

# Interdiffusion and Density Measurements in Some Binary Liquid Mixtures

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**Diffusion coefficients and densities of the three systems *n*-octane-carbon tetrachloride, *n*-decane-carbon tetrachloride, and *n*-dodecane-carbon tetrachloride were determined at 25°C over the complete composition ranges. The average standard error of the diffusion coefficients was about 0.3%, which is comparable with the error of the cell calibration. The measured data were compared with the predictions of some empirical correlations.**

This work represents part of a continuing program (6, 18, 16, 10) intended to supply diffusion data for the testing and formulation of theoretical models describing liquid state behavior.

The diaphragm cell method has been accepted for some time now as one of the most reliable and convenient techniques of measuring diffusion coefficients in liquids (22, 13). For solutions containing volatile constituents, the data normally scatter considerably more than in the case of nonvolatile compounds (6, 18). In the present study the standard error of the diffusion data on three binary systems consisting of *n*-paraffins and carbon tetrachloride has been kept at a comparable level as is usually obtained with nonvolatile systems.

Correlations have been suggested for the prediction of liquid diffusivities in binary solutions at infinite dilutions, among others by Scheibel (20), Wilke and Chang (25), Othmer and Thakar (14), Sitaraman et al. (21), and Lusi and Ratcliff (17). For the estimation of diffusivities over the entire composition range of regular solutions, Vignes (23) and Cullinan (4) have suggested a simple equation. The data obtained in this work have been compared with the predictions of these correlations.

## Experimental

**Apparatus. Balance.** All mass measurements were made with a Mettler Gram-atic semimicro balance having a stated precision of  $2 \times 10^{-5}$  gram. Static electricity, which tended to collect on glassware and produce erroneous weight measurements (10), was dissipated by ionizing the air within the balance case with a radioactive Cesium pencil.

As suggested by Dullien (6), a standard bottle was calibrated to correlate apparent bottle weight to air density, and air buoyancy corrections were made in all precise gravimetric analyses.

**Diffusion cells.** The diffusion cells and the associated stirring device used in this work have been patterned after those of Dullien (6) and were constructed in this lab by Puri (16). A schematic diagram of a cell is shown in Figure 1.

**Cell support and stirring apparatus.** Figure 2 shows a cross-sectional view of the stirring mechanism and one of the six cell supports. The support consists of a copper sleeve (1), a molded Plexiglas base (4), and three teflon screws (5).

Surrounding each sleeve is a brass gear (9) mounted with Alinco magnets (8). The magnets are rotated at 80 rpm (10) by a central brass gear (10) coupled to a variable speed motor (Gerald K. Heller, Model 6T 60-20; motor controller, Model CX-25) by means of a drive shaft (11) and a flexible rubber coupling. A central aluminum supporting structure containing two ball bearings (13 and 14) stabilized the drive shaft. The structure also supported a linen laminated phenol formaldehyde resin plate (15) (trade name Garlite) on which rested all the brass gears. The entire setup is contained in an oil bath, the details of which have been described (24).

**Density apparatus.** Initially, modified Sprengel pycnometers (6) were used to determine organic solution densities. The use of pycnometers was later superseded by a precision density meter (24).

**Materials.** The organic chemicals were obtained from the sources listed below. The manufacturer's minimum purity specifications have been included with the results of gas chromatographic analysis. No attempts were made to purify these materials.

Chemical	Supplier	Specifications, min	Gc, mass %
<i>n</i> -Octane	Phillips Petroleum Co.	99 mol %	99.9
<i>n</i> -Decane	Phillips Petroleum Co.	99 mol %	99.6
<i>n</i> -Dodecane	Phillips Petroleum Co.	99 mol %	98.3
Carbon tetrachloride	Fisher Scientific Co.	ACS	99.97

The potassium chloride which was used for calibration purposes was supplied by J. T. Baker Chemical Co. and had a stated purity of 99.9 mass %.

**Procedure. Calibration of diffusion cells.** The diaphragm diffusion cells were calibrated with Woolf and Tilly's data (26) for the diffusion of potassium chloride into water according to the method of Stokes (22).

In each calibration, a 0.5*N* KCl solution diffused into initially pure water. Much of the diffusion runs followed standard procedure (described in detail in refs. 24, 6, and 18).

**FILLING THE CELLS.** To suppress bulk flow, the denser KCl solution was normally placed in the bottom compartment. In filling the bottom compartment, all valves of Figure 1 were closed except I and IV. The end of stem 4 was submerged in a 100-cc beaker of solution, and a vacuum was applied at stem 1 until the bottom compartment, the diaphragm, and approximately 2 cm of the top compartment had been filled. Valve I was then closed, valve III opened, and the solution forced to completely fill stem 3 by use of the vacuum at 3. At the end of this procedure, valve III was closed.

After the solution and diaphragm were degassed (24), the cell was first forced air cooled and then placed in the oil bath for approximately 20 min. Stirring was allowed to occur within the cell to achieve rapid temperature equilibrium. At the end of this period, the bottom compartment was checked to ensure that no air bubbles were present; then with only valves III and IV closed, the KCl

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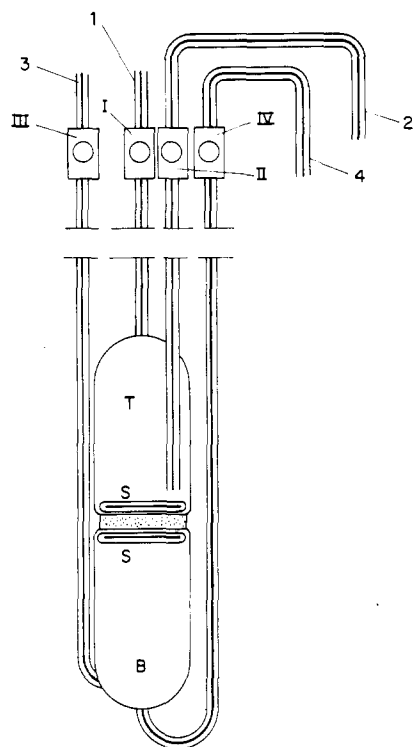


Figure 1. Diaphragm diffusion cell

solution was drained out of the top compartment by applying vacuum on stem 2. As much solution as possible was removed by inclining the cell; then the few remaining drops of solution were drained by completely inverting the cell and quickly drawing off the solution through stem 1. Residual solution was removed by twice rinsing the compartment with 15-cc quantities of cool, freshly boiled, deionized water. In each case, the liquid was drained as above. The top compartment and stems were then completely filled with pure water by again applying vacuum on stem 1 and drawing water in through stem 2.

This marked the beginning of the preliminary diffusion period. At the end of this time, the top compartment was again drained, rinsed, and filled as described above.

The quasi steady-state assumption used in the diaphragm diffusion cell formula (6, 18, 13, 8, 19) specifies that a linear concentration gradient exists within the diaphragm. This is attained in a satisfactory approximation (8) after letting diffusion take place for a time approximately given by the formula  $t = 1.2 l^2/D$ , where  $l$  is the effective path length of diffusion in the diaphragm. In the present work, about 2.5 hr were allowed for preliminary diffusion.

Since small changes occurred in the concentrations during this time, it was necessary to replace the contents of the top compartment with pure water before the actual run began. To allow for any small changes in volume during both the preliminary and actual runs, valve I was always left open. The rest of the valves were closed.

The diffusion runs were timed with an accurate wrist-watch. The beginning of the run was marked by the start of the final filling of the top compartment. The end of the run was taken to be the instant when the sample from the top compartment was taken. Robinson (18) has shown that the minimum error in determining diffusivities occurs at the optimum time  $t_{opt} = 1.2/\beta D$ , where  $\beta$  is the "cell constant." The error minimum, however, is quite

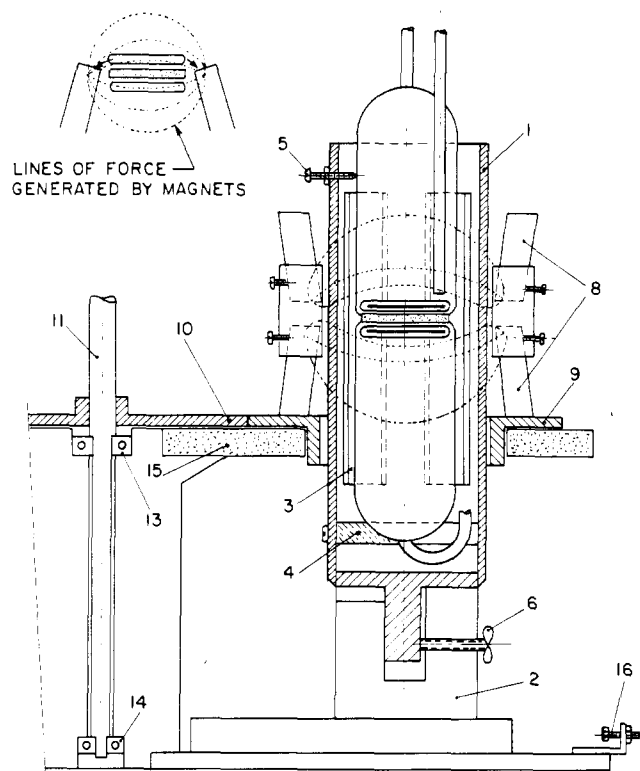


Figure 2. Sectional drawing of cell support and stirring mechanism

broad and deviations of up to 40% from  $t_{opt}$  do not increase the error in  $D$  by more than 20%.

**SAMPLING.** Before samples were taken, any solution in the stems above valves I and III was removed with fine plastic capillary tubing and a syringe. To prevent any solution from draining into the bottom compartment while it was being sampled, the top compartment was always sampled and drained first.

The top compartment was sampled by opening only valves I and II (Figure 2) and introducing compressed air through stem 1. Since the liquid in stem 2 has essentially the initial concentration, the first few cc's emerging from the stem were discarded. The remainder was collected in the sample bottle described earlier. Any liquid which remained in the top compartment was then drained off by inverting the cell and applying vacuum to stem 1.

Before sampling the bottom compartment, only valve II was closed, and compressed air was forced into the bottom compartments through stem 3 displacing a few cc's of solution from that compartment and the diaphragm. Once this occurred, valve I was closed, valve IV was opened, and after the first cc's of sample were discarded, the bottom compartment sample was collected and sealed in a second sample bottle.

The initial KCl concentration in the top compartment is always zero. Therefore, by measuring the top and bottom final concentrations, the bottom initial concentration may be determined from a mass balance.

Samples were taken as soon after the run was stopped as possible. The analysis consisted of evaporation of the solution to dryness and weighing, following a standard procedure (12, 24).

**Diffusion runs with organic solutions.** As a result of the volatility of the organic solutions, the top compartment was not filled by applying vacuum on stem 1. Instead, the solution was forced into the compartment through stem 2 with a syringe and a hypodermic needle fitted with a short length of teflon tubing.

At the end of the diffusion run, the top compartment was sampled first. After removing any stagnant solution above valve I with a syringe and capillary tubing, valve II was opened, and the contents of stem 2 were flushed out by applying a slight air pressure at stem 1. The end of a length of teflon tubing was then snugly inserted into stem 2 and a 35-cc sample was withdrawn with a syringe connected to the tubing.

Since air could easily leak between the dry walls of the cylinder and piston and thus come into contact with the contents of the syringe, an effective seal was created by closing valve II after a few cc's of solution had entered the syringe and then compressing the contents. This forced the contents between the walls of the cylinder and piston, producing the desired seal with no danger of contaminating the sample.

Once the top compartment sample was taken, that compartment was completely drained. Stem 3 was then drained as far as its valve using fine capillary tubing and a syringe. It was then opened and compressed air applied to force any solution held in the diaphragm into the top compartment.

As soon as air began to bubble through the diaphragm, valve IV was opened and the first few cc's of solution were discarded. The teflon tubing was then inserted in stem 4, and valves I and II were closed (to prevent air from bubbling through the bottom compartment and thus producing stripping). Approximately 35 cc's of sample were collected.

All samples taken in the organic diffusion runs were analyzed with the precision density meter. The initial concentration of the bottom compartment was always evaluated with a mass balance.

**Calibration of density meter.** The density of a fluid filling the oscillator is related to its period of oscillation  $T$  by the expression

$$\rho = AT^2 + B \quad (1)$$

However, the manufacturers (7) state that this expression is only valid within an interval of 0.05 g/cc. Within this range and with temperature control to  $\pm 0.01^\circ\text{C}$ , the stated precision is  $\pm 1.5 \times 10^{-6}$  g/cc.

Outside this density range, a reproducible deviation of up to  $10^{-3}$  g/cc from absolute density may be observed. The manufacturers state that this behavior follows because the oscillator is not suspended from an infinite mass. Implicating a finite mass into the calculation, they state that the resultant relationship between density and period is

$$\rho = \frac{AT^2}{1 + CT^2} + B \quad (2)$$

Since densities in this work ranged from 0.70 to 1.58 g/cc, the instrument was calibrated by use of Equation 2.

Water and air were chosen as two of the standards since they were readily available and their densities were accurately known. Since a similarly reliable third standard was not available, organic densities, which had been determined independently with pycnometers, for three pure materials were used as secondary standards. Thus, the three constants were determined as the best estimates fitting the densities of *n*-octane, *n*-decane, and carbon tetrachloride, in addition to water and air.

The sample temperatures, as measured by a mercury bulb thermometer inserted directly into the measuring cell housing through a well in the cover of the apparatus, were maintained at  $25.00 \pm 0.01^\circ\text{C}$  throughout this work.

## Results and Discussion

Diffusion data were obtained over the entire composition range for each of the following systems at  $25.00^\circ\text{C}$

and at atmospheric pressure ranging from 720 to 740 mm Hg: *n*-octane-carbon tetrachloride, *n*-decane-carbon tetrachloride, and *n*-dodecane-carbon tetrachloride. Density-composition curves were also prepared and used for composition determination of the organic systems.

In this work four diffusion cells were calibrated. Volumes of the top and bottom compartments ( $\sim 50$  cc) were determined in duplicate with a standard deviation of 0.0241 cc. Diaphragm volumes, which were determined two or three times each, had a standard deviation of 0.0086 cc. Stem volumes were determined only once.

The diffusion cells were each calibrated from two to four times. Final KCl concentrations were determined from the residue weights left after drying 10-cc aliquots of sample. Each solution was measured at least three times. The standard deviations in determining residue weights were  $1.00 \times 10^{-4}$  and  $1.77 \times 10^{-4}$  gram for the top and bottom compartments, respectively.

The cell constants  $\beta$ , defined by the usual logarithmic formula (24)

$$\bar{D} = \frac{1}{\beta t} \ln \frac{C_B^0 - C_T^0}{C_B - C_T} \quad (3)$$

where  $\bar{D}$  is the "integral diffusion coefficient",  $t$  is the duration of diffusion run, and  $C$  is the concentration of solute ( $B$  and  $T$  refer to bottom and top cell compartment, respectively, and superscript "0" refers to initial values), were calculated in two ways. The first was to ignore the effects of the contents of stems 1 and 3; the second method was to include these effects (24).

As has been discussed extensively by Dullien and co-workers (19, 7), Equation 3 is based on the validity of Fick's law of diffusion, i.e., on the assumption that volume changes on mixing are absent or negligible. By the same authors, rigorous equations have been developed to replace Equation 3 when Fick's law is not valid. Computations performed with the ethanol-water system have shown (19, 7) that for small initial concentration differences of the order of 0.05 mole fraction units (such as those used also in the present work), the error committed by neglecting the effects of volume changes on mixing by using Equation 3 are insignificant.

The method for calculating  $\bar{D}$  was that of Stokes (24), using an integrated form of the equation for true diffusivity  $D$ , given by Woolf and Tilley (26). The densities of duplicate samples of *n*-octane- $\text{CCl}_4$  and *n*-decane- $\text{CCl}_4$  solutions were obtained with pycnometers. The respective standard deviations for the two systems were  $1.65 \times 10^{-4}$  g/cc for 12 measurements and  $1.25 \times 10^{-4}$  g/cc for 16 measurements.

In addition, pycnometers were also used to determine the density of *n*-octane, *n*-decane, and carbon tetrachloride. The standard deviations of seven *n*-alkane samples and nine carbon tetrachloride samples were  $1.48 \times 10^{-5}$  and  $8.46 \times 10^{-5}$  g/cc, respectively.

The *n*-dodecane- $\text{CCl}_4$  system was entirely calibrated with the density meter with a standard deviation of  $0.46 \times 10^{-4}$ . The instrument was also used to obtain additional data for the other two systems. Quadruplicate samples were normally measured. The data for the three systems at  $24.82^\circ\text{C}$  were empirically fitted to the equation

$$W_A = \sum_{i=0}^4 \frac{a_i}{\rho^i} \quad (4)$$

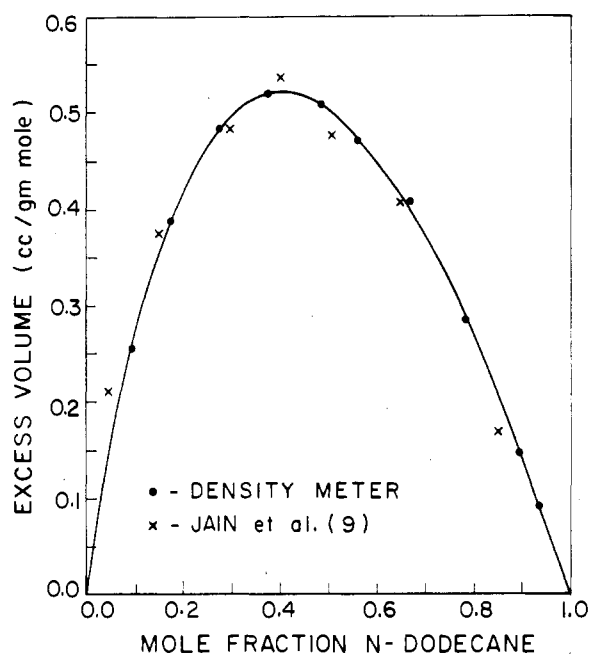
where  $W_A$  is the mass fraction of *n*-alkane and  $\rho$  is the solution density.

The coefficients,  $a_i$ , were determined by a least-squares fit (with the 360/75 Fortran IV library subroutine, CFWOP) and are reported in Table I. Standard deviations for the three curves are contained in the same table.

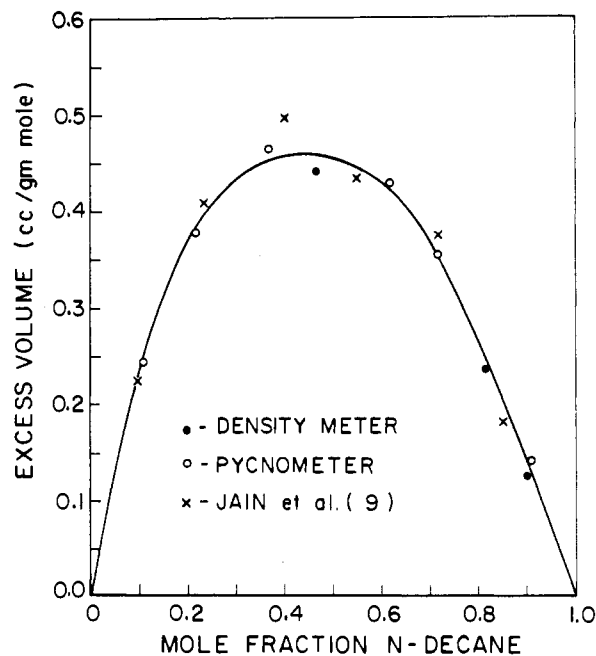
**Table I. Coefficients for Equation 4**

$t = 24.82^\circ\text{C}$

System	SD	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$
<i>n</i> -Octane- CCl <sub>4</sub>	$16.52 \times 10^{-6}$	-0.7310316	1.0536031	0.2352766	-0.1262512	0.0265743
<i>n</i> -Decane- CCl <sub>4</sub>	$12.47 \times 10^{-6}$	-0.7741344	1.1026317	0.2726956	-0.1379426	0.0277989
<i>n</i> -Dodecane- CCl <sub>4</sub>	$4.62 \times 10^{-6}$	-0.7963513	1.0945278	0.3746897	-0.1999065	0.0421807



**Figure 3.** Excess volume of mixing for *n*-octane-CCl<sub>4</sub> system at 25°C



**Figure 4.** Excess volume of mixing for *n*-decane-CCl<sub>4</sub> system at 25°C

Molar excess volumes  $V^E$  at 25°C for the three systems were calculated from

$$V^E = \frac{M_{AXA} + M_{CX C}}{\rho} - \frac{M_{AXA}}{\rho_A} - \frac{M_{CX C}}{\rho_C} \quad (5)$$

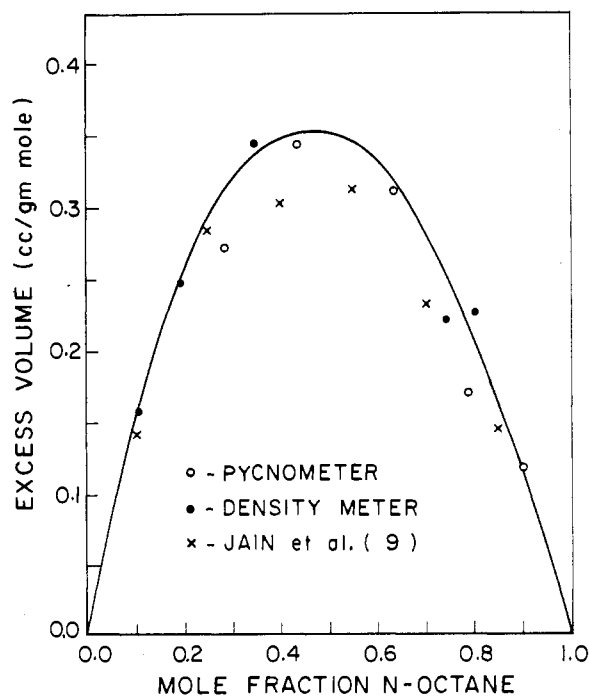
where  $M_i$  and  $\rho_i$  are molecular weights and component densities, respectively.

The results are illustrated in Figures 3-5. The data of Jain et al. (9) have been included for comparison. These plots show good agreement and an apparently great precision of the density measurements. The excess volumes were used to make sure that the neglect of volume changes of mixing, by application of Equation 3, did not introduce measurable errors into the diffusion coefficient determination.

All density measurements made during the diffusion experiments were obtained with the density meter. Samples were usually measured in quadruplicate with errors of less than  $\pm 2 \times 10^{-5}$  g/cc.

The integral diffusivities were calculated in two ways. As with the cell calibration, calculations were made by first neglecting stem volumes and then including them. In each case, diffusivities were calculated with cell constants which had been obtained in a corresponding manner.

Experimental diffusivities calculated from corrected concentrations are shown in Tables II-IV. The column la-



**Figure 5.** Excess volume of mixing for *n*-dodecane-CCl<sub>4</sub> system at 25°C

beled "Concentration" is the value of the concentration at which the integral diffusivity,  $\bar{D}$ , is numerically equal to the true diffusion coefficient  $D$ .

The true diffusivities were calculated by two methods. The first was to equate the true diffusivity at the mean concentration of the experiment to the integral diffusivity.

**Table II. Diffusion Coefficients for *n*-Octane-CCl<sub>4</sub> System at 25°C**

Run	Integral diffusion coeff, cm <sup>2</sup> /sec × 10 <sup>5</sup>	Average concn, g-mol <i>n</i> -octane/l.	Concn, g-mol <i>n</i> -octane/l.
...	1.254 <sup>a</sup>	...	0
8-6	1.343	0.8318	0.8522
8-7	1.445	1.4839	1.5379
8-16	1.700	2.9249	2.9331
8-22	1.967	4.1627	4.1641
8-15	2.019	4.3159	4.3198
8-14	2.173	4.8986	4.9002
8-11	2.441	5.7748	5.7757
8-10	2.444	5.7766	5.7776
...	2.558 <sup>a</sup>	...	6.1166

<sup>a</sup> Extrapolated to pure component by use of Equation 6.

**Table III. Diffusion Coefficients for *n*-Decane-CCl<sub>4</sub> System at 25°C**

Run	Integral diffusion coeff, cm <sup>2</sup> /sec × 10 <sup>5</sup>	Average concn, g-mol <i>n</i> -decane/l.	Concn, g-mol <i>n</i> -decane/l.
...	1.074 <sup>a</sup>	...	0
10-1	1.137	0.7270	0.7346
10-8	1.149	0.7742	0.7827
10-12	1.200	1.2063	1.2248
10-9	1.321	2.3874	2.3920
10-20	1.418	3.0669	3.0692
10-13	1.507	3.5498	...
10-21	1.551	4.1195	4.1216
10-17	1.640	4.6647	4.6663
10-27	1.641	4.6355	4.6372
...	1.710 <sup>a</sup>	...	5.1061

<sup>a</sup> Extrapolated to pure component by use of Equation 6.

**Table IV. Diffusion Coefficients for *n*-Dodecane-CCl<sub>4</sub> System at 25°C**

Run	Integral diffusion coeff, cm <sup>2</sup> /sec × 10 <sup>5</sup>	Average concn, g-mol <i>n</i> -dodecane/l.	Concn, g-mol <i>n</i> -dodecane/l.
...	0.959 <sup>a</sup>	...	0
12-1	0.996	0.6680	0.6713
12-4	0.997	0.6691	0.6724
12-3	1.058	1.7698	1.7732
12-6	1.096	2.4546	2.4553
12-9	1.097	2.3084	...
12-8	1.131	2.6643	...
12-12	1.150	3.1611	3.1617
12-7	1.155	2.9177	...
12-11	1.184	3.6465	3.6469
12-10	1.198	3.8906	3.8910
12-5	1.206	4.1398	4.1401
...	1.229 <sup>a</sup>	...	4.3763

<sup>a</sup> Extrapolated to pure component by use of Equation 6.

This method is valid, provided the diffusivity is linear over the concentration range of the experiment. The second method is an iterative procedure suggested by Mills et al. (13) and will give precise values provided a suitable form of equation is chosen. As seen in Tables II-IV, it was only for the *n*-octane-CCl<sub>4</sub> system that the iterative method was actually needed.

The data for both the integral and the true diffusion coefficients have been fitted to the equation

$$D = \sum_{i=0}^2 b_i C_A^i \quad (6)$$

where  $C_A$  is *n*-alkane concentration g-mol/l., and the coefficients  $b_i$  have been obtained with the least-squares curve fitting subroutine "CFWOP". These coefficients and the average absolute deviations associated with each curve have been reported (24). The observed deviations of the true diffusivities from the best fitting curves are as follows:

System	Average absolute dev, %
<i>n</i> -Octane-CCl <sub>4</sub>	0.23
<i>n</i> -Decane-CCl <sub>4</sub>	0.35
<i>n</i> -Dodecane-CCl <sub>4</sub>	0.29

These compare favorably with the predicted error of 0.45%, and it appears that there are no major sources of error which have been overlooked (3, 5).

These results contrast with those of previous workers (6, 18, 10, 2) who found that the predicted error in organic diffusivities was significantly less than the experimental ones. These authors all suggested sampling as one major source of error. The present results, therefore, attest to the effectiveness of the experimental procedure.

The true diffusion coefficients extrapolated to zero alkane concentrations by use of Equation 6 are reported in Table V. They may be compared to corresponding values obtained by Dewan and von Holde (5) using the Rayleigh interferometric method.

The diffusivities reported here have been calculated by making corrections for the small changes in concentrations which occurred when the contents of stems 1 and 3 were flushed into the compartments. The limiting diffusion coefficients calculated from corrected and uncorrected concentrations agreed well within experimental errors for the systems *n*-octane-CCl<sub>4</sub> and *n*-decane-CCl<sub>4</sub> but differed significantly for *n*-dodecane-CCl<sub>4</sub>.

A possible explanation for this behavior is that in the first two systems, the diffusion times of the organic and calibration times were approximately the same proportion of the optimum times (19). However, the diffusion times of the *n*-dodecane-CCl<sub>4</sub> runs were much shorter. Therefore, it appears that the effects of the stem volumes are accounted for in the cell constant when similar procedures are followed in the calibration and the diffusion runs. Deviations from similar procedures may, however, introduce significant errors when concentration corrections are ignored.

The cells were calibrated at two different times during this work. The total operating time between the two sets of calibrations were less than 1000 hr for each of the cells. In most cases, the redetermined values lay within the experimental error of determining the cell constant.

The periodic bath temperature fluctuations of ±0.01°C create only a fluctuation of ±0.0025°C in the cells (24). This effect is probably the result of damping of the fluctuations by the cell walls.

The contents of the cell have a temperature which is about 0.05°C higher than the bath temperature (24). This is probably the result of the conversion of mechanical en-

ergy within the cell to thermal energy. In this case, water was used in the cell when the temperature was measured, and the heating effect was small. However, in more viscous systems the effect may be more pronounced. In this work the diffusivity data have been reported at the bath temperature.

The effect of fluctuations in the bath temperature may be serious because they are capable of generating bulk flow owing to volume changes in the solution. The following calculations show the magnitude of the error caused by a change of 0.2°C in the cell temperature.

For simplicity, assume: the stem volumes are negligible; the diaphragm volume is negligible; the compartment volumes are each 50 cc; each concentration is determined independently; the solution has a volume coefficient of expansion of  $10^{-3}$  cc/cc °C; and perturbation occurs just before the final concentrations are measured.

When the contents warm, bulk flow occurs in the top compartment as a result of expansion. Flow to the top compartment is

$$V_B \cdot \frac{1}{V} \frac{\partial V}{\partial T} \cdot \Delta T = 50 \times 10^{-3} \times 0.2 = 0.01 \text{ cc} \quad (7)$$

Therefore, the measured concentration in the top compartment is

$$C_T' = \frac{50 C_T + 0.01 C_B}{50.01} \quad (8)$$

**Table V. Comparison of Experimental Limiting Diffusivities**

System	Limiting diffusivity, $D^\circ \times 10^5$ cm <sup>2</sup> /sec, this work	Limiting diffusivity, $D^\circ \times 10^5$ cm <sup>2</sup> /sec, independent method (5)
n-Octane-CCl <sub>4</sub>	1.254	1.260
n-Decane-CCl <sub>4</sub>	1.074	1.085
n-Dodecane-CCl <sub>4</sub>	0.959	0.964

**Table VI. Comparison of Predicted and Experimental Diffusivities at Infinite Dilution**

Equation	Alkane, A	$D_{AC}^\circ$ , cm <sup>2</sup> /sec $\times 10^5$	$D_{CA}^\circ$ , cm <sup>2</sup> /sec $\times 10^5$	Av absolute error, %
Exptl	n-Octane	1.254	2.558	
	n-Decane	1.074	1.710	
	n-Dodecane	0.959	1.229	
Scheibel	n-Octane	0.92	3.50	32
	n-Decane	0.78	2.38	
	n-Dodecane	0.68	1.66	
Wilke and Chang	n-Octane	1.32	2.84	8
	n-Decane	1.16	1.89	
	n-Dodecane	1.04	1.30	
Othmer and Thakar	n-Octane	0.69	1.78	41
	n-Decane	0.59	1.08	
	n-Dodecane	0.54	0.68	
Sitaraman et al.	n-Octane	1.12	2.65	4
	n-Decane	1.03	1.77	
	n-Dodecane	0.97	1.22	
Lusis and Ratcliff	n-Octane	0.92	1.56	28
	n-Decane	0.82	1.68	
	n-Dodecane	0.74	1.80	

where  $C_T$  is the corresponding value that would have been measured in the absence of the disturbance, and  $C_B$  is the concentration measured in the bottom compartment.  $C_B$  is obviously not affected by the flow of the solution from the bottom to the top compartment.

The calculated diffusivity is then by Equation 3:

$$\bar{D}' = \frac{1}{\beta t} \ln \frac{C_T^\circ - C_B^\circ}{C_T' - C_B} \quad (9)$$

Therefore,

$$e^{\beta \bar{D}' t} = \frac{C_T^\circ - C_B^\circ}{C_T' - C_B} = \frac{C_T^\circ - C_B^\circ}{\frac{50}{50.01}(C_T - C_B)} \quad (10)$$

The corresponding expression for the case where no perturbation occurs is

$$\frac{C_T^\circ - C_B^\circ}{C_T - C_B} = e^{\beta \bar{D} t} \quad (11)$$

Therefore,

$$e^{\beta \bar{D} t} = \frac{50.01}{50} e^{\beta \bar{D}' t} \quad (12)$$

Allowing the experiment to proceed to an optimum time  $t = 1.2/\beta \bar{D}$  (18), there follows:

$$\frac{\bar{D}' - \bar{D}}{\bar{D}} = \frac{\ln \frac{50.01}{50}}{1.2} \times 100\% = 0.017\% \quad (13)$$

This error can still be considered negligible. Had the diffusion time been considerably shorter, or the temperature disturbance greater, however, the error might have been significant. In addition, if the temperature fluctuations occur repeatedly or even periodically, each disturbance will contribute an error of similar magnitude, and the final error will be the sum of the errors caused by all the disturbances. It would seem logical to consider the error caused by the observed temperature fluctuation in the cells (0.0025°C) in the time interval corresponding to a half-period of the periodic temperature fluctuation in the cell (about 6 min). This would give an error of the order of 1% in  $D$ . It must be considered at the same time, however, that the corresponding advance of the solution out of the diaphragm is only about 0.2  $\mu$  which is well inside the viscous sublayer; thus, it escapes the mixing effect of the stirrer. Hence, only temperature variations which exceed the value observed in the present experiments by a considerable amount would represent any threat to the accuracy of the measurements.

The diffusivities at infinite dilution as calculated by various predictive equations (17) are shown in Table VI. In the case of the Wilke and Chang correlation (25), the association parameter has been set equal to 1.0 in all cases.

There is a large variation in the agreement between predicted and experimental results. The differences may be partly attributable to the simplifying assumptions which were originally made in the formulation of the correlations. Furthermore, as Lusis and Ratcliff (11) and others have pointed out, the mechanism of diffusion for long straight-chain molecules may be different from other species.

In Table VII are shown the "experimental" diffusivity values interpolated by Equation 6 at  $x_A = 0.2, 0.4, 0.6,$  and  $0.8,$  together with the values predicted by the formula

$$D = (D_{AC}^\circ)^{x_C} (D_{CA}^\circ)^{x_A} \frac{d \ln a_i}{d \ln x_i} \quad (i = A, C) \quad (14)$$

**Table VII. Comparison of Experimental Diffusivities with Those Predicted by Vignes-Cullinan Correlation**

System	Mole fraction alkane, $x_A$	$D$ , exptl, $\text{cm}^2/\text{sec} \times 10^5$	$D$ by Equation 14, $\text{cm}^2/\text{sec} \times 10^5$
<i>n</i> -Octane- $\text{CCl}_4$	0.2	1.49	1.45
	0.4	1.76	1.67
	0.6	2.02	1.92
	0.8	2.30	2.22
<i>n</i> -Decane- $\text{CCl}_4$	0.2	1.25	1.18
	0.4	1.40	1.29
	0.6	1.53	1.42
	0.8	1.65	1.56
<i>n</i> -Dodecane- $\text{CCl}_4$	0.2	1.04	1.01
	0.4	1.11	1.06
	0.6	1.16	1.11
	0.8	1.19	1.17

first suggested by Vignes (11). Here,  $D_{AC}^\circ$  and  $D_{CA}^\circ$  are the values of  $D$  as  $x_A \rightarrow 0$  and  $x_C \rightarrow 0$ , respectively, and  $a_i$  is the activity of either component. Since thermodynamic activities were not available for the systems studied here,  $d \ln a_i / d \ln x_i$  was arbitrarily set equal to 1 in every case.

As the *n*-alkane- $\text{CCl}_4$  mixtures approximate regular solutions, one could have estimated the activities by the formula (15)

$$RT \ln \gamma_A = V_A \Phi_C^2 (\delta_A - \delta_C)^2 \quad (15)$$

where

$$\Phi_C = \frac{x_C V_C}{x_A V_A + x_C V_C} \quad (16)$$

with  $\gamma_A$  the activity coefficient,  $V_A$  and  $V_C$  the molar volumes of the pure components, and  $\delta_A$  and  $\delta_C$  the "solubility parameters".

From Equations 15 and 16,

$$\frac{d \ln a_i}{d \ln x_i} = 1 - \frac{2 x_A x_C (V_A V_C)^2 (\delta_A - \delta_C)^2}{RT (x_A V_A + x_C V_C)^3} \quad (17)$$

with the result that for regular solutions  $d \ln a_i / d \ln x_i < 1$ .

From the data in Table VII, Equation 14, with  $d \ln a_i / d \ln \gamma_i$  assumed to be 1, predicted lower values than the measured diffusivities in every case. Hence, the use of Equation 17 in Equation 14 would result in even greater discrepancies between the predicted and measured quantities.

### Conclusions

The following conclusions may be reached from this study.

The diffusion coefficients of three *n*-alkane- $\text{CCl}_4$  systems were determined as a function of composition at 25°C with an average standard error of about 0.3%.

Evaporational losses during sampling appear to be a major source of error encountered by previous workers. The procedure outlined in this work appears to eliminate this source of error and for this reason is recommended in future work. Especially noteworthy is the accuracy obtainable when the procedure is used in conjunction with a precision density meter.

Correction for concentration changes caused by slushing stem contents into the compartment does not appear to be necessary when the same procedure is used in the calibration and diffusion runs.

The cell contents appear to be at a higher temperature than that of the bath during diffusion runs. This effect requires additional investigation, especially in the case of viscous solutions.

The temperature fluctuation inside a diaphragm cell is considerably less than the corresponding fluctuation in the bath temperature.

The error in the diffusion coefficient introduced by temperature fluctuations was estimated.

The diffusion coefficients were fitted to a power series in the concentration, and the diffusion coefficients at infinite diffusion calculated. These agreed well (within 1%) with the results determined by other investigators using an independent method.

The limiting diffusion coefficients were estimated by five different empirical correlations. The accuracy of the predictions varied greatly from one method to another.

The diffusion coefficients were predicted by use of the limiting values by Vignes' correlation over the entire concentration range. The Vignes correlation did not accurately predict the measured values.

By use of the density determinations performed on the three *n*-alkane-carbon tetrachloride solutions, the excess volumes were calculated as a function of composition.

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### Nomenclature

- $A$  = constants in Equations 1 and 2
- $a_i$  = thermodynamic activity of component  $i$
- $a_i$  = constants in Equation 4
- $B$  = constants in Equations 1 and 2
- $b_i$  = constants in Equation 6
- $C$  = constant in Equation 2
- $C$  = concentration, gmol/l.
- $D$  = diffusion coefficient,  $\text{cm}^2/\text{sec}$
- $l$  = effective path length of diffusion in diaphragm, cm
- $M$  = molecular weight
- $R$  = universal gas constant, cal/g-mol K
- $T$  = period of oscillation, sec
- $T$  = temperature, K
- $t$  = time, sec
- $V$  = molar volume, cc/g-mol
- $V^E$  = excess volume, cc/g-mol
- $W$  = mass fraction
- $x$  = mole fraction

### Greek Letters

- $\beta$  = cell constant,  $\text{cm}^{-2}$
- $\gamma$  = activity coefficient
- $\delta$  = solubility parameter,  $(\text{cal}/\text{cc})^{1/2}$
- $\rho$  = density, g/cc
- $\Phi$  = quantity defined by Equation 16

### Subscripts

- $A$  = *n*-alkane
- $B$  = bottom compartment
- $C$  = carbon tetrachloride
- $i$  = dummy index
- $T$  = top compartment

### Superscripts

- $i$  = dummy index
- = integral value
- $^\circ$  = initial condition
- $^\circ$  = infinite dilution

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## Diffusion Coefficients in Binary Liquid *n*-Alkane Systems

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**Binary diffusion coefficients were measured for four *n*-alkane systems, *n*-heptane-*n*-decane, *n*-heptane-*n*-dodecane, *n*-heptane-*n*-tetradecane, and *n*-octane-*n*-tetradecane over the full range of concentrations at 25°C. The diaphragm diffusion cell method was employed. Experimental data obtained followed the relationship shown by Shieh and Lyons. Equations were developed for correlating the limiting diffusion coefficients in binary *n*-alkane systems in terms of the number of carbon atoms in the system and values of the self-diffusion coefficients of the solvent.**

Diffusion coefficients in hydrocarbon systems are fundamental data in a number of engineering applications and in the study of mass transfer. In the recovery of oil from a petroleum reservoir utilizing a bank of solvent followed by dry gas, diffusion coefficients of the components involved, oil (liquid hydrocarbons), solvent (mixture of methane and propane), and dry gas (mainly methane), are some of the data required for estimating the amount of solvent to be injected to displace the oil under miscible conditions to achieve high recovery.

The objective of this study was to supplement the meager data available for binary diffusion coefficients in liquid *n*-alkanes. A number of empirical and semiempirical equations, each subject to some limitations, have been proposed for estimating diffusion coefficients. For *n*-alkanes the application of these equations is not satisfactory. Lulis and Ratcliff (9) have indicated that large errors may be expected when the equation they developed was applied to the diffusion of long straight-chain solutes in a similar type of solvents of greater chain length.

Leffler and Cullinan (8) found that their modified Vignes equation correlates experimental data of a large number of substances well, except for liquid *n*-alkanes. From consideration of activation energy, van Geet and Adamson (27) have pointed out that long straight-chain hydrocarbons may flow and diffuse in segments of a few

carbons. Hence, the number of carbon atoms involved in the elementary displacement would be the same for both components in the binary system. A separate study of diffusion in liquid *n*-alkanes has been conducted by Shieh and Lyons (16). They showed that the diffusion coefficient is a function of the density of the mixture and is related to the average number of carbon atoms in the system. However, more data are needed to further confirm these relationships and to establish the accuracy of these correlations.

### Experimental

**Diaphragm cell method.** The diaphragm cell method was developed based on the pseudo-steady state diffusion through a porous diaphragm. A nearly steady concentration gradient is established across the porous diaphragm separating two miscible solutions of different composition. After a known period of diffusion, the concentrations of the two solutions are analyzed. The diffusion coefficient is calculated from the following equation:

$$\bar{D}_{12} = \frac{1}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \quad (1)$$

Derivations of Equation 1 can be found in a number of publications such as van Geet and Adamson (21). The diffusion coefficient obtained from the diaphragm cell measurements is actually a double average over concentration and time termed the integral diffusion coefficient

$$\bar{D} = \frac{1}{t} \int dt \frac{1}{c_1 - c_2} \int_{c_2}^{c_1} D dc \quad (2)$$

Gordon (4) has shown that Equation 2 can be treated without any serious error as the ordinary integral diffusion coefficient taken over the initial concentration range.

$$\bar{D} = \frac{1}{c_1 - c_2} \int_{c_2}^{c_1} D dc \quad (3)$$

To establish a concentration gradient in the diaphragm and to attain steady state conditions, a period of prediffu-