strictly, these conditions pertain only to the case for which  $\sigma = 0$ ; however, no appreciable error is introduced as long as  $\sigma$  is negligible relative to the convective mass circulation rate in the column. This is the case for most experimental conditions

of interest, especially for those involving isotopic mixtures.

Relatively simple expressions can be obtained for the column coefficients if the assumption is made that the physical properties of the fluid, other than density, are constant and equal to the values at the arithmetic average temperature, and if the hot and cold walls of the column are assumed to be plane parallel surfaces. The density is allowed to vary with a constant thermal expansion coefficient in the solution of Eq. (5) and is otherwise assumed to be constant, e. g., in Eqs. (2)–(4). With these restrictions the following expressions are obtained for the column coefficients:

$$H = a^3 \rho^2 \alpha_T \beta g B (T_1 - T_2)^2 / 6! \eta \bar{T}, \quad (7)$$

$$K_c = a^7 g^2 \beta^2 \rho^3 B (T_1 - T_2)^2 / 9! \eta^2 D_{12}, \quad (8)$$

$$K_d = a \rho D_{12} B, \quad (9)$$

where  $\bar{T}$  is the arithmetic average temperature,  $a$  is the horizontal spacing between the hot and cold walls.  $B$  is the width of the column, and  $\beta$  is the thermal expansion coefficient. Equations (7)–(9) are good approximations for the typical cylindrical liquid column for which  $a$  is small relative to the radii of the hot and cold walls; thus,  $B$  is taken as the average circumference of the column.

For the static, steady-state case ( $\tau_1 = 0, \sigma = 0$ ) the concentration gradient in the column can be obtained from Eq. (1):

$$dw_1/dz = H w_1 w_2 / (K_c + K_d). \quad (10)$$

If  $K_d$  is taken to be negligible (usually the case), then substitution of 7 and 8 into 10 yields

$$dw_1/dz = 504 \alpha_T \eta D_{12} / a^4 g \rho \beta \bar{T}. \quad (11)$$

For the case  $a \ll r_1$  this result is identical to that obtained by Horne and Bearman,<sup>19</sup> provided that the contribution of the forgotten effect is omitted.

In general it would appear to be preferable to avoid the somewhat restrictive assumptions leading to Eqs. (7)–(9), especially if large temperature differences prevail between the hot and cold walls of the columns. The direct numerical integration of Eqs. (2)–(5) is relatively easy to accomplish; hence, column coefficients can be based on tabulations of the physical properties of the fluid as functions of temperature. This approach has been used extensively by the author in previous work on gas phase thermal diffusion.

### III. EXPERIMENTAL APPARATUS

The liquid thermal diffusion column used in this investigation was designed explicitly for measurement of isotopic separations. The dimensions and operating temperatures were chosen to yield large

separation factors which could be readily measured in a mass spectrometer of limited precision. The column was provided with two interchangeable hot walls of different dimensions so that measurements could be made at two values of the spacing between the hot and the cold walls. The apparatus included a calibrated pumping system for establishing a known steady-state flow rate through the column. It was designed to operate at pressures as high as 70 atm.

The column, Fig. 1, was 61 cm in length between the end ports. The cold wall was a water-cooled stainless steel tube, 5 cm o. d. and  $1.907 \pm 0.0002$  cm i. d. at 20 °C. The hot wall was a steam-heated stainless steel tube 1.27 cm i. d. and either  $1.8272 \pm 0.0005$  or  $1.8529 \pm 0.0005$  cm o. d. at 25 °C, according to whether a gap width of 0.254 or 0.383 mm was desired. Uniformity of the gap was established by piano wire spacers spot welded at 5-cm intervals along the hot wall. At each vertical location six spacers, each 0.5 cm long, were placed around the circumference of the tube.

Clearance for assembly of the hot wall into the cold wall resulted from the fact that the hot wall was some 0.003 cm smaller in diameter at the assembly temperature of 25 °C than at the operating temperature. In the strictest sense, correct spacing between hot and cold walls occurs at a single hot wall temperature, a temperature such that the expansion of the hot wall is just sufficient to allow all spacers to contact the cold wall. In this connection it should be pointed out that the rather common practice of heating the outside wall of the

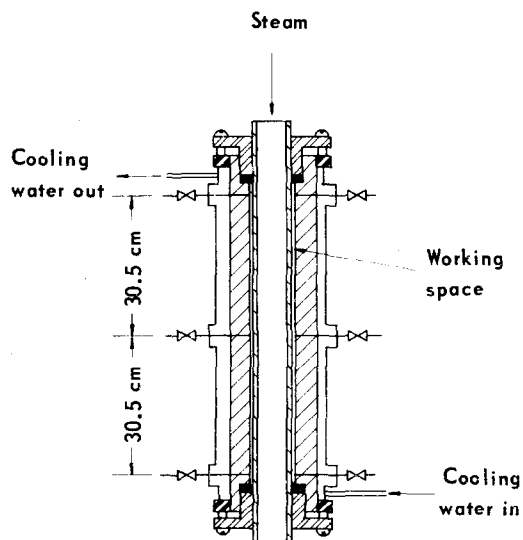


FIG. 1. Liquid thermal diffusion column.

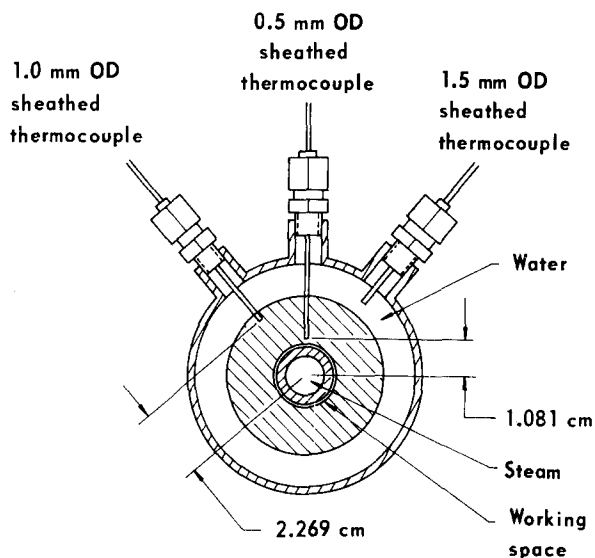


FIG. 2. Cross sectional view of experimental liquid thermal diffusion column showing locations of thermocouples.

column and cooling the inside wall leads to exaggerated errors in spacing, and the annular gap in such a device will be nonuniform in width to the extent of the sum of the assembly tolerance and the thermal expansion effect.

The experimental column contained no internal reservoirs. It was provided with three pairs of connecting ports. The end ports, which were 61 cm apart, were positioned 2.5 cm from the top and bottom of the column, respectively. The third set of ports was in the middle of the column. Each port was connected to a  $\frac{1}{16}$  in. miniature high pressure valve by a length of 0.5-mm-i.d. tubing.

Thermocouples were placed in the column wall and in the cooling water at two vertical positions 46 cm apart. As shown in Fig. 2 three thermocouples were emplaced at each of the two positions. Thermal calibration runs with fluid of known thermal conductivity (helium gas) were used to determine the several thermal resistances between the condensing steam on the hot side and the cooling water on the cold side. The inner and outer cold wall temperatures and the temperature of the condensing steam were sufficient for the evaluation of the horizontal heat flux and of the hot and cold temperatures at the boundaries of the annular gap. Because high heat fluxes were involved in material of low thermal conductivity, the boundary temperatures were appreciably different from the condensing steam and cooling water temperatures, respectively.

Auxiliary equipment (Fig. 3) for the column included a system for preparing and supplying degassed feed liquid, a buffer vessel to maintain the system at a pressure above the bubble point pressure at the column hot wall temperature, and a pumping system to establish known, controlled flow rates of liquid through the column.

The buffer vessel was a particularly important feature of the apparatus. It provided the small amount of volumetric capacity necessary to sustain system pressure after removal of samples and during fluctuations caused by temperature variations, pump switching, and other disturbances. Thus, it was possible to operate the system with low molecular weight fluids having normal boiling points well below the hot wall temperature of the column.

Several attempts to use buffer vessels with diaphragms or pistons to separate the liquid from an auxiliary source of compressed gas were failures as the result of gas migration across the barrier. The design finally adopted was highly successful. It consisted simply of a vertical thimble maintained at a temperature somewhat higher than the hot wall temperature of the column. The liquid thus came in contact only with its own vapor. The pressure remained constant as long as the thimble contained both liquid and vapor.

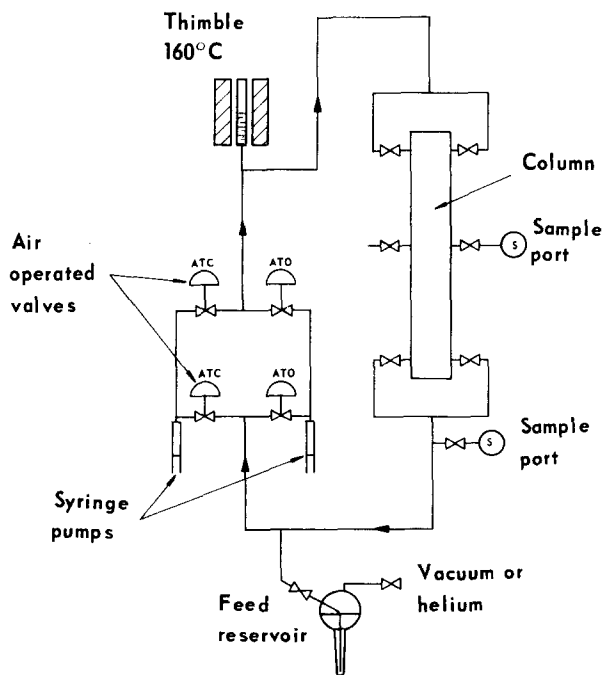


FIG. 3. Flow diagram for liquid thermal diffusion experiments.

The pumping system was based on two alternately operating syringe pumps driven through change gears by synchronous motors. The syringes had a single stroke capacity of 3.5 ml and were specially fabricated from stainless steel. A system of air-operated valves switched the syringes between intake and discharge. Time delays were built into the switching system so that both intake and discharge valves were never open simultaneously. By choice of the gear ratio the pumping rate of the tandem system could be varied between 0.0232 and 115.9 ml/hr.

#### IV. EVALUATION OF THE THERMAL DIFFUSION FACTOR FROM COLUMN MEASUREMENTS

The separation experiments were designed to obtain experimentally derived values of the initial transport coefficient  $H$  and the total remixing coefficient  $K = K_c + K_d$ . (For the conditions of this investigation  $K_d$  is negligible; hence,  $K = K_c$ .) The procedure involves (1) measurement of the separation factor of the column at static, steady-state conditions and (2) measurement of the separation factor of the column as a function of an imposed flow rate  $\sigma$ .

The ratio  $H/K$  is evaluated from the static, steady-state separation measurement. Under these conditions the separation factor of the column is given by the integral of Eq. (10); thus,

$$\ln q_e = \ln \left( \frac{(w_1/w_2)_T}{(w_1/w_2)_B} \right) = \frac{HL}{K}, \quad (12)$$

where  $q_e$  is the static separation factor and  $L$  is the length of the column section. The subscripts  $T$  and  $B$  refer to the top and bottom of the column section, respectively.

The initial transport coefficient  $H$  is obtained from measurements of separation as a function of flow rate. The solution of Eq. (1) for the steady flow case ( $\sigma \neq 0$ ) is given by Jones and Furry<sup>25</sup> for flow in the downward ( $-z$ ) direction as

$$\tanh \left( \frac{bY}{2} \right) = \frac{b(w_{1B} - w_{1T})}{w_{1B} + w_{1T} - (\sigma/H)(w_{1B} - w_{1T}) - 2w_{1B}w_{1T}}, \quad (13)$$

where

$$b = \{ [1 + (\sigma/H)]^2 - (4\sigma w_{1B}/H) \}^{1/2} \quad (14)$$

and

$$Y = HL/K. \quad (15)$$

The experimental value of  $H$  is taken as that value which yields the best least squares fit of Eq. (13) to the flow separation data. The experimental value of the coefficient  $K$  is subsequently calculated from Eq. (12).

The thermal diffusion factor is obtained from the experimental value of  $H$ . The average value of the thermal diffusion factor over the temperature range between the hot and cold walls is given by

$$\bar{\alpha}_T = 2\pi \int_{T_1}^{T_2} \frac{\alpha_T G(T) dT}{T} / 2\pi \int_{T_1}^{T_2} \frac{G(T) dT}{T}. \quad (16)$$

If a quantity  $\xi$  is defined by

$$\xi = 2\pi \int_{T_1}^{T_2} [G(T)/T] dT, \quad (17)$$

then

$$\bar{\alpha}_T = H/\xi. \quad (18)$$

The experimental value of  $\alpha_T$  is obtained by insertion of the experimental value of  $H$  in Eq. (18). The quantity  $\xi$  is evaluated from theory.

In order for the above procedure to be valid it is necessary to provide independent confirmation that the behavior of the column is adequately described by theory. This can be supplied by comparison of the experimentally derived value of the remixing coefficient  $K_c$  with the value predicted from theory. The theoretical expression for  $K_c$  does not involve the thermal diffusion factor; hence, *a priori* knowledge of the thermal diffusion factor is not required to demonstrate validity of the column theory. In the rigorous sense this comparison is not conclusive, and compensating errors or effects may be present even when good agreement is obtained.

In its essential features this method for determining isotopic thermal diffusion factors from column measurements is similar to the procedure used in earlier work by the author on isotopic and nonisotopic gas mixtures.

#### V. RESULTS

Isotopic separation measurements were made under static and flowing conditions with the following compounds: benzene, cyclohexane, carbon disulfide, and 1-chloropropane. A single static separation measurement was made for bromoethane. The column operating conditions for these measurements are given in Table I. In order to avoid sampling difficulties the flow separation measurements pertained only to the lower half of the column and were based on samples taken from the middle and bottom ports. Some of the systems were examined at both of the two available gap dimensions, 0.254 and 0.383 mm. In general, the more readily separable systems were studied with the larger gap and the less readily separable systems with the smaller gap. For all experiments separation factors were evaluated from mass spectrometrically determined isotope ratios.

The benzene isotopic system was a prepared

TABLE I. Dimensions and operating conditions for liquid thermal diffusion experiments.

Compound	$t_H$ (°C)	$t_c$ (°C)
I. $a=0.383$ mm, $r_H=0.9154$ cm, $r_c=0.9537$ cm.		
Benzene	127	40
Cyclohexane	129	37
1-Chloropropane	130	35
Bromoethane	131	35
II. $a=0.254$ cm, $r_H=0.9282$ cm, $r_c=0.9537$ cm		
Benzene	139	53
Carbon disulfide	137	55
1-Chloropropane	143	46

mixture of 2%  $C_6D_6$  in ordinary benzene. Separation of the mass 84 species from the mass 78 species was determined as a function of flow rate for both configurations of the experimental column. These data are plotted in Fig. 4. (Most of the points plotted in Fig. 4 and in subsequent figures are averages of several measurements made over a period of several days.) Initial transport coefficients were evaluated from the experimental results for each annular spacing, and experimental values of  $\alpha_T$  were subsequently calculated using Eq. (18). These results and the experimentally derived values of the remixing coefficient are given in Table II. For the evaluation of  $\xi$  the references listed in Table III were used as sources for the required physical properties. Where it was necessary to extrapolate the density to higher temperatures the correlation given in Ref. 34 was employed. The other properties were extrapolated according to the following rules:

$$\eta(T) = \eta(T_0)e^{-A/T}, \quad (19)$$

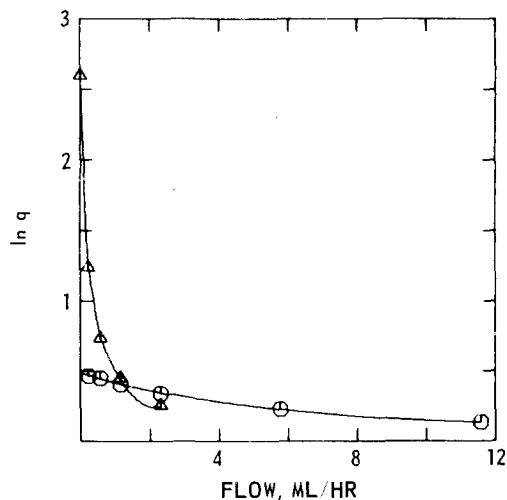


FIG. 4. Separation as a function of flow rate for the  $C_6H_6-C_6D_6$  system in the liquid thermal diffusion column. The triangles are data for a spacing of 0.254 mm and the circles are for a spacing of 0.383 mm. The solid lines are best fits for Eq. (13).

$$D_{12}(T) = T D_{12}(T_0) \eta(T_0)/\eta(T) T_0, \quad (20)$$

$$\lambda(T) = \lambda(T_0) [V(T)/V(T_0)]^{4/3}, \quad (21)$$

where  $A$  is a constant and  $V$  is the molar volume.

All calculations leading to the column coefficients and the quantity  $\xi$  were done by numerical integration of the appropriate expressions, e.g., Eqs. (2)–(5) and (15). Smoothed tables of the necessary physical properties as functions of temperature were used as input for these calculations.

The separation of the mass 79 species of benzene (primarily  $^{13}C^{12}C_5H_6$ ) from the mass 78 species was also measured for static conditions only. The

TABLE II. Column parameters and thermal diffusion factors derived from liquid thermal diffusion experiments.

Compound	Gap (mm)	Isotope pair	$H$ , exptl (g/sec)	$K$ , exptl (g·cm/sec)	$K$ , theory (g·cm/sec)	$\alpha_T$	$\alpha_0$
Benzene	0.383	$C_6D_6-C_6H_6$	$4.2 \times 10^{-4}$	0.026	0.032	0.15 <sup>a</sup>	4.1
	0.254	$C_6D_6-C_6H_6$	$1.54 \times 10^{-4}$	0.0018	0.0020	0.18 <sup>a</sup>	4.8
	0.383	$^{13}C^{12}C_5H_6-^{12}C_6H_6$	...	...	...	0.015 <sup>b</sup>	2.3
	0.254	$^{13}C^{12}C_5H_6-^{12}C_6H_6$	...	...	...	0.019 <sup>b</sup>	2.9
Cyclohexane	0.383	$C_6D_{12}-C_6H_{12}$	$4.7 \times 10^{-4}$	0.020	0.019	0.25 <sup>a</sup>	3.7
	0.383	$^{13}C^{12}C_5H_{12}-^{12}C_6H_{12}$	...	...	...	0.017 <sup>b</sup>	2.9
Carbon disulfide	0.254	$C^{32}S_2-C^{32}S^{34}S$	$1.28 \times 10^{-4}$	0.0077	0.0071	0.062 <sup>a</sup>	4.9
1-Chloropropane	0.383	$C_3H_7^{35}Cl-C_3H_7^{37}Cl$	...	...	...	0.030 <sup>b</sup>	2.4
	0.254	$C_3H_7^{35}Cl-C_3H_7^{37}Cl$	$4.6 \times 10^{-5}$	0.0055	0.0062	0.021 <sup>a</sup>	1.7
Bromoethane	0.383	$C_2H_5^{79}Br-C_2H_5^{81}Br$	...	...	...	0.020 <sup>b</sup>	2.1

<sup>a</sup>From measurement of initial transport coefficient.

<sup>b</sup>From static separation factor.

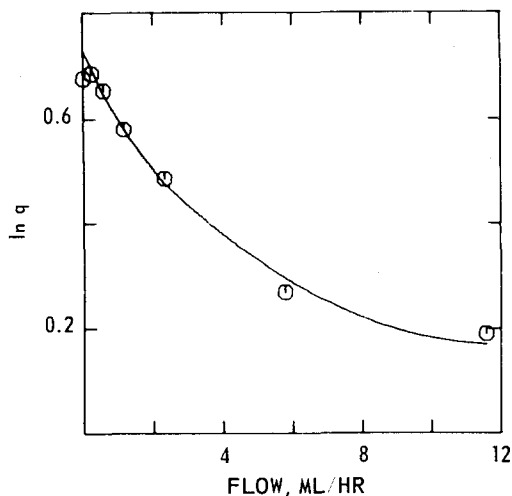


FIG. 5. Separation as a function of flow rate for the  $C_6H_{12}-C_6D_{12}$  system in the liquid thermal diffusion column. The points are data for the 0.383-mm spacing. The solid line is the best fit of Eq. (13).

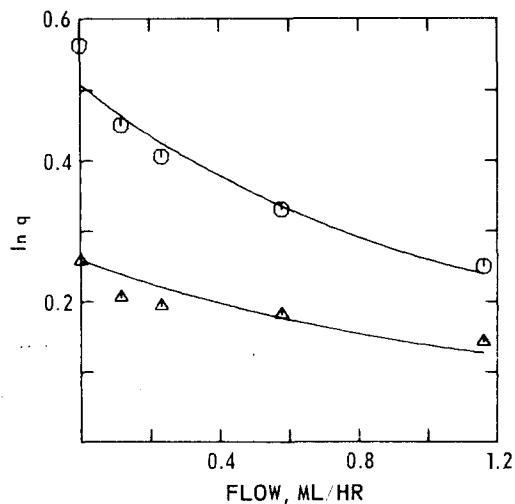


FIG. 6. Separation as a function of flow rate for carbon disulfide and 1-chloropropane in the liquid thermal diffusion column at a spacing of 0.254 mm. The circles are data for carbon disulfide and the triangles are data for 1-chloropropane. The solid lines are best fits of Eq. (13).

thermal diffusion factor for the mass 79 species was evaluated on the basis of static separation measurements; thus,

$$[\alpha_T]_{79-78} = [\alpha_T]_{84-78} [\ln q_e]_{79-78} / [\ln q_e]_{84-78} \quad (22)$$

Cyclohexane separation measurements were carried out for a mixture of 2%  $C_6D_{12}$  in  $C_6H_{12}$ . The results appear in Fig. 5 and Table II. For this system the separations were much larger than in the case of benzene, and it proved impractical to use the 0.254-mm annular gap; thus the results pertain only to the 0.383-mm gap. The data were processed in the same manner as for benzene, and a value of  $\alpha_T$  was likewise obtained for the  $^{13}C^{12}C_5H_{12}-^{12}C_6H_{12}$  pair by a procedure similar to that given in Eq. (22).

Carbon disulfide, 1-chloropropane (Fig. 6) and bromoethane were studied as natural isotopic mixtures. For these systems the separations were much smaller, and the precision of the re-

sults is accordingly somewhat less. As indicated in Table II, the value of  $\alpha_T$  for the bromoethane system was evaluated from static measurements only. Inasmuch as the experimental results for  $K$  agree reasonably well with column theory for all of the other systems, this procedure should be accurate. Unfortunately, however, the separation for bromoethane was extremely small; and the resulting value of  $\alpha_T$  is substantially more uncertain than is the case for the other systems.

Assessment of the over-all precision of the data given in Table II for the thermal diffusion factor is difficult. The agreement between theory and experiment for the remixing coefficient, which is more sensitive to experimental conditions, suggests that an estimate of  $\pm 15\%$  would not be unreasonable. The two sets of measurements of the thermal diffusion factor for benzene support this estimate of the error.

TABLE III. Sources of physical property data.

Compound	Density	Viscosity	Diffusion coefficient	Thermal conductivity
Benzene	26, 27	28, 29, 27	30, 31, 32, 33	28, 34, 29, 35, 36
Cyclohexane	37, 38, 27	39, 40, 37, 28, 27	41, 42	36
Carbon disulfide	43, 37	37, 28	44	37
1-Chloropropane	45, 46, 29, 34	34	47 <sup>a</sup>	37
Bromoethane	37, 45, 46, 29	37, 26, 45	30, 47	35, 48

<sup>a</sup> Based on value of  $D\eta/kT$  for similar compounds in Ref. 47 ( $k$  is the Boltzmann constant).

TABLE IV. Re-evaluation of Korsching experiment on separation of  $C_6D_6$  from  $C_6H_6$  by liquid thermal diffusion.

Column length	9.6 cm
Column spacing	0.25 mm
Hot wall temperature	71 °C
Cold wall temperature	30 °C
$\ln q_e$ , observed	4.702
$\alpha_T$ , from original calculation	0.22
$\xi/K$ , recalculated	0.490 $cm^{-1}$
$\alpha_T$ , recalculated	0.15

## VI. DISCUSSION

On the basis of the results of this work as given in Table II, it appears that the theory of the thermal diffusion column in its present form is satisfactory. For several systems and two different values of the spacing parameter, agreement within the estimated precision of the experiments was obtained for the column remixing coefficient. This coefficient is directly related to the internal convective circulation rate which is in turn a sensitive function of the experimental geometry and column operating conditions. In addition, the observed relationship between the separation factor and flow rate as well as the static separation factor are well represented by the use of a single value of  $H$ , the initial transport coefficient.

The isotopic separation of benzene in the thermal diffusion column was measured by Korsching<sup>9</sup> many years ago, and a value of the thermal diffusion factor for the  $C_6D_6$ - $C_6H_6$  pair was reported. The value reported, however, was based on calculations involving physical property data which have since been superseded. Specifically, the self-diffusion coefficient of benzene is now much more accurately known. Accordingly, the calculation of the thermal diffusion factor from the Korsching separation measurement was redone on the basis of the property data assembled for the present investigation. The necessary column coefficients were evaluated by numerical integration of Eqs. (2)–(5), and the thermal diffusion factor was calculated from the following relationship:

$$\alpha_T = \frac{\ln q_e}{\xi L/K} \quad (23)$$

The results of the calculation are given in Table IV. A significant difference is noted between the old and the new values of  $\alpha_T$  obtained from the separation data. The new value is in quite good agreement with the results of this investigation.

The recent work of Rabinovich<sup>6</sup> indicates that the reduced thermal diffusion factor  $\alpha_0$ , defined by

$$\alpha_0 = \alpha_T (m_1 + m_2)/(m_1 - m_2), \quad (24)$$

where  $m$  and  $m_2$  are the molecular weights of 1 and 2, is a constant approximately equal to 5.4. This semiempirical result is based on published data for several systems including organic compounds, liquid metals, molten salts, and  $UF_6$ . The published data show a wide variation from the average value of 5.4; they range from  $\alpha_0 = 2.8$  to  $\alpha_0 = 9.3$ .

The reduced thermal diffusion factors for the several measurements of this investigation are given in Table II. The values are all smaller than the value of 5.4 suggested by Rabinovich. Moreover, they show rather sizeable deviations from constancy; and the deviations are appreciably greater than the estimated experimental error. The possibility of a simple mass dependence for the thermal diffusion factor can apparently be eliminated on the basis of the data involving  $^{13}C$  and deuterium substitutions in the same compound. If any experimental bias exists, it will be reflected equally in the calculation of the two sets of data. The not surprising conclusion is that the thermal diffusion factor must involve more than a molecular mass dependence.

The chlorine and bromine substituted compounds used in this work do not afford a direct comparison with results obtained by Alexander and co-workers<sup>5,7,8</sup> for other compounds. Generally, the reduced thermal diffusion factors for the compounds listed in Table II are substantially lower by a factor of 3 or 4. There does not appear to be any reason to attribute this discrepancy to imperfections in the apparatus used by Alexander, although he did not make use of an independent check of the behavior of the column with respect to theory. Column imperfections generally lead to low separation factors; hence, thermal diffusion factors for columns of poor geometry are similarly low. Alexander and co-workers determined isotopic concentrations at the ends of the columns by means of density measurements. This procedure may have resulted in some error in the determination of the separation factors. Mass spectrometric measurement of the isotopic concentration, as used in the present work, is felt to be more accurate.

It is of some interest to compare column coefficients evaluated by numerical integration of Eqs. (2)–(5) with those obtained from the much simpler approximate relationships of Eqs. (7)–(9). Test calculations for benzene under the conditions used in this work showed a difference of 3% for the initial transport coefficient, 0.5% for the convective remixing coefficient, and 4.4% for the diffusive remixing coefficient. At the present level of experimental accuracy, it does not appear that any

important error is incurred in using the simple relationships.

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<sup>1</sup>G. R. Grove, USAEC Report MLM-1088, 1959.

<sup>2</sup>J. E. Powers, "Separation of Liquids by Thermal Diffusion," University of California Radiation Laboratory Report UCRL-2618, August 1954.

<sup>3</sup>P. H. Abelson, N. Rosen, and J. I. Hoover, *Liquid Thermal Diffusion* (USAEC Technical Information Service, Oak Ridge, TN, 1951).

<sup>4</sup>K. Clusius and G. Dickel, *Naturwissenschaften* **26**, 546 (1938).

<sup>5</sup>K. F. Alexander, *Fortschr. Phys.* **8**, 1 (1960).

<sup>6</sup>G. D. Rabinovich, *Inzh.-Fiz. Zh.* **15**, 1014 (1968).

<sup>7</sup>K. F. Alexander and U. Krecker, *Kernenergie* **1**, 437 (1958).

<sup>8</sup>K. F. Alexander and R. Dreyer, *Z. Naturforsch. A* **10**, 1034 (1955).

<sup>9</sup>H. Korsching, *Naturwissenschaften* **31**, 348 (1943).

<sup>10</sup>H. Korsching and K. Wirtz, *Naturwissenschaften* **27**, 367 (1939).

<sup>11</sup>I. Prigogine, L. de Brouckere, and R. Buess, *Physica (Utr.)* **18**, 915 (1952).

<sup>12</sup>W. H. Furry, R. C. Jones, and L. Onsager, *Phys. Rev.* **55**, 1083 (1939).

<sup>13</sup>I. Prigogine, L. de Brouckere, and R. Amand, *Physica (Utr.)* **16**, 577 (1950), *Physica (Utr.)* **16**, 851 (1950).

<sup>14</sup>W. J. Korchinsky and A. H. Emery, Jr., *AIChE J. (Am. Inst. Chem. Eng.)* **13**, 224 (1967).

<sup>15</sup>H. Korsching, *Z. Naturforsch. A* **18**, 669 (1963).

<sup>16</sup>F. H. Horne and R. J. Bearman, *J. Chem. Phys.* **37**, 2842 (1962).

<sup>17</sup>F. H. Horne and R. J. Bearman, *J. Chem. Phys.* **37**, 2857 (1962).

<sup>18</sup>F. H. Horne and R. J. Bearman, *J. Chem. Phys.* **46**, 4128 (1967).

<sup>19</sup>F. H. Horne and R. J. Bearman, *J. Chem. Phys.* **49**, 2457 (1968).

<sup>20</sup>A. Beyerlein and R. J. Bearman, *J. Chem. Phys.* **49**, 5022 (1968).

<sup>21</sup>D. J. Stanford and A. Beyerlein, *J. Chem. Phys.* **58**, 4338 (1973).

<sup>22</sup>W. M. Rutherford, *J. Chem. Phys.* **54**, 4542 (1971).

<sup>23</sup>W. M. Rutherford, *J. Chem. Phys.* **58**, 1613 (1973).

<sup>24</sup>W. M. Rutherford, *J. Chem. Phys.* **53**, 4319 (1970).

<sup>25</sup>R. C. Jones and W. H. Furry, *Rev. Mod. Phys.* **18**, 151 (1946).

<sup>26</sup>*Landolt-Börnstein Physikalisch-Chemische Tabellen* (Springer

Verlag, Berlin, 1936), 5th ed.

<sup>27</sup>F. D. Rossini *et al.*, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* (Carnegie, Pittsburgh, PA, 1953).

<sup>28</sup>*American Institute of Physics Handbook* (McGraw-Hill, New York, 1963), 2nd ed.

<sup>29</sup>*Handbook of Chemistry and Physics* (Chemical Rubber, Cleveland, OH, 1961), 44th ed.

<sup>30</sup>K. Graupner and E. R. S. Winter, *J. Chem. Soc. (Lond.)* **1952**, 1145.

<sup>31</sup>H. Hiraoka, J. Osugi, and W. Jono, *Rev. Phys. Chem. Jap.* **28**, 52 (1968).

<sup>32</sup>R. E. Rathburn and A. L. Babb, *J. Phys. Chem.* **65**, 1072 (1961).

<sup>33</sup>W. Dietrich, B. Gross, and R. Kosfeld, *Z. Naturforsch. A* **25**, 40 (1970).

<sup>34</sup>*Chemical Engineers Handbook* (McGraw-Hill, New York, 1963), 4th ed.

<sup>35</sup>J. E. S. Venart, *J. Chem. Eng. Data* **10**, 239 (1965).

<sup>36</sup>J. K. Horrocks, E. McLaughlin, and R. Ubbelohde, *Trans. Faraday Soc.* **59**, 1110 (1963).

<sup>37</sup>*International Critical Tables* (McGraw-Hill, New York, 1926).

<sup>38</sup>S. E. Wood and J. A. Gray III, *J. Am. Chem. Soc.* **74**, 3729 (1952).

<sup>39</sup>K. M. Khalilov, *Russ. J. Phys. Chem.* **36**, 1341 (1962).

<sup>40</sup>J. A. Dixon and R. W. Schiessler, *J. Phys. Chem.* **58**, 430 (1953).

<sup>41</sup>M. V. Kulkarni, G. F. Allen, and P. A. Lyons, *J. Phys. Chem.* **69**, 2491 (1965).

<sup>42</sup>D. W. McCall, D. C. Douglas, and E. W. Anderson, *J. Chem. Phys.* **31**, 1555 (1959).

<sup>43</sup>*Encyclopedia of Chemical Technology* (Wiley, New York, 1964), 2nd ed., Vol. 4.

<sup>44</sup>R. C. Koeller and H. G. Drickamer, *J. Chem. Phys.* **21**, 267 (1953).

<sup>45</sup>J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds* (Elsevier, New York, 1950), Vol. I.

<sup>46</sup>S. A. Mumford and J. W. C. Phillips, *J. Chem. Soc. (Lond.)* **1950**, 75.

<sup>47</sup>L. H. Stein and P. C. Carman, *J. S. African Chem. Inst.* **9**, 55 (1956).

<sup>48</sup>J. E. S. Venart, *J. Sci. Instrum.* **41**, 727 (1964).