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lated value of  $D$  is in all cases higher than for the corresponding mixture involving a  $n$ -paraffin, which is contrary to experiment. Furthermore the calculated diffusivity for  $n$ -C<sub>7</sub>- $n$ -C<sub>18</sub> is larger than that for  $n$ -C<sub>7</sub>- $n$ -C<sub>12</sub>, whereas experiment shows the former to

be much smaller. In general it must be stated that this relationship does not appear to be in any way consistent with the data for hydrocarbon mixtures. At present the only really useful relationship is the semi-empirical one of Arnold.

## Thermal Diffusion in Binary Liquid Hydrocarbon Mixtures

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Thermal diffusion coefficients have been measured for a series of binary mixtures of paraffin hydrocarbons and of paraffin hydrocarbons with benzene. The temperature dependence of the thermal diffusion coefficient is shown to be small. The results are correlated quite satisfactorily by assuming that the mobility of a molecule is inversely proportional to the product of the molecular mass and molecular cross section in the direction of flow.

### NOMENCLATURE

- $B$  = mean circumference of the column, cm.  
 $C_1, C_2$  = mole fractions of components 1, 2.  
 $D$  = coefficient of diffusion cm<sup>2</sup>/sec.  
 $D_T$  = coefficient of thermal diffusion cm<sup>2</sup>/sec.  
 $g$  = acceleration of gravity cm<sup>2</sup>/sec.  
 $L$  = length of column cm.  
 $m$  = molecular mass.  
 $v$  = convection velocity of entire fluid, cm/sec.  
 $v_1$  = convection velocity of molecules of Type 1, cm/sec.  
 $V_+$  = volume of one reservoir cm<sup>3</sup>.  
 $\omega$  = one-half the annular spacing—cm.  
 $\bar{T}$  = average temperature.  
 $\Delta T$  = temperature difference between hot and cold wall.  
 $\alpha$  = thermal diffusion ratio.  
 $\beta = -\partial\rho/\partial T$ .  
 $\rho$  = density g/cm<sup>3</sup>.  
 $\eta$  = viscosity, poises.  
 $\sigma$  = molecular cross section.  
 $x$  = probability of finding a molecule in the hot region.

**T**HERMAL diffusion in the liquid phase was first observed by Ludwig<sup>1</sup> in 1856. When a temperature gradient was maintained in a uniform aqueous solution of sodium sulfate he found that a concentration gradient was established. Later Soret<sup>2</sup> discovered the effect independently, and as a result thermal diffusion in the liquid phase is now termed the Ludwig-Soret effect or the Soret effect.

If a temperature gradient is impressed on a mixture of gases a partial separation of the gases will generally occur, but it was early shown that no simple picture of molecular interaction would predict such an effect. When the other transport properties, viscosity, thermal conductivity and diffusion, can be predicted satisfactorily by assuming simple molecular interaction laws it becomes apparent that thermal diffusion is a second-

order effect which is very sensitive to slight differences in interaction between molecules. It is therefore possible to obtain more specific information about how molecules behave in the gas phase by studying thermal diffusion rather than one of the other transport properties.

In liquids and liquid mixtures a simple theory of binary collisions is not sufficient to describe the molecular behavior because the molecules are closely packed and are probably influenced by several neighbors simultaneously. Accordingly, it is considered that binary collisions as conceived in gases are of minor importance compared to the complex force field about each molecule in a liquid. Due to the complexity of the problem a complete mathematical theory of the liquid state has not yet been realized. It is possible, however, that thermal diffusion data for liquids may yield more specific information about the liquid state than the other transport properties as is the case for gases. On this premise thermal diffusion has been adopted as the tool in a study of liquid mixtures.

Scanty data on the Soret effect are available for aqueous solutions of electrolytes but few experiments have involved solutions of organic compounds. The present work is confined to a study of the Soret effect in binary mixtures of unreactive hydrocarbons which form almost ideal solutions. It is desired to discover what fundamental properties of the pure compounds determine the magnitude and direction of the thermal diffusion constant.

### KINETIC THEORY

There is at present no kinetic theory of liquids adequate to explain thermal diffusion, but the following argument is consistent with the modern theory of liquids and with the experimental results.

Let us consider a liquid as a network of equilibrium

<sup>1</sup> C. Ludwig, *Akad. Wiss. Wien*, **20**, 539 (1856).

<sup>2</sup> Ch. Soret, *Auh. Sci. Phys. Nat.*, Geneve (3) **2**, 48 (1879).

TABLE I. Thermal diffusion data obtained with a concentric tube column for 50 mole percent liquid mixtures.

Mixtures	$l/3600$	$T_H$	$T_C$	$100\Delta c^*$	$\alpha^{**}$
Ph— <i>n</i> -C <sub>7</sub>	4.50	298.8	293.4	-0.500	-1.19
	10.50	298.8	293.4	-0.579	
	0.02	—	—	-0.072	
	0.06	—	—	-0.128	
	0.12	308.9	303.4	-0.250	
	0.25	309.0	303.5	-0.364	-1.20
	1.00	309.0	303.6	-0.486	
	4.00	308.9	303.7	-0.571	
	4.30	308.9	303.5	-0.543	
	10.00	308.9	303.3	-0.557	
	11.00	308.8	303.5	-0.550	-1.06
	4.00	324.0	318.7	-0.443	
	10.00	323.9	318.7	-0.536	
	3.00	339.0	334.1	-0.510	
	10.80	340.4	334.3	-0.525	
	4.00	311.7	300.9	-0.585	-1.24
	6.00	311.7	300.9	-0.560	
	13.00	311.8	301.0	-0.568	
	4.30	314.8	298.3	-0.607	
	5.30	314.7	298.4	-0.603	-1.28
	12.00	314.7	298.4	-0.553	
Ph— <i>n</i> -C <sub>10</sub>	4.00	299.0	293.3	-0.118	-0.22
	8.00	298.9	293.3	-0.145	
	4.00	308.8	303.4	-0.245	
	9.50	308.9	303.4	-0.231	-0.41
	4.00	323.9	318.5	-0.318	
	8.00	323.8	318.4	-0.190	
	4.00	338.7	333.4	-0.281	-0.47
	7.30	338.8	333.2	-0.213	
	3.50	353.4	348.2	-0.454	-0.68
	7.50	353.6	348.1	-0.268	
Ph— <i>n</i> -C <sub>12</sub>	4.30	308.9	303.6	-0.230	-0.31
	8.00	308.9	303.5	-0.189	
	11.50	308.9	303.6	-0.189	
Ph— <i>n</i> -C <sub>14</sub>	4.00	308.9	303.5	-0.164	-0.41
	4.50	308.9	303.6	-0.164	
	11.00	308.9	303.6	-0.124	
Ph— <i>n</i> -C <sub>16</sub>	4.00	308.9	303.4	+0.025	-0.001
	4.00	308.9	303.6	-0.007	
	12.00	309.0	303.6	-0.043	

\* In this table a positive  $\Delta c$  indicates that the first-named component concentrated at the hot wall.

\*\* Mean values of  $\alpha$  are given at each temperature. Only points where the steady state was reached were used in calculating.

positions, in which a molecule is held as in a "cage" by the potential energy field of the surrounding molecules. The liquid differs from the solid in that the kinetic energy of the molecules is larger and the surrounding potential barrier is lower and subject to much greater fluctuations. Thus the "retention time" of a molecule in any equilibrium position is relatively short. Higher temperatures correspond to greater kinetic energy, and larger cages with more flexible and penetrable walls, i.e., to shorter retention times. To describe the motion we must consider the tendency to escape from an equilibrium position, the direction in which, on the average, it will move, the possibility of location in a new position, and the probability of moving back toward the old position.

In general, the higher the temperature the greater the mobility, so that all molecules have a tendency to move toward the lower temperature which accounts for

TABLE I.—Continued.

Mixtures	$l/3600$	$T_H$	$T_C$	$100\Delta c^*$	$\alpha^{**}$
Ph— <i>n</i> -C <sub>18</sub>	4.00	308.9	303.6	+0.105	+0.07
	4.00	308.9	303.6	+0.059	
	14.00	308.7	303.4	+0.053	
<i>n</i> -C <sub>7</sub> — <i>n</i> -C <sub>12</sub>	4.30	298.9	293.5	0.370	+0.57
	10.20	298.9	293.5	0.394	
	4.00	308.8	303.5	0.430	
	7.80	308.9	303.4	0.370	+0.61
	4.00	323.8	318.4	0.287	
	7.50	323.8	318.4	0.382	
	4.00	338.9	333.6	0.323	+0.56
	8.40	338.8	333.5	0.335	
	4.30	353.7	348.8	0.215	+0.44
	7.60	353.9	348.6	0.263	
<i>n</i> -C <sub>7</sub> — <i>n</i> -C <sub>14</sub>	4.00	308.5	303.6	0.552	+0.90
	10.00	309.2	303.6	0.717	
	4.00	325.1	318.5	0.601	
	10.00	324.2	318.3	0.679	+0.93
	4.00	340.2	333.3	0.881	
	10.00	339.3	333.3	0.553	
	4.00	313.2	303.1	0.727	+0.88
	10.30	314.4	304.2	0.514	
	4.50	308.9	303.6	0.735	+1.03
	5.50	308.9	303.6	0.778	
<i>n</i> -C <sub>7</sub> — <i>n</i> -C <sub>18</sub>	12.00	308.9	303.6	0.778	+0.95
	4.00	308.9	303.6	0.752	
	4.30	309.0	303.7	0.838	
<i>i</i> -C <sub>7</sub> — <i>n</i> -C <sub>12</sub>	11.00	308.8	303.6	0.900	+0.43
	4.00	308.9	303.6	0.308	
	4.00	308.9	303.6	0.237	
<i>i</i> -C <sub>7</sub> — <i>n</i> -C <sub>16</sub>	10.50	308.8	303.4	0.216	+0.22
	4.00	308.9	303.6	0.107	
	4.00	308.8	303.4	0.161	
Ph— <i>i</i> -C <sub>7</sub>	12.00	308.7	303.4	0.199	-0.59
	4.50	308.9	303.5	-0.256	
	5.00	308.9	303.5	-0.262	
	12.00	308.8	303.6	-0.246	

the density gradient. If all molecules at the same temperature level have the same kinetic energy, the heavier molecules have the higher momentum and thus the greater tendency to move in the direction of the temperature gradient.

In addition, one must consider a steric effect. The greater the cross section in the direction of the motion the more difficult the motion. This would seem to inhibit the tendency of the large molecules to move in the direction of the temperature gradient, but this effect is overshadowed by the fact that the relative difficulty of movement against the temperature gradient is even greater for large molecules. When moving from hot to cold region the molecules have the advantage of the higher kinetic energy consistent with their higher "temperature" and are able to force themselves into relatively small holes. By the end of a retention time it may be assumed that the molecules have come to thermal equilibrium with the surroundings and have less kinetic energy and a smaller chance of escaping. This "trapping" effect is much more efficient on large molecules more nearly the size of the cage.

The probability of finding a high concentration of a given species in the hot region can be written

$$\chi = k'/m\sigma, \quad (1)$$

where  $m$  is the mass and  $\sigma$  the cross section in the direction of flow. The thermal diffusion ratio is proportional to the difference in these probabilities for the two species.

$$\alpha = K[(k_1'/m_1\sigma_1) - (k_2'/m_2\sigma_2)], \quad (2)$$

or

$$\alpha = (k_1/m_1\sigma_1) - (k_2/m_2\sigma_2). \quad (2')$$

In accord with the above discussion regarding the effect of molecular mass on the direction of thermal diffusion we shall consider that a positive  $\alpha$  corresponds to a movement of the heavy molecule to the cold wall and a negative  $\alpha$  corresponds to a movement of the heavy molecule to the hot wall.

### THEORY OF THE THERMAL DIFFUSION COLUMN

The coefficient of thermal diffusion  $D_T$  is defined by the equation of diffusion

$$c_1(\mathbf{v}_1 - \mathbf{v}) = -D \text{grad} c_1 - (D_T/T) \text{grad} T. \quad (3)$$

In the case of gases it has been shown that the coefficient of thermal diffusion is proportional to the product  $c_1 c_2$ , and therefore a thermal diffusion ratio  $\alpha$  is introduced and defined by the relation

$$D_T = D c_1 c_2 \alpha. \quad (4)$$

In terms of  $\alpha$  Eq. (3) becomes

$$c_1(\mathbf{v}_1 - \mathbf{v}) = D(-\text{grad} c_1 - \alpha(c_1 c_2/T) \text{grad} T). \quad (5)$$

From this equation and the Navier-Stokes equation, Furry, Jones, and Onsager<sup>3</sup> have developed a theory of the thermal diffusion column which results in the following equation for the steady state separation factor.

$$\ln q_s = \left[ \frac{63\alpha D \eta L}{2\bar{T}\omega^4 \beta g} \right] \left[ \frac{1}{1 + 5670(\eta D/g\omega^3 \beta \Delta T)^2} \right], \quad (6)$$

where

$$q_s = (c_1/c_2)_{\text{top}}(c_2/c_1)_{\text{btm}}. \quad (7)$$

The development of the transport equation is based on the assumption of laminar flow. Furry, Jones, and Onsager define the Reynolds number

$$R_e = \frac{\omega^3 g \rho^2 \Delta T}{4\gamma \eta^2 \bar{T}}, \quad (8)$$

employing an average value for the convection velocity and considering the annular space as the characteristic length. For flow between plane surfaces Onsager and Watson<sup>4</sup> have shown experimentally that the critical  $Re$  is about 25.

An approximate equation for the rate of approach to the stationary state has been developed by Jones and

<sup>3</sup> Furry, Jones, Clark, and Onsager, Phys. Rev. **55**, 1083 (1939).

<sup>4</sup> L. Onsager and W. W. Watson, Phys. Rev. **56**, 474 (1939).

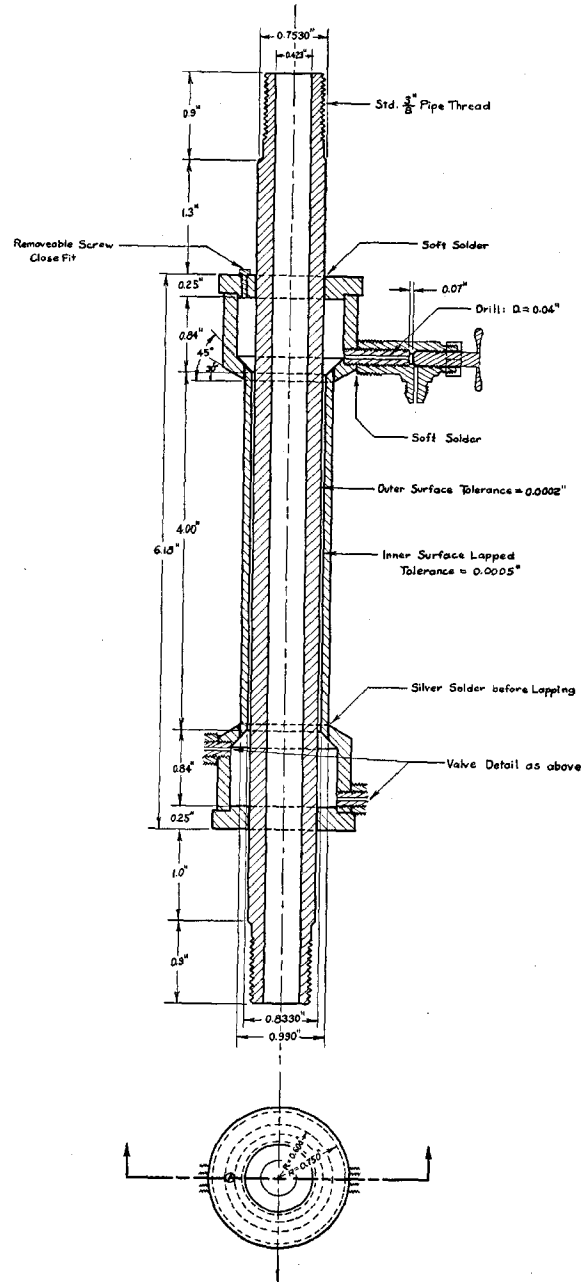


FIG. 1. Thermal diffusion column.

Furry<sup>5</sup> by assuming that the volume of each reservoir is large compared to the volume between the walls of the column. For the special case in which  $c_1 c_2 \cong \text{constant}$  they have derived a simple exponential approach to the steady state

$$(\Delta c/\Delta c_s) = 1 - \exp(-t/t_r), \quad (9)$$

for which the relaxation time is

$$t_r = \frac{V + L}{(2\omega^3 g^2 \beta^2 B(\Delta T)^2 / 2835 \eta^2 D) + 4\omega DB}. \quad (10)$$

<sup>5</sup> Jones, Clark, and Furry, Rev. Mod. Phys. **18**, 151 (1946).

## EXPERIMENTAL METHODS AND RESULTS

The systems studied and the analytical methods used were the same as those discussed in the previous paper on diffusion.<sup>6</sup>

The thermal diffusion column was designed with a calculated relaxation time of less than an hour to obtain the stationary state in a reasonable time. A small value for  $\Delta T$  was chosen to make possible a study of the temperature dependence of  $\alpha$ . As a result of this limitation it was necessary to use a relatively large annular space with correspondingly small equilibrium separations. This situation arises from the fact that  $\ln q$  is inversely proportional to the fourth power of the gap and  $t_r$  is inversely proportional to approximately the seventh power of the gap. The column is shown in the accompanying drawing.

From (8) it is readily shown that these dimensions will give rise to laminar flow in the column.

The column was mounted in a water thermostat, and water from a second thermostat was circulated through the inner tube at a velocity of about 5 feet per second by a positive displacement pump. Water temperatures were regulated to better than  $0.1^\circ\text{C}$ , and wall temperatures of the column were measured by copper-constantan thermocouples clamped against the walls. A Leeds and Northrup portable precision potentiometer was used for temperature measurements. No attempt was made to calculate temperature drops through the walls because the term involving  $\Delta T$  in (6) seldom makes a significant contribution to  $\alpha$  for our choice of column

and operating variables and consequently accurate values of  $\Delta T$  are not required.

The method of column operation was as follows. Having drained the water from the bath the column was filled with liquid from a brass reservoir attached by a copper tube and screwed fitting to the lowest valve. The filling reservoir and tube were then removed and a screwed fitting with a closed end was connected to each valve to prevent water entering the valve. After filling the bath with water and adjusting its temperature, circulation from the second bath was begun. At the end of a run, which usually lasted 4 to 10 hours, half the water was drained from the bath and the upper sampling cock was dried with filter paper. The protecting fitting was removed from the cock and the contents of the upper reservoir were drained. The remaining water was siphoned from the bath, cocks were dried with filter paper and the contents of the column and lower reservoir were drained. It was considered important that sampling be done as rapidly as possible and for this reason a rubber blow-tube was connected to the top of the column. The bath could be drained in about 30 seconds and the entire sampling procedure completed in  $2\frac{1}{2}$  to 3 minutes.

The concentration of all mixtures was initially 50 mole percent and in most runs the  $\Delta T$  was about  $5^\circ\text{C}$ . All runs were carried out in duplicate or triplicate, and data are recorded in Table I. In calculating  $\Delta c$  the assumption was made that refractive index varies linearly with mole fraction, an excellent approximation over the small range of concentrations involved.

In calculating values of  $\alpha$  from Eq. (6) values are

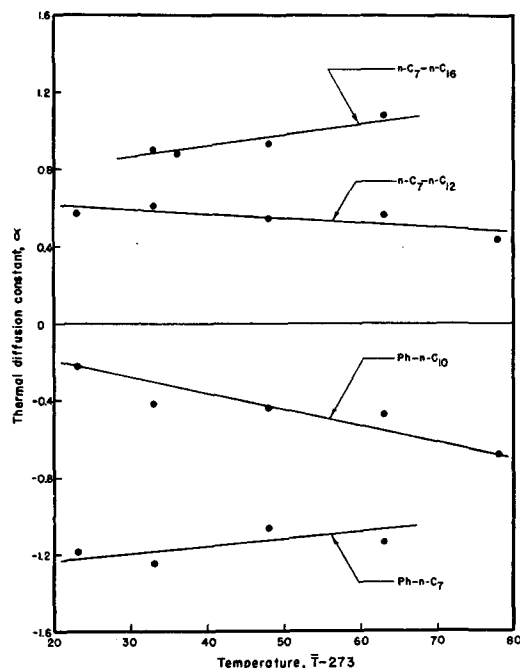


FIG. 2. Variation of thermal diffusion constants with temperature for mixtures of liquid hydrocarbons.

<sup>6</sup> D. J. Trevo and H. G. Drickamer, J. Chem. Phys. 17, 1117 (1949).

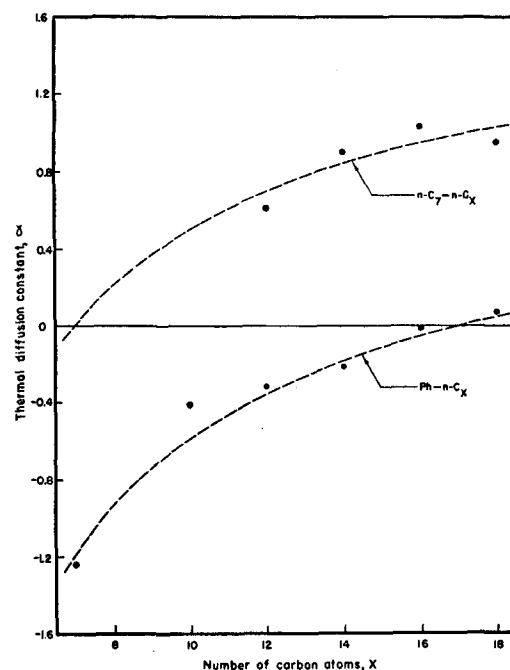


FIG. 3. Comparison of thermal diffusion constants obtained experimentally with those calculated by Eq. (2).

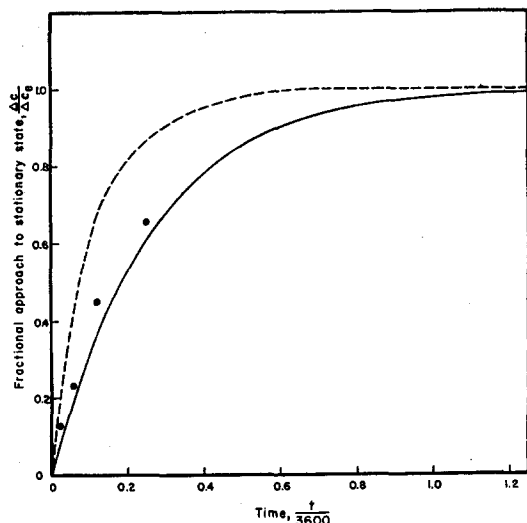


FIG. 4. A comparison of the rate of approach to the stationary state with that predicted theoretically in a thermal diffusion column. Values calculated by (10) are joined with a broken line.

needed for the diffusion coefficient, the coefficient of viscosity, and the temperature coefficient of density. The measured diffusion coefficients are discussed in the previous article.<sup>6</sup> The viscosities of the mixtures have been published earlier.<sup>7</sup> Density data were taken from standard sources<sup>8,9</sup> and the temperature coefficient calculated on an additive basis. The data are shown in Table I.

#### DISCUSSION OF RESULTS

As predicted by (4) for our choice of column and operating variables  $\alpha$  is substantially independent of  $\Delta T$ . A study of Table I shows this to be true for benzene—*n*-heptane mixtures over a threefold range of  $\Delta T$ , and for *n*-heptane—*n*-tetradecane over a twofold range.

To illustrate the temperature dependence of  $\alpha$ , data taken from Table I for four systems are plotted in Fig. 2. While the data for each system are consistent, within experimental error,  $\alpha$  increases slightly with increasing temperature in some cases and decreases slightly in others. For this reason one cannot generalize

regarding the dependence of  $\alpha$  on temperature although it appears that it does not vary rapidly with temperature over a range of 55°C.

The upper curve in Fig. 3 compares experimental values of  $\alpha$  at 303°K with those calculated from Eq. (2') on the assumption that  $k$  is independent of chain length. The agreement shown implies that the normal paraffins up to  $C_{18}$  move in the liquid state in the same zigzag chain in which they occur in the solid state.

Using  $k = 2.75 \times 10^{-22}$  for the normal paraffins, as obtained from the paraffin-paraffin series, we obtain a value of  $k = 9.04 \times 10^{-22}$  for benzene. The lower curve in Fig. 3 indicates that this value is a constant for the entire benzene-paraffin series. From the above data one can see that  $(k/\sigma)$  for benzene is about three times that for the paraffins. It is interesting to note that cross section of a benzene molecule taken edgewise is about twice that of a zigzag paraffin chain, while the cross section flatwise is about four times that of the paraffin chain. This is an indication that  $k$  is substantially constant from compound to compound. This low mobility for benzene is consistent with its high viscosity and relatively low diffusivity in many mixtures.

From what is known of the structure of iso-paraffins one would predict a larger cross section and therefore a lower mobility for *i*- $C_7$  relative to *n*- $C_7$ . On this basis  $\alpha$  for *i*- $C_7$ —*n*- $C_x$  series should be less than  $\alpha$  for the corresponding *n*- $C_7$ —*n*- $C_x$  series. Also  $|\alpha|$  for *i*- $C_7$ —Ph should be less than that for *n*- $C_7$ —Ph. This is confirmed by experiment as indicated in Table I.

#### APPROACH TO STATIONARY STATE IN DIFFUSION COLUMN

From data given in Table I for the system Ph—*n*- $C_7$  the rate of approach to the stationary state may be compared with that predicted theoretically. The broken line in Fig. 4 represents the rate of approach calculated by (10) while the solid line is that obtained using the mean relaxation time determined by experiment. From (10)  $t_r = 379$  seconds and from experiment the mean of five values is  $t_r = 936$  seconds. The derivation of (10) involves several assumptions one of which is that the volume between hot and cold walls is small compared to the volume of the reservoirs. For the present column this assumption is not valid and one would expect the calculated relaxation time to be too small. For this reason agreement between theory and experiment is considered very satisfactory.

<sup>7</sup> D. J. Trevoy and H. G. Drickamer (to be published).

<sup>8</sup> G. Egloff, *Physical Constants of Hydrocarbons* (Reinhold Publishing Corporation, New York, 1941).

<sup>9</sup> *International Critical Tables* (McGraw-Hill Book Company, Inc., New York).