SOLUBILITY AND DIFFUSIVITY OF HIGH MOLECULAR WEIGHT SOLID PARAFFINS IN PARAFFIN SOLVENTS

by

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SUMMARY

In this work solubilities and diffusivities of the high molecular weight solid paraffins, tetracosane and dotriacontane, were measured in the low molecular weight liquid paraffin solvents, hexane and dodecane. A method for measuring the solubilities of solids in liquids has been developed using a simple titration technique. The volume of solvent required to dissolve a known quantity of solid, has been measured using laboratory glassware and visual determination. It has proven to be not only simple and rapid but also accurate.

A method for measuring diffusivities in liquid solutions using a modified diaphragm cell has also been developed. The accuracy of the cell was tested using previously measured data. Agreement was generally good. Furthermore diffusion coefficients were measured for dotriacontane and tetracosane in hexane and octane solutions for which there were no available data in literature. The new diffusion cell can be described as a multi-tube diaphragm cell with its two compartments having different volumes. It has distinct advantages over the old diaphragm cell in that it does not require a prior calibration and it can be used both in the steady-state and transient mode for experimental determinations.

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NOMENCLATURE

a	activity
A	constant in Equation (12)
A_{cap}	diffusion area, cm^2
B	constant in Equations (1) and (12)
c	molar concentration, gm-mole/ml
C_{av}	arithmetic average concentration between the top and bottom compartments, gm-mole/ml
C_o	initial concentration, mole fraction
$\bar{C}_o$	average concentration of the diffusant in the top compartment, mole fraction
C_{oF}	final concentration in the top compartment, mole fraction
$C_{(x,t)}$	variable dependent on x, t
d	displacement in differential refractometer
Δd	reading of total displacement
$d_2 - d_1$	differential refractometer reading for the solution
$d_2' - d_1'$	zero reading for the solvent
D, D_{AB}	diffusion coefficient, cm^2/sec
H	heat content, Kcal/gm-mole
ΔH^F	heat of fusion, Kcal/gm-mole
J	molar flux relative to average velocity, gm-mole/sec-cm^2
K	calibration constant of the differential refractometer

m	an integer
M	molecular weight
M_t	total amount of diffusant transferred in time t
n	refractive index
Δn	refractive index difference
N_A	molar flux relative to fixed point, gm-mole/sec-cm^2
N_{A_o}	N_A at $x = 0$
R	universal gas law constant, 1.987 cal/gm-mole-°K
t	time, secs
T	temperature, °K
T_{NBP}	temperature at the normal boiling point, °C (Table 1)
$T_{(t)}$	variable depended only on t; T' refers to differentiation with respect to t
v	volume of the top compartment, ml
V	molal volume at the normal boiling point V_1 for solvent, V_2 for solute, ml/gm-mole
x	mole fraction; distance in x direction
X	association parameter in Wilke-Chang equation
$X_{(x)}$	variable depended only on x; X'' refers to differentiation with respect to x.
$y_{A_{lav}}$	arithmetic average mole fraction of the diffusant in the top compartment
y_{A_2}	mole fraction of the diffusant in the bottom compartment
z	variable in Equation (50)

Greek Letters

γ	activity coefficient
μ	viscosity, cps (table 1)
ρ	density, gm/ml (table 1)
ϕ	mass, gm
ω_{A_1}	mass fraction of the diffusant in the top compartment $\frac{\rho_A}{\rho}$

Subscripts

A	solute
B	solvent
m	melting point
S	steady-state
t_D	diffusion time, secs
t_w	washing time, secs
T	transient

INTRODUCTION

When considering the solubility of solids in liquids it is noted that certain thermodynamic properties can characterize the behavior of solutions. Thus an ideal solution is formed if the mixing process takes place at constant temperature and pressure without change in energy or volume. There are many pairs of molecular species so nearly alike in their attractive forces that their liquids mix with little or no heat effect. Such solutions are designated as athermal or semi-ideal. "A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged " as stated by Hildebrand and Scott [10] who indicated that regular solutions obey the relation:

$$RT \ln \gamma_2 = B x_1^2 \qquad (1)$$

In the present work, ideal solubilities were calculated by the aid of the equation also derived by Hildebrand and Scott [10] :

$$\log \frac{1}{x_2} = \frac{\Delta H^F}{4.575}\left(\frac{T_m - T}{T_m \cdot T}\right) \qquad (2)$$

Equation (2) gives the solubility of a solid in any solvent in which it forms an ideal solution. It was derived from the general relation:

$$\frac{d \ln a^s}{dT} = \frac{H^\ell - H^s}{RT^2} = \frac{\Delta H^F}{RT^2} \qquad (3)$$

By integration of Equation (3) and making use of the assumption that the heat of fusion ΔH^F was constant the following equation was obtained:

$$\ln a^s = -\frac{\Delta H^F}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad (4)$$

Finally Equation (2) was obtained by substituting x_2 for a^s and by rearranging the term containing the negative logarithm since $x < 1$.

In the first part of this work, solubilities were determined at different temperatures using a simple technique. The volume of solvent from a burette necessary to dissolve a known quantity of solid in a volumetric flask was determined visually at the point when the solid completely disappeared. When the solid was nearly dissolved, the solvent was added very slowly, drop-wise, to ensure that the end-point was not exceeded. The solubility of dotriacontane in hexane and in dodecane were available from the literature at certain temperatures for comparative purposes. Additional solubility measurements were made over a wider temperature range for dotriacontane as well as for tetracosane in the same solvents. The range of temperature chosen was based on the melting point of the solutes and also on the freezing point and boiling point of the solvents.

In previous solubility measurements, investigators[8,13] used a technique based on the disappearance of a solid in a sealed ampule containing a synthesized solid-solvent system. A precise bracketing of the temperature at which the solvent saturation took place was performed by measurements of the temperature at which some solid remained undissolved and another temperature slightly above, at which no solid remained. The solution temperature used in the method was the average of these two temperatures. This technique was found to be tedious and time consuming. The method described in this thesis largely overcomes the above disadvantages.

The basic formulas of mole and mass fraction were used to calculate experimental solubilities.

$$w_B = \frac{\phi_B}{v_A \rho_A + \phi_B} \tag{5}$$

$$x_B = \frac{\phi_B/M_B}{v_A \rho_A/M_A + \phi_B/M_B} = \frac{\phi_B}{\phi_B + v_A \rho_A M_B/M_A} \tag{6}$$

Fick's law describes diffusion phenomena. For a binary mixture of compounds A and B, the diffusive flux is given by:

$$J_A = - D_{AB} \frac{\partial C_A}{\partial x} \tag{7}$$

The flux of component A is measured relatively to the molar average velocity. By considering the effect of bulk flow the flux can be converted to one relative to a fixed position.

$$N_A = (N_A + N_B) \frac{C_A}{C} - D_{AB} \frac{\partial C_A}{\partial x} \tag{8}$$

Analogous expressions can be written for component B. It may be shown that $D_{AB} \equiv D_{BA}$ [21, 28], which means that the diffusion coefficient, usually known as mutual or interdiffusion coefficient, is the same value regardless of which component is being considered.

Current theories proposed to describe diffusion process have either hydrodynamic, kinetic, statistical-mechanical or thermodynamic foundations. Of these, the first two have probably had the greatest direct application.

The Stokes-Einstein equation was based on hydrodynamic principles. The diffusivity and solvent viscosity were found to be inversely related, as would be expected for the process for large molecules diffusing in a low molecular weight solvent. The equation should be applicable to describe diffusion strictly for spherical or nearly spherical molecules in solvents of considerable smaller molecules. It has thus become general practice to calculate the size of the diffusing particles using the Stokes-Einstein equation.

According to the Eyring theory [35], on the other hand, diffusion was considered as an activated rate process, taking place by jumping of individual molecules from one position to another, under a force arising from the gradient of the chemical potential. An important inherent assumption, that the free energies of activation for diffusion and viscous flow were equal, was subsequently found to be invalid even for many ideal or nearly ideal systems. However, the Eyring kinetic theory was at least partially successful in describing the temperature coefficient of diffusivity.

A number of empirical correlations are available for the prediction of diffusivity. The correlations of Wilke and Chang, Lusis and Ratcliff, Scheibel, and the hypothesis of Hayduk and Cheng have been considered in this work, as being useful in describing the diffusivities in binary liquid systems.

The empirical equation of Wilke and Chang [27] is:

$$D_{AB} = 7.4 \times 10^{-8} \frac{(X M_B)^{1/2} T}{\mu V^{0.6}} \qquad (9)$$

The application of this equation is limited because no rigorous treatment of solute-solvent interaction was considered in its derivation.

Scheibel [18] proposed a modification of the Wilke-Chang relation in which the association parameter of solvent was eliminated.

$$D_{AB} = 8.2 \times 10^{-8} T\left[1 + \left(\frac{3 V_1}{V_2}\right)^{2/3}\right]/\mu V_1^{1/3} \quad (10)$$

The more recent Lusis and Ratcliff correlation [30] also avoided the use of any interaction parameter.

$$\frac{D_{AB}\,\mu}{T} = \frac{8.52 \times 10^{-8}}{V_1^{1/3}}\left[1.40\left(\frac{V_1}{V_2}\right)^{1/3} + \left(\frac{V_1}{V_2}\right)\right] \quad (11)$$

The equation was shown to give slightly better results than the previous correlations.

Hayduk and Cheng [34] chose the hypothesis that the diffusivity of a particular dilute species in any solvent depended only on the solvent viscosity, provided that there was no molecular aggregation of either the solute or solvent on mixing. This hypothesis suggested that a relationship existed between a particular diffusing species in a range of solvents, temperatures, and solvent compositions, depending only on the solvent viscosity.

$$D_{AB} = A\,\mu^{B} \quad (12)$$

A number of experimental devices and methods have been developed for the determination of diffusivities in liquids. Perhaps the most common is the diaphragm - cell technique which was first developed by Northrop and Anson (1929) [43] later improved by Gordon (1937) [47] and brought by Stokes (1950) [48] to a stage where

it became recognized as an exact method for the measurement of diffusion coefficients. Another reliable method for measuring liquid diffusivity was described by Hollander and Barker (1963) [49] using radioactive tracer components. In this method the concentrations were monitored outside the diaphragm cell. The contents of the diaphragm cell were circulated periodically through a scintillation counting chamber and the concentration differences measured.

Recently Sanni and Hutchison [44] described a modified diaphragm-cell in which the composition in the top compartment was determined continuously by measuring changes in the conductivity or capacitance of the solution. Witherspoon and Saraf [25] used the capillary-cell method perfected by Wang [52] in a modified way. Whereas the former experiments were conducted at steady-state, the latter workers used the transient method requiring less time per experiment.

Other workers [32] measured diffusion coefficients using a Mach-Zehnder diffusiometer. This equipment measured refractive index gradients, which were proportional to concentration gradients over narrow concentration ranges, by means of interference fringes. With this device it was possible to measure local concentrations along the diffusion path.

Haluska and Colver [36], Hiss and Cussler [41] later, used the technique of Savart plate interferometer to measure diffusion coefficients in binary nonideal liquid systems, in which an experiment was conducted by forming a horizontal interface between two solutions in a flowing junction test cell. Measurement of the product of the refractive index of the solution and the geometrical length through the diffusion cell was related to the solution of Fick's second law for determination of the diffusion coefficient.

Hahn [29] demonstrated successfully the applicability of the NMR phenomenon for diffusion measurements. NMR phenomenon can be observed with molecules, that contain atomic nuclei with both magnetic moment and angular momentum. The procedure required the calculation of the ratio of the echo amplitudes for two different, known field gradients.

In this work diffusion measurements were conducted both under steady-state and transient conditions. The corresponding mathematical analyses for the diffusivity measurements were based on Fick's first and second laws.

Integration and manipulation of Fick's first law, Equation (7) yielded an expression as follows:

$$D = \frac{N_A L}{C (y_{A_2} - y_{A_{1\,av}})} \tag{13}$$

For application in Equation (13) the flux was expressed by:

$$N_A = \frac{\omega_{A_1} v_1 \rho_1}{M t A_{cap.}} \tag{14}$$

Substitution of Equation (14) into Equation (13) yielded the following expression for the diffusion coefficient for the steady-state process:

$$D = \frac{\omega_{A_1} v_1 \rho_1}{M t A_{cap}} \cdot \frac{L}{C_{av} (y_{A_2} - y_{A_{1\,av}})} \tag{15}$$

The time required to obtain a steady-state concentration profile within a certain depth of liquid was calculated from a knowledge of the diffusion path length and an estimated diffusivity, using Crank's [33] Equation:

$$Dt = 0.45\ L^2 \tag{16}$$

In many cases the determination of diffusivity in liquids using transient methods is advantageous. Since diffusion in liquids is slow, in steady-state experiments it is difficult to measure the relatively low diffusive flux and long periods of time are required. Transient experiments circumvent both these disadvantages. The solution which applies in such cases is based on Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{17}$$

The concentration profile within a semi-infinite liquid is expressed as:

$$\frac{C_1 - C}{C_1 - C_o} = \text{erf}\left(\frac{x}{2\sqrt{D t}}\right) \tag{18}$$

The molar flux at the boundary is given by:

$$N_{A_o} = \frac{D (C_1 - C_o)}{\sqrt{\pi D t}} \tag{19}$$

Then the total amount having left the tube in time t per unit area, is a combination of Equations (18) and (19)

$$M_t = \frac{2}{\sqrt{\pi}} \sqrt{D t}\ (C_1 - C_o) \tag{20}$$

Derivation of Equation (20) is shown in Appendix A. According to the penetration theory for constant diffusivity D and a given time t, a penetration depth δ can be determined from the expression derived by Danckwerts [17]:

$$\delta = 3.6 \quad Dt \tag{21}$$

In the transient process for measuring diffusivities the contact time between the liquid components is short, so that the penetration of the dissolved solid is essentially the same as if it occurred into an infinitely long column of liquid. The "depth of penetration" has been arbitrarily defined as the depth at which the rise in concentration is 1/100 of the maximum concentration, and given by Equation (21).

Fick's second law, Equation (17), has also been solved for a finite diffusion path length. Details of this solution are also given in Appendix A. The instantaneous flux and total amount of material transferred upto time t per unit area are given by Equations (22) and (23), respectively:

$$N_{A_{x=0}} = D\,(\partial C/\partial x)_{x=0} = D\left[\frac{C_1}{L} + \frac{2C_1}{L}\sum_{1}^{\infty}(-1)^n \exp\left[-\left(\frac{n\pi}{L}\right)^2 Dt\right] + \frac{4C_o}{L}\sum_{o}^{\infty}\exp\left[-\left(\frac{(2n+1)\pi}{L}\right)^2 Dt\right]\right] \tag{22}$$

$$M_t = \frac{DC_1 t}{L} + \frac{2C_1 L}{\pi^2}\sum_{1}^{\infty}\frac{(-1)^n}{n^2}\left[1 - \exp\left[-\left(\frac{n\pi}{L}\right)^2 Dt\right]\right] + \frac{4C_o L}{\pi^2}\sum_{o}^{\infty}\frac{1}{(2n+1)^2}\left[1 - \exp\left[-\frac{(2n+1)\pi}{L}\right)^2 Dt\right]\right] \tag{23}$$

Of the two transient solutions outlined above, the former was found the more useful. It was necessary to ensure that the conditions of that solution were met. Hence, transient diffusion experiments were limited to diffusion times which were less than those for which the penetration depth was equal to the diaphragm thickness ($\delta < L$).

Diffusivities were calculated as follows. Equation (15) was applied for measurements at steady-state. The concentration of the mixture in the bottom compartment was considered constant because of its relatively large volume and the slow rate of diffusion. The arithmetic average concentration of the diffusant in the top compartment over the time interval for the experiment was used to calculate the average concentration driving force.

Equation (20) was applied when the transient mode was used. In that case the washing time for the top compartment was considered because of its influence on the diffusion rate. The initial diffusion rate was greater when the washing time was neglected. For example for a diffusion time of 5 hours and washing time of 1 minute the diffusivity was 11% greater if the 1 minute was not included in the calculations. Thus for diffusivity determinations the following equation was applicable:

$$M_{t_D} - M_{t_w} = \frac{2}{\sqrt{\pi}} A \text{ cap } \sqrt{D} \left[\sqrt{t_D} (C_1 - \bar{C}_o) - \sqrt{t_w} (C_1 - \bar{C}_o) \right] = V C_{oF} \quad (24)$$

The volume of the top compartment was different for each experiment because of the flexibility of the two rubber O-rings at both sides of the teflon diaphragm. The initial concentration in the top compartment was always zero because of the flushing operation.

MATERIALS AND THEIR PROPERTIES

The solvents hexane, cyclohexane and carbon tetrachloride were purchased from Fisher Scientific, New Jersey and were specified to be of spectrophotometric quality. Octane and dodecane were purchased from Matheson Coleman and Bell, Ohio and were certified to have a minimum purity of 99 mole %. The melting points and normal boiling points as given by Ross and Hildebrand [11] for hexane are -95°C, and 68.95°C, and for dodecane are -9.6°C, and 216.3°C respectively [11].

Tetracosane and dotriacontane were obtained from the Eastman Organic chemicals, New York, in the laboratory pure grade. The melting point of tetracosane was 50.9°C [11] with the heat of fusion of 13.12 Kcal/gm mole. For the dotriacontane, Seyer and Fordyce [3] had noted that it undergoes a transition from the β-form to α-form at a temperature of about 55°C. Hildebrand and Negishi [5] found the melting point of dotriacontane to be 70.2°C and the transition point 63.5°C. The solubility data suggests that the latter transition temperature is the more accurate.

The viscosities, densities and Le Bas molal volumes [48] at the normal boiling point of the materials utilized which were required in the course of this work are listed for the pertinent temperatures in Table 1. The numbers appearing in the table 1 are from the literature. Le Bas molal volumes were used to calculate diffusion coefficients because of similar molal volumes were considered in the empirical correlations which are referred in this thesis.

TABLE 1

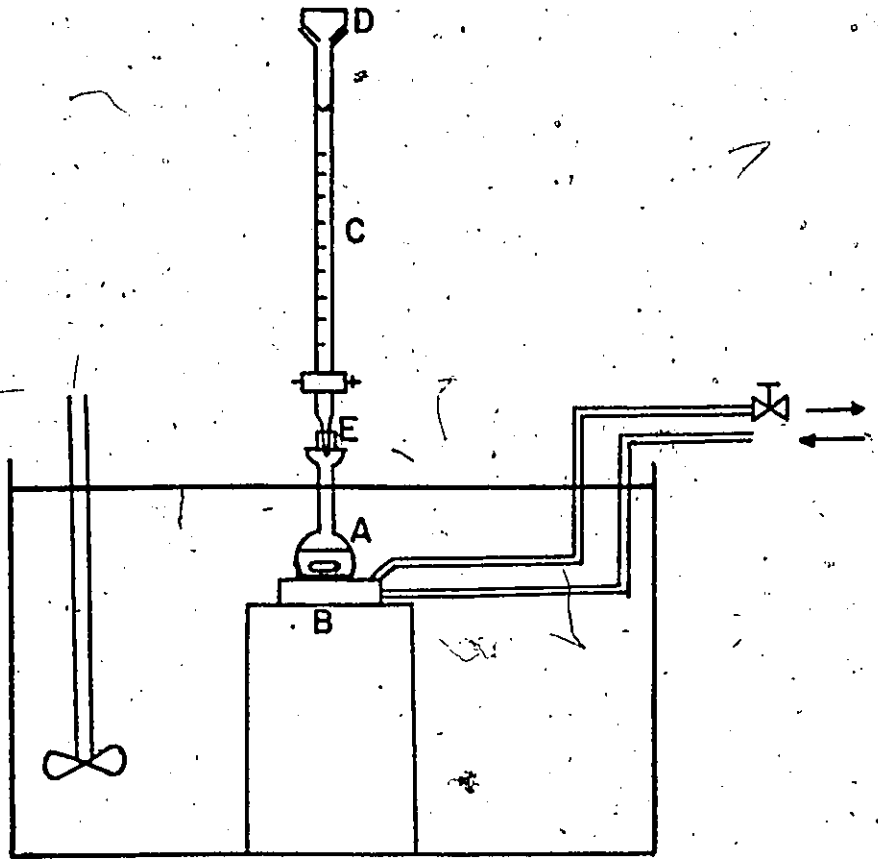
Viscosity, Density and Molal Volume of Compounds

Compound	Properties	T_{NBP}	Temp, °C						
			0	25	47.5	50	65	75	100
cyclohexane	μ			0.8980					
	ρ			0.77383					
	V	118.0							
carbon-tetrachloride	ρ			1.58452					
	V	102.0							
n-hexane	μ			0.2985					
	ρ		0.6769	0.6549	0.6342	0.6316			
	V	141.0							
n-octane	μ			0.5151				0.3134	0.2555
	ρ			0.69849				0.6571	0.6352
	V	185.0							
n-dodecane	μ			1.3780					
	ρ		0.7637	0.74516	0.7288	0.7271	0.7161		
	V	274.8							
n-tetracosane	V	540.2							
n-dotriacontane	V	718.0							

APPARATUS AND PROCEDURE FOR SOLUBILITY DETERMINATIONS

Solubility measurements were performed on a semi-micro scale. The solubility apparatus which is shown in Figure 1, consisted basically of a 10 ml precision solvent burette and 10 ml volumetric flasks. An amount of solute was weighed into the flask and then gradually dissolved while the flask was immersed in a constant temperature bath, by slower adding solvent from the burette. Weighings were performed by means of an electrical balance manufactured by the Mettler company. The precision of the solvent burette was 0.01 ml while the solute weights were determined to 10 micrograms. The temperature bath could be kept at any predetermined temperature to within 0.05°C. A water-driven magnetic stirrer was used for stirring the solution inside the flask. The water used for stirring was also supplied at constant temperature by means of a circulating bath purchased from Neslab Instruments. The thermometer used for measuring temperature was an A.S.T.M. thermometer graduated in intervals of 0.1°C and readable to 0.01°C. To achieve temperatures lower than room temperature a refrigeration unit purchased from Neslab Instruments, was used to cool the aqueous ethylene glycol coolant that was prepared for this purpose. To obtain temperatures as low as 0°C the bath was insulated to minimize the heat intake. For this purpose the outside of the bath was covered with styrofoam sheeting.

The procedure for measuring the solubility involved the accurate determination of the mass of the solute and the volume of solvent that was required to dissolve it. The advantage of this method was that a difficult analysis of the saturated solution, a procedure which is rather uncertain in the case of most organic substances as



A solution flask, 10 ml
B water driven magnetic stirrer
C solvent burette, 10 ml
D stopper
E cork

Figure 1 Solubility apparatus

discussed by Garner et al [2], was avoided. A gravimetric analysis of the equilibrated solution was attempted. The solvent was to be evaporated from a measured volume of solution and the residue was to be weighed. However it was found difficult to expel the last traces of solvent from the solute residue.

The first step in making a solubility determination was to tare the 10 ml flask and then to weigh the solute which was added through a funnel. Both tetracosane and dotriacontane were in a fine powder form. The flask was then placed on the magnetic stirrer immersed in the constant temperature bath underneath the burette. Solvent was added slowly to the solute from the burette while the mixture in the flask was stirred. The last drops were added one every ten minutes until all the solid particles disappeared. That "end-point" was observed carefully using a travelling telescope while the flask was illuminated with a powerful light positioned at right angles to the axis of observation. The end point of the solubility measurement was checked by lowering the temperature about 1°C which usually resulted in the formation of tiny crystals or finely divided precipitate of the hydrocarbon solute in a white suspension form. When the temperature was again revised to the particular experimental temperature, the white suspension disappeared and the solution became clear again. The lowering and arising of the temperature was conducted according to a slow procedure of a change in temperature of 0.5°C requiring up to 30 min.

SOLUBILITY RESULTS

The experimental observations are recorded in Tables 2 and 3 in which are tabulated the solubilities for dotriacontane and tetracosane respectively, in hexane and dodecane solvents expressed in grams per 100 gm of solvent, in mole fraction and in mass fraction. Determinations were made in duplicate or in triplicate so that the average solubilities are given. Taking in consideration all the possible errors such as those associated with determining the point of disappearance of the solid particles, measuring the solvent volume, weighing the solute, a possible error in temperature and the reported solvent density, the overall error in the solubility measurements is estimated to be less than 3%.

Figure 2 represents the log of solubility versus the reciprocal of the absolute temperature which has long served well as a means of correlating and interpreting experimental solubility data. Departure from linearity increases as solutions deviate more and more from ideality. A plot of the log solubility versus the log of the absolute temperature gives a more linear relation as shown in Figure 3. In Figure 4 the log of solubility versus the number of carbon atom of the paraffin solvents is shown [3, 6].

TABLE 2

Average values of solubility of dotriacontane, in grams per 100 gm of solvent, in mole fraction and in mass fraction

	Hexane, Solvent			Dodecane, Solvent		
Temp. °C	Grams	Mole fraction	Mass fraction	Grams	Mole fraction	Mass fraction
0	0.127	$2.43 (10^{-4})$	0.00183	0.0426	$1.61 (10^{-4})$	$5.23 (10^{-4})$
25	4.10	0.00775	0.0588	1.57	0.00592	0.0206
50	98.1	0.158	0.608	43.9	0.142	0.376
65	-	-	-	396	0.612	0.847

TABLE 3

Average values of solubility of tetracosane, in grams per 100 gm of solvent, in mole fraction and in mass fraction

	Hexane, Solvent			Dodecane, Solvent		
Temp. °C	Grams	Mole fraction	Mass fraction	Grams	Mole fraction	Mass fraction
0	2.58	0.00653	0.0367	0.919	0.00460	0.0118
25	42.4	0.0973	0.393	17.7	0.0820	0.192
47.5	1076	0.732	0.944	511	0.730	0.875

DISCUSSION OF SOLUBILITY RESULTS

For the purpose of checking the accuracy of the technique and apparatus used, the results obtained in this work were compared with data available from the literature. The observations are recorded in Table 4 and are shown in a distinct way in Figure 2 in which can be seen that solubilities of this work for dotriacontane fall close to those of Seyer [6] and Hildebrand [4]. The maximum difference is 4.22%. The reproducibility of duplicate or triplicate determinations was estimated at less than 1%. This leads to the conclusion that the utilized technique and apparatus gives results with a maximum deviation of 5.0%. It appears possible that the results of this work and those in the literature differ because of the difference in the techniques used. Perhaps some solute crystals, unobserved, stuck on the inside wall of the flask and remained undissolved thus explaining the slight difference in the solubilities. The fact that determination of solid solubilities is more difficult than that of gas solubilities explains bigger deviations between experimental and literature data.

The broken lines in Figures 2 and 3 represent the ideal solubilities which were obtained by application of Equation (2). The solubilities of tetracosane fall below the ideal solubility line. Hildebrand [8] observed that in the case of dotriacontane a curve for the ideal solubulity should be drawn with due regard to the transition point occuring at 63.5°C for this substance and the melting point at 70°C. Garner, van Bibber and King [2] determined the heats of transition and fusion of normal paraffins with 22, 26, 30, 34 and 35 carbon atoms from which they estimated by interpolation that for dotriacontane the

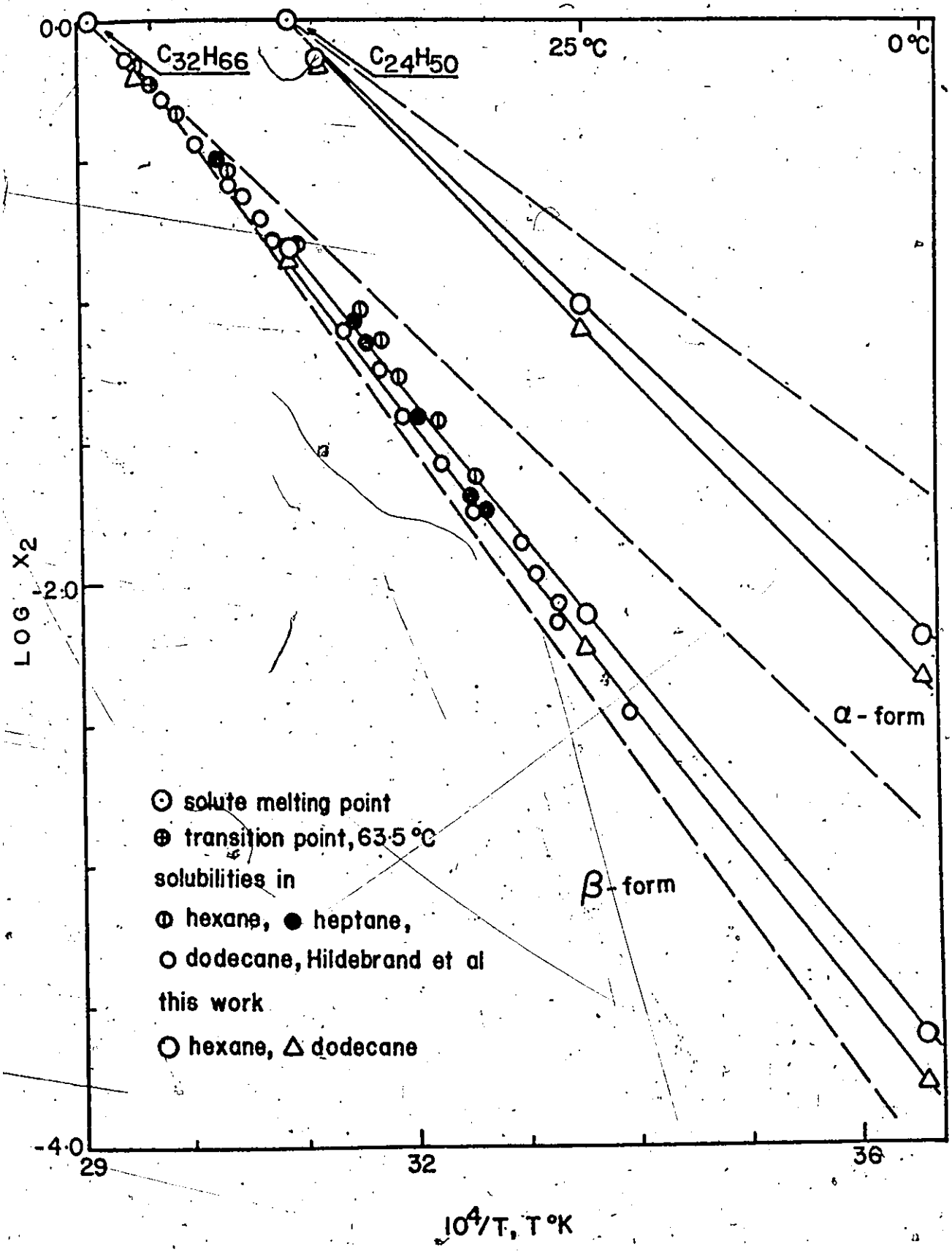


Figure 2 Solubility of n-tetracosane and n-dotriacontane

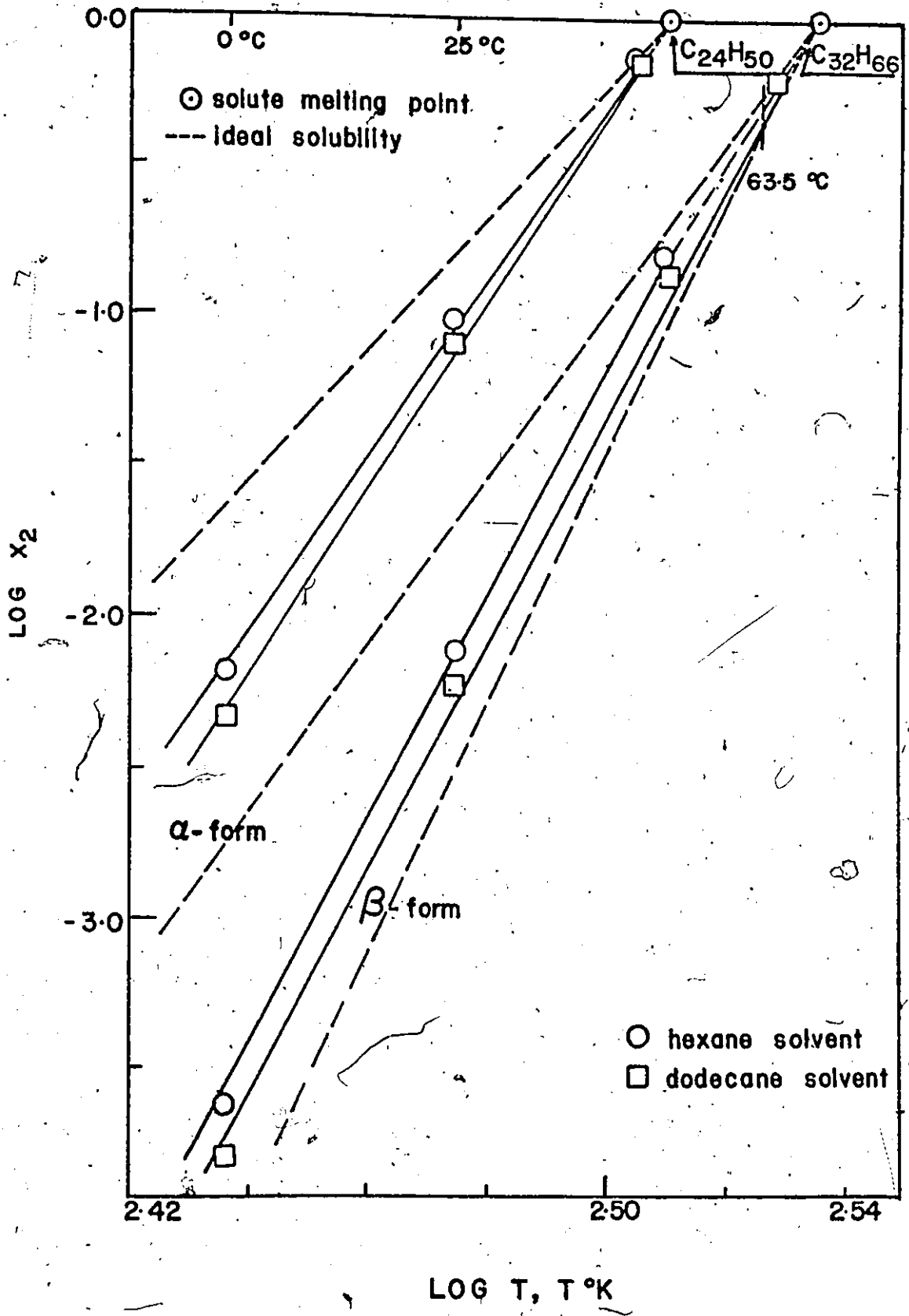


Figure 3. Solubility of n-tetracosane and n-dotriacontane

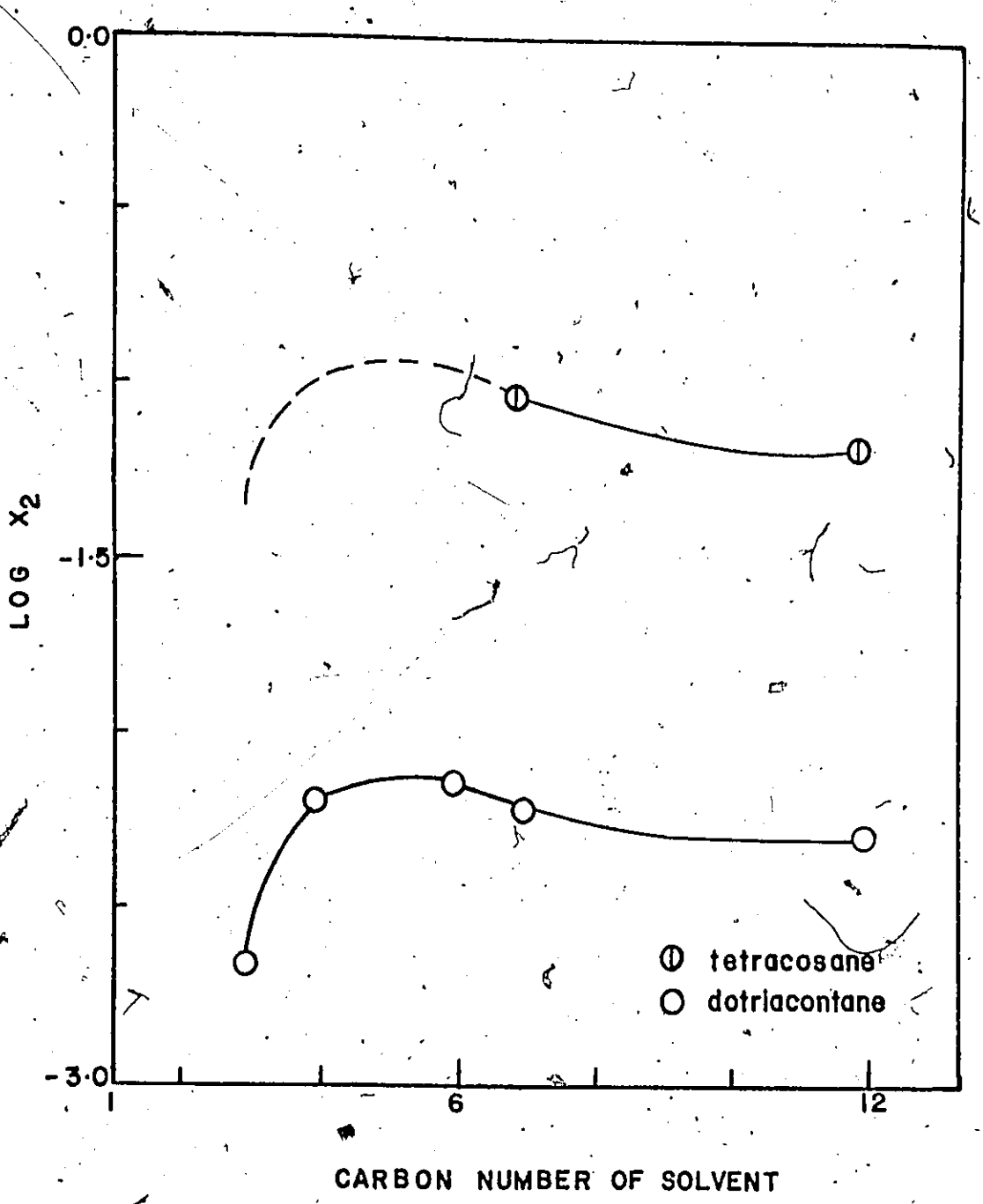


Figure 4 Solubility of n-tetracosane and n-dotriacontane

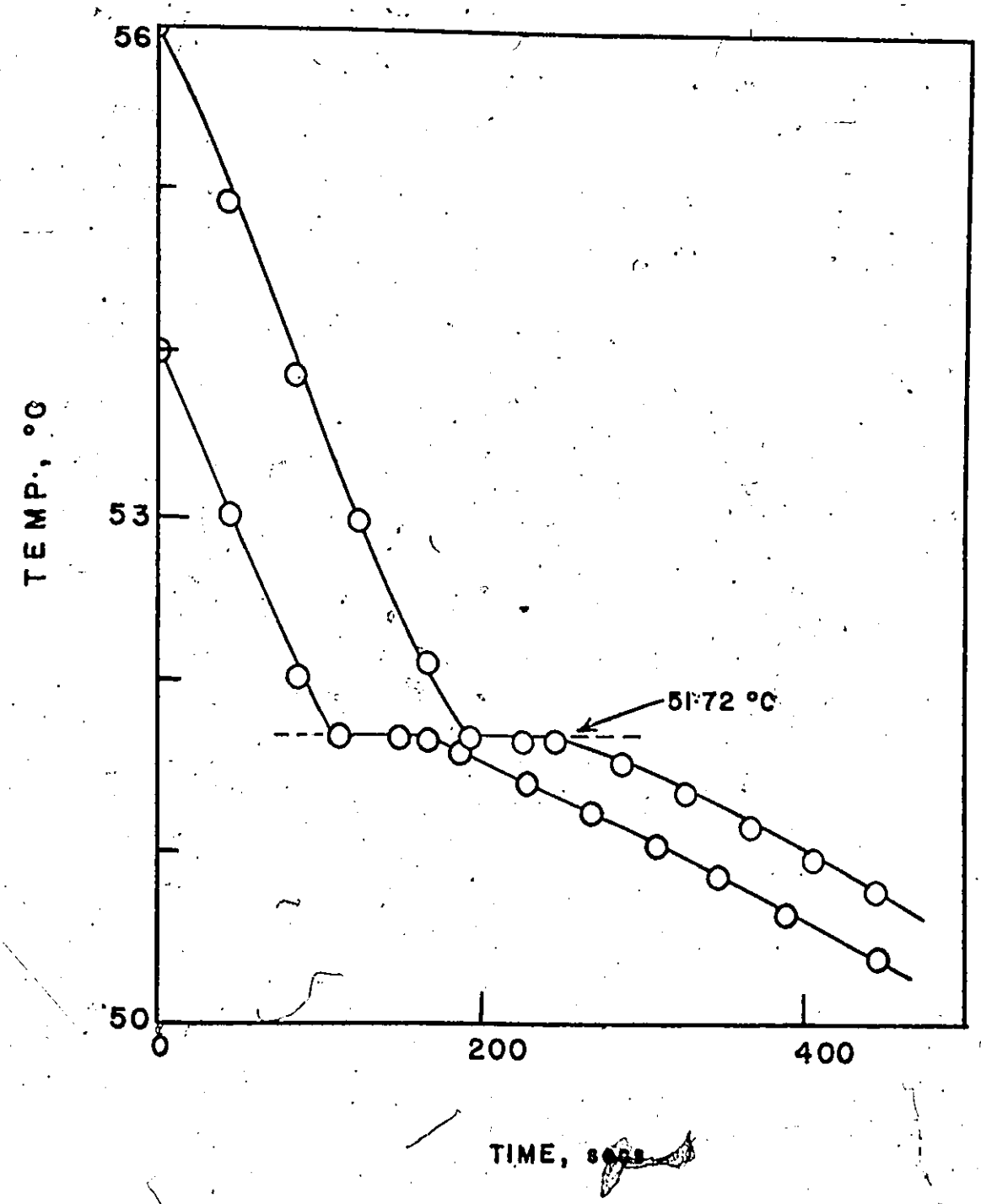


Figure 5 Freezing point plot for dotriacontane in dodecane as solvent ($X_{C_{32}H_{66}} = 0.194$)

TABLE 4

Comparison of solubilities of dotriacontane obtained in this work with literature values

Temp. °C	Hexane, Solvent			Dodecane, Solvent		
	Mole fraction This work	Solubility Literature (6)	% difference	Mole fraction This work	Solubility Literature (6)	% difference
0	$2.43\ (10^{-4})$	-	-	$1.61\ (10^{-4})$	$1.55\ (10^{-4})$	3.87
25	0.00775	0.00750	3.33	0.00592	0.00575	2.95
50	0.158	0.163	3.16	0.142	0.148	4.22
65	-	-	-	0.612	0.634	3.60

molal heats of transition and fusion were 10.4 Kcal and 17.6 Kcal which corresponded to the slope of the ideal solubility line for an α-form, as drawn in Figure 2. The slope of the line for a β-form downward from the transition point corresponds to 28.0 Kcal [10]. The observed solubilities of dotriacontane were found to be between the lines for the α and β-forms. This observed behaviour suggested that the dotriacontane used was probably a mixture of both crystalline forms. An attempt, made at this laboratory to positively detect the presence of these forms by freezing point measurements failed. This is shown in Figure 5 in which the freezing plot of dotriacontane in dodecane is presented with a unique plateau at 51.72 °C instead of two different crystallization temperatures.

Considering the relation between solubility and the temperature as it is shown in Figures 2 and 3 it is almost linear and the lines have regularly increasing slopes in going from the better solvent like hexane to poorer solvent like dodecane. Hildebrand [4] noted that the slope of the line on such a diagram, represented the enthalpy of solution, and hence would be expected to be straight or only slightly curved line over fairly wide ranges of temperature. Such a linear behaviour is characteristic of regular solutions. For both solvents the lines converge to the melting point of the solutes corresponding to $x = 1$.

It can be observed that tetracosane having a lower melting point is more soluble in both hexane and dodecane. Furthermore, both solutes are more soluble in the lower boiling paraffin solvent hexane.

The solubility of dotriacontane in heptane obtained from the literature [4] and dodecane are similar, while the solubility in hexane is slightly higher. It appears probable that the solubility in the remaining paraffin solvents falls between those of hexane and dodecane.

Concerning again Figures 2 and 3, it is evident that these plots can serve to smooth experimental data and can be used to estimate the temperature coefficient of solubility from a single point.

The solubility of dotriacontane was plotted against the carbon number of the solvent as shown in Figure 4. In the case of tetracosane not enough data are available to show the solubility relationship among the paraffin solvents. Seyer and Fondyce [3] investigated the solubility relationship for dotriacontane in propane and butane. The plot indicates the possibility that the solubility of tetracosane varies with the paraffin solvents in a similar manner to that of dotriacontane.

APPARATUS AND PROCEDURE FOR DIFFUSIVITY MEASUREMENTS

Diffusivity measurements have been made using the diaphragm - cell technique. Witherspoon and Saraf [25] used an open-ended capillary-cell method to measure the diffusion coefficients of light hydrocarbons in water at various temperatures. Ross and Hildebrand [24] adopted a steady-state method of measurement. Their diffusion diaphragm consisted of a stainless steel circular plate with a large number of holes, 1 mm in diameter, in it.

The equipment used, shown in the Figure 6, was a modification of the open-ended capillary-cell. Used in conjunction with the diffusion cell was a differential refractometer to analyze the diffusing substance. The diffusion cell diaphragm consisted of a teflon circular plate 8 cm in diameter with a varying height from 2 cm at the perimetry to 1.9 cm at the center, with 252 stainless steel tube holes 2 cm in length and 1 mm in diameter, inserted in holes drilled through the teflon plate, giving a total cross section for diffusion of 1.98 cm^2. The plate was mounted in an apparatus made from stainless-steel as shown schematically in Figure 6. The diameter of the tubes was sufficiently small to eliminate liquid convection within them. Volumes of the two compartments were approximately 25 ml and 205 ml for the top and bottom respectively.

It was necessary to find out in the final experimental runs if there was an appreciable variation in the diffusivity measurements when a stirrer was used in the top compartment of the diffusion cell, particularly during transient measurements. The stirrer was attached to the 1/8 in. O.D. stainless steel central filling tube, supported inside another tube, bigger in diameter (3/8 in. O.D.), with teflon bushing. The tube or stirrer was revolved with a 30 rph motor supplied by Harvard Apparatus Company.

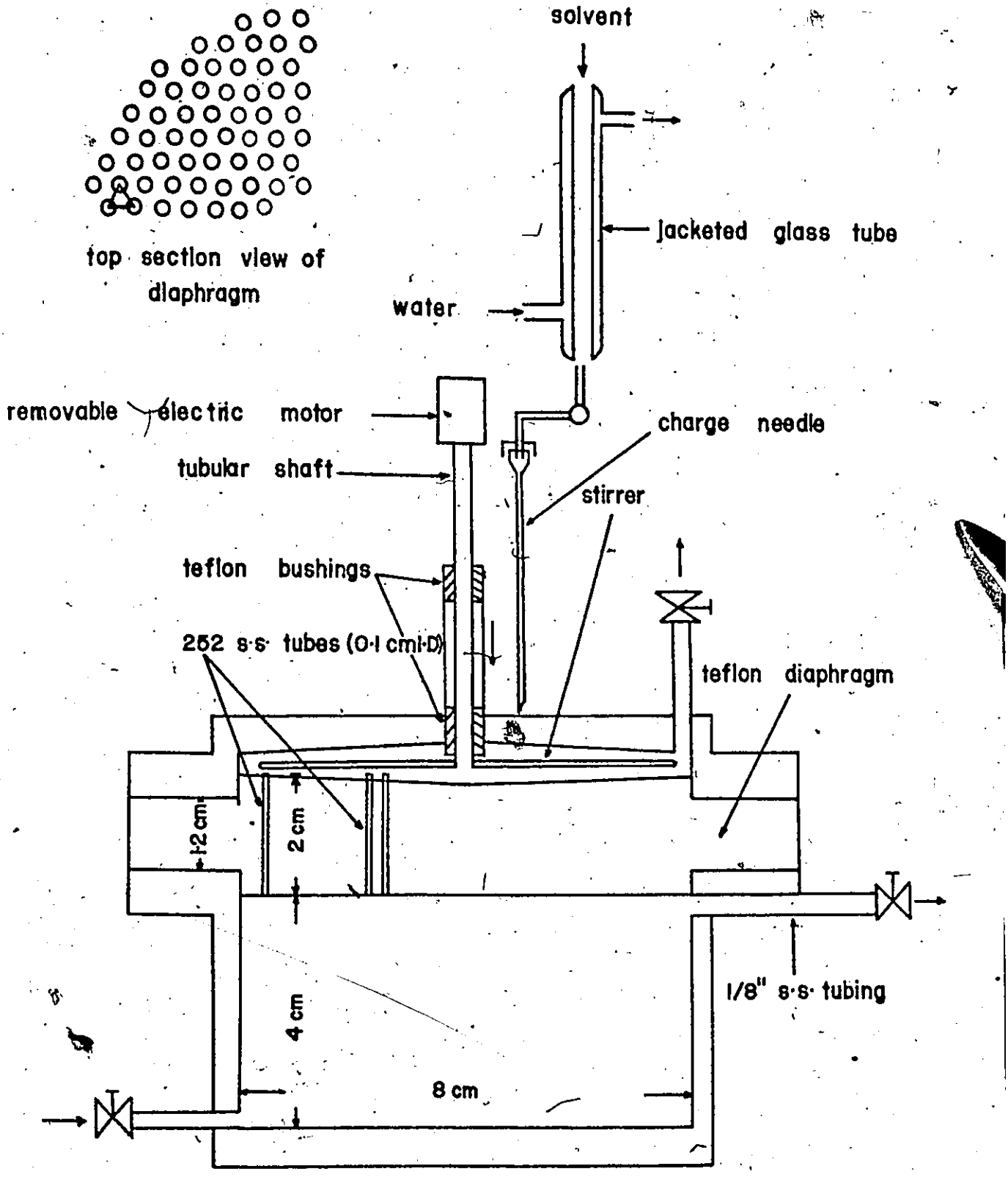


Figure 6 Multi-Tube Diffusion Diaphragm - Cell

Use of the diaphragm cell for a steady-state or transient method for measuring liquid diffusivities assumed that solutions in the upper and lower compartments were of uniform composition. Bulk streaming of the liquids through the tubes was prevented by filling the top compartment with solvent, (less dense liquid), and the bottom with the more dense solution. The upper part of the top compartment was slightly conical, to facilitate the removal of air. The solvent was introduced through the central tube (1/8 in. O.D.), using a needle (1/17 in. O.D.), the tip of which just reached the center of the diaphragm. The same tube and syringe were also used to withdraw the liquid from the top compartment. Use of two rubber O-rings at both sides of the diaphragm prevented any leak between the interior of the cell and the bath liquid. The parts of the cell were fastened tightly together by means of four clamps.

Mutual diffusion coefficients were determined at 25°C for carbon tetrachloride in cyclohexane, each of dodecane, tetracosane, dotriacontane in hexane, and both tetracosane and dotriacontane in octane at 25°C, 75°C and 100°C. The systems carbon tetrachloride-cyclohexane, dodecane-hexane, tetracosane-hexane were conducted at both steady-state and in the transient method. The rest of them dotriacontane-hexane, tetracosane-octane, dotriacontane-octane were conducted only in the transient method.

The procedure for filling the diffusion cell was as follows: solution was first introduced into the bottom chamber and then allowed to completely fill the cell using a hypodermic syringe. The cell was then immersed in a constant temperature bath. After equilibration the solution from the top compartment was withdrawn and the top compartment was rinsed three times with fresh solvent

which had been previously heated to the same temperature as the bath. A jacketed glass tube was used to preheat and deaerate the solvent. Ethylene glycol-water was used as the bath liquid and circulated by means of an immersible pump (Little Giant purchased from Canlab). The method used to remove the dissolved air from the solvent involved preheating the solvent in the jacketed tube and bubbling helium through it for approximately 30 minutes. Deaerating the solvent with helium prevented air bubbles from forming inside the cell which could cause volume changes not associated with the diffusion process. This procedure avoided any thermal volume changes of the solution in the bottom compartment during rinsing and filling of the top compartment and thus eliminated a possible source of thermal mixing. After filling the cell, the filling tubes were closed by means of Swagelock fittings. Special care was needed to avoid disturbing the liquid in the cell when it was filled; otherwise the concentration gradient within the tubes would be altered.

The duration of the experiments depended on whether the diffusion cell was operated at steady-state or in the transient mode. An 8 to 10 hours period was required as a preliminary diffusion time to establish the concentration profile when the steady-state method was used. Typically, the diffusion runs were stopped after 1 to 2 days for the steady-state method. For transient experiments a certain time given by the penetration theory's Equation (22) could not be exceeded. This time was between 4 and 8 hours. Experiments performed using two sets of similar diaphragm cells to reduce the time of the total experimental work.

A method of analysis was carried, based on measurements of concentration difference. The compositions of the hydrocarbon

mixtures from the diffusion runs were determined by means of a differential refractometer. An attempt was made to analyse the solutions, determining the density with a Digital Precision Density Meter (DMA 02C). It was found less sensitive to variations in composition than differential refractometer measurements. The essential parts of the differential refractometer (Brice-Phoenix differential refractometer) are schematically shown in Figure 7. It was designed for the precise measurement of the difference in refractive index between a dilute solution and its solvent. The limiting sensitivity was a difference of about 3 units in the sixth decimal place of refractive index, while the range was 0.01 units. The same technique of analyses was used by van Geet and Adamson [23] in their diffusion studies. Differential refractometry is characterized by high accuracy and relative insensitivity to temperature change. It was essential however, that solution and solvent in the differential cell had the same temperature preferably to 0.01°C. Details about a general description of the instrument have been reported at the operation manual. Worthy of mentioning here is that the refractive index difference is given by the following equations:

$$\Delta n = K \Delta d \tag{25}$$

$$\Delta d = (d_2 - d_1) - (d'_2 - d'_1) \tag{26}$$

The calibration constant K, is obtained by calibrating the instrument with a solution of potassium chloride having a known refractive index. The total slit image displacement (solvent zero reading) Δd, is measured for several concentrations. From a plot of Δd versus Δn, a value of $K = 930 \times 10^{-6}$ with green light (546 mμ) was obtained from a least-square plot of data shown in Figure 8.

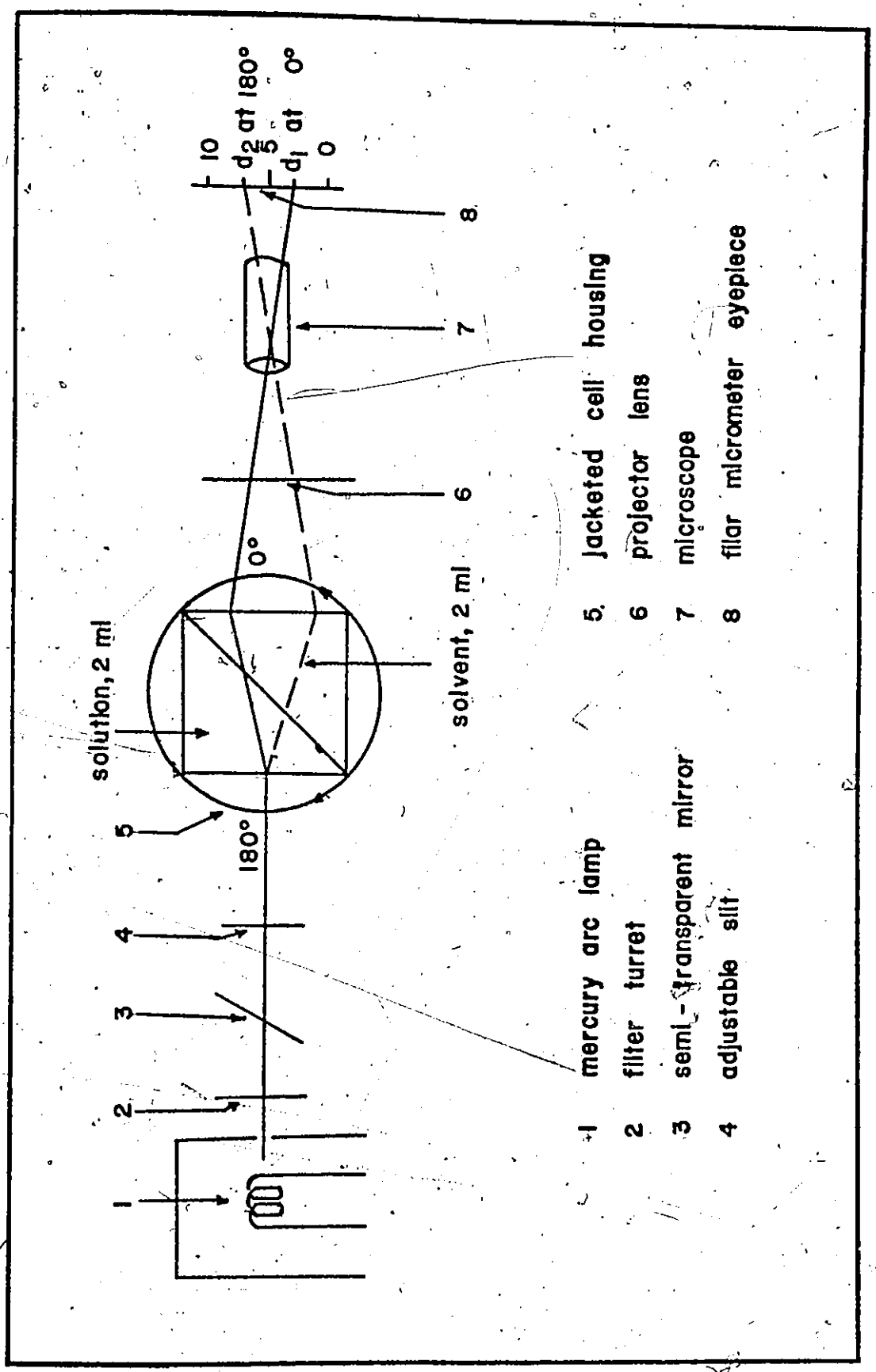


Figure 7 Visual Laboratory Type Differential Refractometer

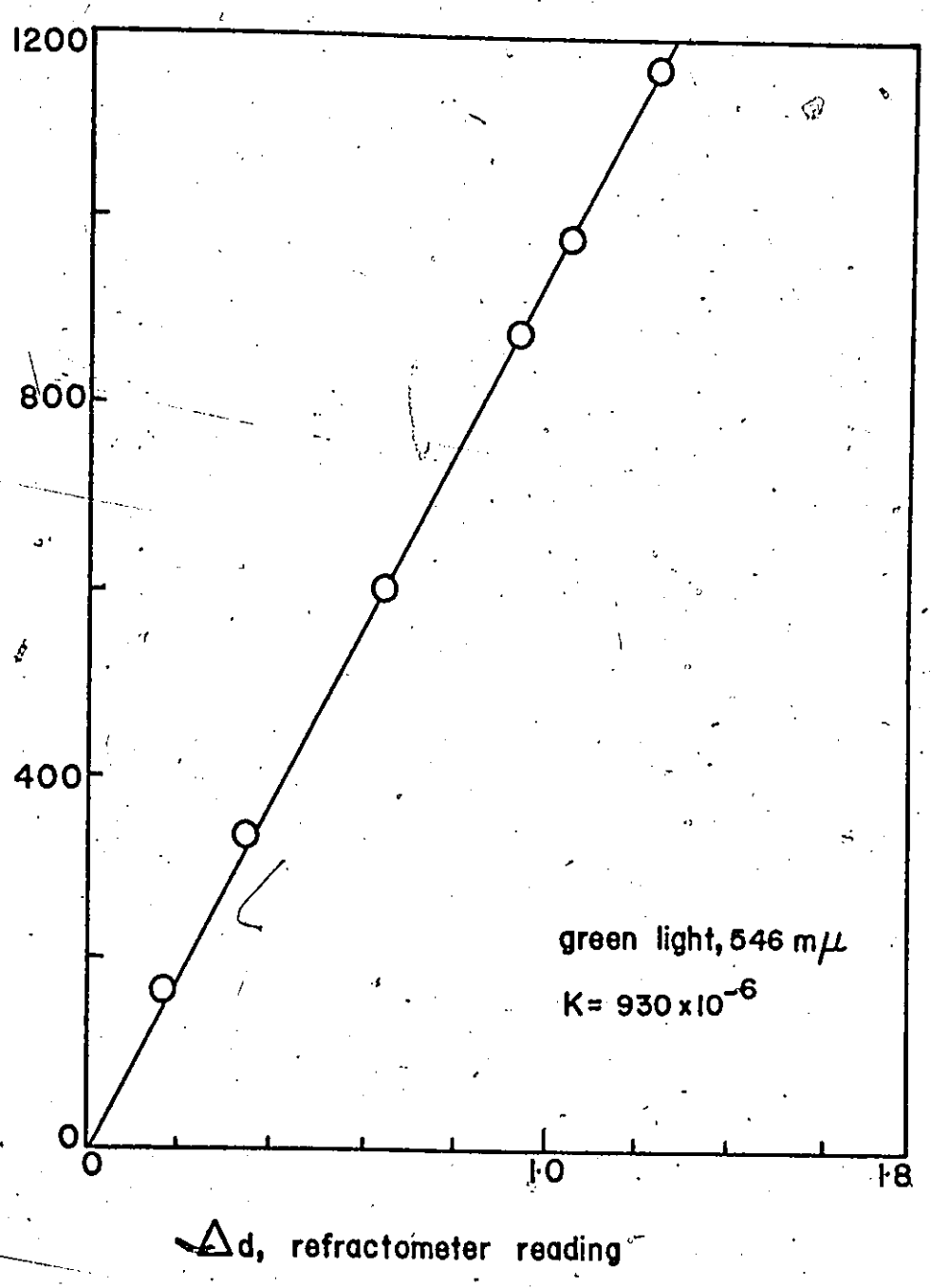


Figure 8 Differential Refractometer Calibration Using Potassium Chloride

Green light instead of blue light (438 mμ) was used because the cross hair within the eyepiece was more distinct. The Δd values of samples from the diffusion cell were used in conjunction with the machine constant K, to obtain the refractive index difference, Δn. A calibration curve of Δn versus concentration for the solutions were used to obtain the solute concentrations from diffusion experiments as shown in Figure 10 in the appendix B.

DIFFUSIVITY RESULTS AND DISCUSSION

The diffusivity results are reported in Table 5. The average diffusivity for carbon tetrachloride in cyclohexane at 25°C measured in this work was 1.44×10^{-5} cm^2/sec compared with 1.48×10^{-5} cm^2/sec reported by Sanni and Hutchison [44], a difference of 2.7%. The average diffusivity for dodecane in hexane at 25°C measured in this work was 2.75×10^{-5} cm^2/sec compared with 2.63×10^{-5} cm^2/sec reported by Shieh and Lyons [31], a difference of 4.5%. These comparisons show that the new diaphragm cell gives results comparable to those of other workers.

The experimental diffusion coefficients were also compared to ones predicted by the Wilke-Chang correlation, Equation (9), the Scheibel correlation, Equation (10), the Lusis and Ratcliff correlation, Equation (11) and the diffusivity - viscosity correlation, Equation (12). This comparison is presented in Table 6. The range of paraffins with 1, 2, 3, 6, 8, 12, 16, 24 and 32 carbon atoms as solutes in different paraffin solvents is presented in Figure 9 as diffusivity versus solvent viscosity on a log-log graph. It should be noted that literature and experimental data obey the diffusivity-solvent viscosity linear relationship as postulated by Hayduk and Cheng [34]. The slope of the lines increases gradually as the number of carbon atoms of the solute increases.

Such an orderly arrangement of diffusivities permits an estimate of diffusivities for other dissolved paraffins in paraffin solvents. It is noteworthy though that diffusivities in other solvents do not follow such a simple pattern. The other empirical correlations tested here, seem to be less satisfactory for the diffusion measured in this work.

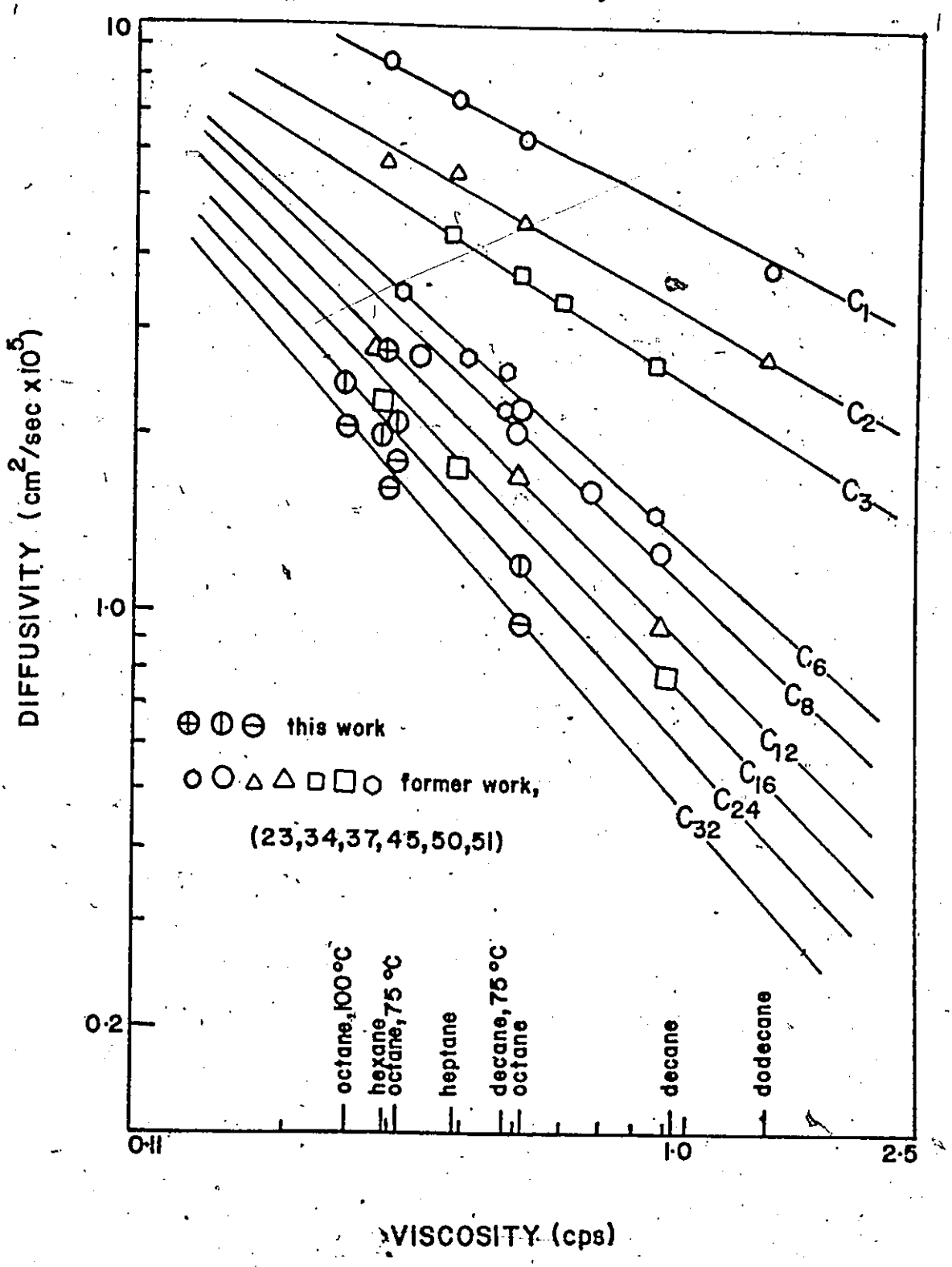


Figure 9 Diffusivity vs Solvent Viscosity at 25°C Unless Otherwise Noted

TABLE 5

Average diffusivities as measured by alternate methods

Solvent: Solute	Concentration gm/100 ml	Temp. °C	Diffusivity ($cm^2/sec \times 10^5$) steady-state	transient with stirring	transient without stirring
cyclohexane: carbon tetrachloride	0.0638	25	1.495	-	1.444
hexane: dodecane	0.052	25	2.712	2.754	2.656
hexane: tetracosane	0.025	25	2.04	-	2.008
hexane: dotriacontane	0.015	25	-	-	1.633
octane: tetracosane	0.025	25	-	1.223	1.153
		75	-	2.096	-
		100	-	2.41	-
octane: dotriacontane	0.01	25	-	0.965	-
		75	-	1.804	-
		100	-	2.07	-

TABLE 6

Comparison of experimental diffusivities with correlations

Temp. (°C)	Experimental	Diffusivities ($cm^2/sec \times 10^5$) Wilke-Chang	Scheibel	Lusis-Ratcliff	Hayduk et al.
cyclohexane: carbon tetrachloride					
25	1.444	1.405	1.827	1.515	-
hexane: dodecane					
25	2.754	2.366	3.677	2.677	2.85
hexane: tetracosane					
25	2.008	1.574	2.910	1.889	2.07
hexane: dotriacontane					
25	1.633	1.326	2.679	1.652	1.70
octane: tetracosane					
25	1.223	1.050	1.681	1.144	1.19
75	2.096	2.015	3.226	2.196	2.00
100	2.41	2.650	4.242	2.887	2.45
octane: dotriacontane					
25	0.965	0.885	1.535	0.994	0.96
75	1.804	1.698	2.945	1.908	1.65
100	2.07	2.233	3.872	2.508	2.02

As indicated in Table 5, deviations between values using stirrer and those without stirrer were less than 5%. The difference should not be neglected however since in every case the diffusivities with stirring were measurably higher. This suggests that convection alone is insufficient to give a completely uniform concentration for the relatively high rates of diffusion obtained with transient experiments. The results obtained at steady-state and by means of transient experiments with mixing of the top compartment are considered equally accurate. The transient method has the advantage of requiring much less time for each experiment.

CONCLUSION

Solubility determinations of tetracosane in hexane and in dodecane are reported for first time through this work.

The solubilities of high molecular weight paraffins in solutions from which chemical interactions are absent, when plotted as log of mole fraction versus log of absolute temperature, yield practically straight lines.

A new technique was developed which is rapid and simple for solubility determinations of any highly soluble solid. Comparison of dotriacontane solubilities shows that the used technique is accurate.

A modified type of tube diaphragm diffusion-cell, was developed and used to measure diffusion coefficients of solid paraffins in liquid paraffins.

The diffusion measurements of carbon tetrachloride in cyclohexane and dodecane in hexane were used to test the new designed diffusion cell. It was concluded that the diaphragm-cell results agreed with literature data for these systems, in dilute solutions. The necessity for stirring was demonstrated by comparing the experimental values.

This modified technique has been developed to a stage where it can be recognized as an exact method for the measurement of diffusion coefficients.

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APPENDIX A

Mathematical Details

(i) The solution for the unsteady-state diffusion rate [40] in a semi-infinite medium using the error function starts with Equation (17), Fick's second law for constant D:

I.C.1: at $x = x$, $t = o$, $c = c_o$

B.C.1.: at $x = 0$, $t = t$, $c = c_1$

B.C.2.: at $x = \infty$, $t = t$, $c = c_o$

The solution is made by substitution of $y = x/t^{1/2}$.

Then

$$\left(\frac{\partial y}{\partial t}\right)_x = -\frac{1}{2}\frac{x}{t^{3/2}} = -\frac{1}{2}(y\,t^{1/2})\frac{1}{t^{3/2}} = -\frac{y}{2t} \quad (27)$$

$$\left(\frac{\partial c}{\partial t}\right)_x = \frac{\partial c}{\partial y}\frac{\partial y}{\partial t} = \frac{\partial c}{\partial y}\left(\frac{-y}{2t}\right) \quad (28)$$

In a similar manner,

$$\left(\frac{\partial^2 c}{\partial x^2}\right)_t = \frac{1}{t}\left(\frac{\partial^2 c}{\partial y^2}\right)_t \quad (29)$$

Substituting Equations (28) and (29) into (17) and calling $p = \partial c/\partial y$,

$$-\frac{p}{2}\,y = D\frac{dp}{dy} \quad (30)$$

This is an ordinary differential equation and, upon integrating once,

$$D \ln p = \frac{-y^2}{4} + D \ln A \quad (31)$$

where A is a constant.

Solving for p,

$$p = \frac{dc}{dy} = A\, e^{-y^2/(4D)} \tag{32}$$

Letting $\lambda = y/(2\sqrt{D})$, then $d\lambda = dy/(2\sqrt{D})$

Substituting this value for dy into Equation (32) and integrating using B.C. 1.,

$$\int_{c_1}^{c} dc = c - c_1 = A\, 2\sqrt{D} \int_{o}^{x/2\sqrt{D\cdot t}} e^{-\lambda^2}\, d\lambda \tag{33}$$

Setting $x = \infty$ and $c = c_o$ from B.C. 2, the value of the integral which is really $(\sqrt{\pi}/2)$ times the error function, is $(\sqrt{\pi}/2)$ (1).

Hence,

$A = (c_o - c_1)/\sqrt{\pi D}$ and Equation (33) becomes

$$\frac{c_1 - c}{c_1 - c_o} = \frac{2}{\pi} \int_{o}^{x/2\sqrt{Dt}} e^{-\lambda^2}\, d\lambda$$

$$= \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{34}$$

Equation (34) can be rearranged to give,

$$\frac{c - c_o}{c_1 - c_o} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{35}$$

To determine the total amount of material that has diffused per unit area from t = o to t = t, the area under the c versus x curve is evaluated as:

$$\int_0^\infty (c - c_o)\, dx \text{ or } 2\sqrt{Dt} \int_0^\infty (c - c_o)\, d\left(\frac{x}{2\sqrt{Dt}}\right) \quad (36)$$

Substituting Equation (35) into Equation (36),

$$\int_0^\infty (c - c_o)\, dx = 2\sqrt{Dt}\,(c_1 - c_o) \int_0^\infty \left[1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] d\left(\frac{x}{2\sqrt{Dt}}\right) \quad (37)$$

From the mathematical tables, the definite integral has a value of $1/\sqrt{\pi}$.

Hence,

$$\text{total amount diffusing} = \frac{2}{\sqrt{\pi}} \sqrt{Dt}\,(c_1 - c_o) \quad (38)$$

ii) Considering again, as in the preceding solution, Fick's second law or Equation (17), it was attempted to find a solution[20,33] for a finite medium. The solution could be considered similar to that for a combination of diffusion rates out of a slab and diffusion through a membrane.

We assume that the solution of Equation (17) is of the following form, which is the product of two variables;

$$C_{(x,t)} = X_{(x)}\, T_{(t)} \quad (39)$$

Substituting Equation (39) into Equation (17) gives,

$$T'/T = DX''/X = -\lambda^2 D \quad (40)$$

Equation (40) is chosen equal to $-\lambda^2 D$, for convenience. For a finite solution $\lambda^2 > 0$ for all values of t. The general solution is:

$$C = X_{(x)} T_{(t)} = [A \sin \lambda x + B \cos \lambda x] \exp(-\lambda^2 Dt) \quad (41)$$

The values of λ will be restricted to an infinite set of discrete positive values.

First we consider a system with constant initial concentration, the concentrations at both faces are kept at zero for $t > 0$.

$$\begin{aligned} &C = C_o \text{ for } 0 < x < L \text{ at } t = 0 \\ &C = 0 \text{ for } x = 0 \text{ and } x = L \text{ at } t > 0 \end{aligned} \quad (42)$$

The boundary conditions are fulfilled for

$$B = 0, \quad \lambda = n\pi/L \quad (43)$$

The general solution is of the form

$$C = \sum_{n=1}^{\infty} A_n \exp\left[-\frac{n^2 \pi^2 Dt}{L^2}\right] \sin \frac{n\pi x}{L} \quad (44)$$

The arbitrary constants A_n are determined using Fourier's theorem.

$$C_o = \sum_{1}^{\infty} A_n \sin \frac{n\pi x}{L}, \text{ for } 0 < x < L \text{ at } t = 0 \quad (45)$$

After multiplying Equation (45) by $\sin \frac{n\pi x}{L}$ and integrating with respect to x from 0 to L,

$$A_n = \frac{2}{n L} \int_o^L C_o \sin \frac{n\pi x}{L} \, dx \quad (46)$$

It follows that,

$$A_n = 4 C_o/(2m + 1)\pi, \quad m = 0, 1, 2.... \quad (47)$$

and

$$C = \frac{4 C_o}{\pi} \sum_{m=0}^{\infty} \frac{1}{2 m + 1} \sin \frac{(2 m + 1) \pi x}{L} \exp \left[- \left(\frac{(2 m + 1) \pi}{L} \right) D t \right] \quad (48)$$

For the next step the initial and boundary conditions for diffusion through a membrane are considered:

$$\begin{aligned} &C = C_o \text{ for } 0 < x < L \text{ at } t = 0 \\ &C = C_1 \text{ for } x = 0, \; C = C_2 \text{ for } x = L \text{ at } t > 0 \end{aligned} \quad (49)$$

The problem is solved by putting

$$C = C_S + C_T = z_1 + z_2 \quad (50)$$

Considering that the diffusion process consists of a steady-state and a transient mode, z_1 and z_2 are chosen in such a way as to conform with the above conditions, Equation (49).

Evaluating Fourier coefficients An for initial conditions, Equation (44) gives:

$$- C_1 \frac{x}{L} = \sum_{1}^{\infty} A_n \sin \frac{n \pi x}{L}, \text{ for } 0 < x < L \text{ at } t = 0 \quad (51)$$

After multiplying Equation (51) by $\sin \frac{n \pi x}{L}$ and integrating with respect to x from 0 to L it follows:

$$A_n = \frac{- 2 C_1}{L^2} \int_o^L x \sin \frac{n \pi . x}{L} \, d x \quad (52)$$

and

$$A_n = \frac{2 C_1}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \quad , n = 1, 2, 3... \qquad (53)$$

$$z_2 = \frac{C_1 x}{L} + \frac{2 C_1}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi x}{L} \exp\left[-\left(\frac{n\pi}{L}\right)^2 D t\right]$$

(54)

The solution for z_1 is that given by Equation (48).

Finally:

$$C = \frac{C_1 x}{L} + \frac{2 C_1}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi x}{L} \exp\left[-\left(\frac{n\pi}{L}\right)^2 D t\right]$$

$$+ \frac{4 C_o}{\pi} \sum_{m=0}^{\infty} \frac{1}{2 m + 1} \sin \frac{(2 m + 1)\pi x}{L} \exp\left[-\left(\frac{(2 m + 1)\pi}{L}\right)^2 D\right.$$

(55)

The rate at which the diffusant emerges from unit area of the face, $x = 0$, of the membrane is given by $D (\partial C/\partial x)\, x = 0$, which is deduced from Equation (55). By integrating them with respect to t, the total amount M_t of diffusing substance which has passed through the membrane in time t is obtained and given by Equation (23).

APPENDIX B

TABLE 7

Differential Refractometer Calibration Data

Green Light (546 m μ), using Potassium Chloride

Sol'n conc'n gm/100 ml	d'_1 water	d'_2 water	d_1 sol'n	d_2 sol'n	Δd	$\Delta n \times 10^6$
1.2836	4.910	4.908	3.950	5.871	1.923	1760
0.8557	4.900	4.899	4.281	5.514	1.234	1165
0.7192	4.900	4.899	4.350	5.402	1.053	980
0.6225	4.900	4.899	4.409	5.355	0.947	880
0.4323	4.900	4.899	4.541	5.185	0.645	600
0.2490	4.900	4.899	4.706	5.052	0.347	340
0.1283	4.900	4.899	4.841	4.992	0.152	175

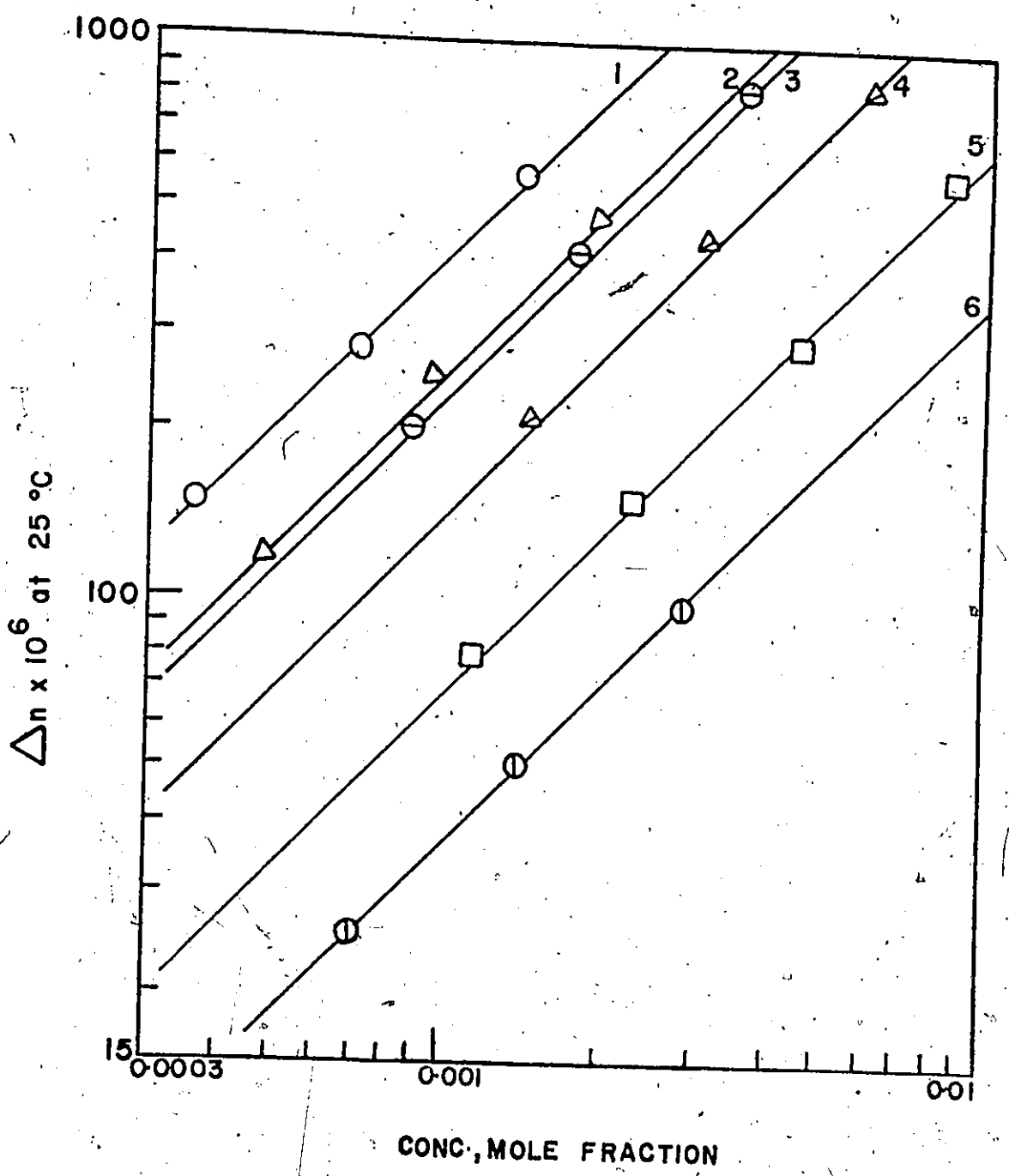

Figure 10 Diffusivity calibration curves for the systems:

1. hexane (S) - dotriacontane, 2. hexane (S) - tetracosane
2. octane (S) - dotriacontane, 4. octane (S) - tetracosane
5. hexane (S) - dodecane, 6. cyclohexane (S) - carbon tetrachloride

(S) is solvent

Raw experimental data for Solubility measurements

Solubility of dotriacontane at 0°C

Solvent	Trial	Weight of Solute	Volume of Solvent
Hexane	1	.01576 gm	18.40 ml
	2	.00712 gm	8.60 ml
Dodecane	1	.00471 gm	14.88 ml
	2	.00799 gm	25.24 ml

Solubility of dotriacontane at 25°C

Solvent	Trial	Weight of Solute	Volume of Solvent
Hexane	1	.08092 gm	3.00 ml
	2	.17105 gm	6.33 ml
Dodecane	1	.02024 gm	1.73 ml
	2	.04033 gm	3.45 ml
	3	.08076 gm	6.88 ml

Solubility of dotriacontane at 50°C

Solvent	Trial	Weight of Solute	Volume of Solvent
Hexane	1	0.24474 gm	0.38 ml
	2	0.91532 gm	1.42 ml
	3	1.46526 gm	2.25 ml
Dodecane	1	0.16286 gm	0.50 ml
	2	0.11153 gm	0.34 ml

Solubility of dotriacontane at 65°C

Solvent	Trial	Weight of Solute	Volume of Solvent
Dodecane	1	0.73705	0.25 ml
	2	2.53552	0.86 ml

Solubility of tetracosane at 0°C

Solvent	Trial	Weight of Solute	Volume of Solvent
Hexane	1	0.02996 gm	1.76 ml
	2	0.03810 gm	2.24 ml
Dodecane	1	0.01876 gm	2.75 ml
	2	0.02894 gm	4.22 ml

Solubility of tetracosane at 25°C

Solvent	Trial	Weight of Solute	Volume of Solvent
Hexane	1	0.06426 gm	0.23 ml
	2	0.15177 gm	0.54 ml
	3	0.37033 gm	1.33 ml
Dodecane	1	0.10070 gm	0.76 ml
	2	0.10795 gm	0.82 ml

Solubility of tetracosane at 47.5°C

Solvent	Trial	Weight of Solute	Volume of Solvent
Hexane	1	0.35474 gm	0.05 ml
	2	3.40558 gm	0.48 ml
Dodecane	1	0.15210 gm	0.04 ml
	2	2.43366 gm	0.64 ml

Raw experimental data for diffusivity measurements

A	A_{cap} diffusion area, 1.98 cm^2
C	C_{av}, arithmetic average concentration
D	diffusion coefficient, cm^2/sec
DIP	$D1'$, d'_1 , displacement in differential refractometer for solvent at 0°
D2P	D'_2, d'_2, displacement in differential refractomer for solvent at 180°
D1, D2	d_1, d_2 , displacement in differential refractometer for the solution at 0°, and 180°
DDP	DD', Δd, reading of total displacement
DN	Δn, refractive index difference
M	molecular weight of diffusant
L	diffusion path length, 2 cm
P	$\sqrt{3.1416}$ (unsteady-state program)
P	w_1, mass fraction of the diffusant $\frac{\rho_A}{\rho}$
R	ρ_1, density of solvent, gm/ml
T_1	diffusion time, secs (transient mode)
T_2	washing time, secs (transient mode)
T	diffusion time, secs (steady-state mode)
V	volume of the top compartment, ml

Y1, C1	y_{A_2}, mole fraction of the diffusant
Y2, C2	mole fraction of the diffusant after diffusion time t at the top compartment
Y3	$y_{A_{1av}}$, arithmetic average mole fraction of the diffusant Y2/2
C3	$\frac{C2}{2}$.

```
      $JOB   $WA81180 S.IOAKIMIDIS                                  WATFIV JOB CARD
 1            REAL L,M
 2            DIMENSION ZP(4), ZY2(4), ZD1(4), ZD2(4), ZDN(4), DIFF(4), ZT(4)
 3            DIMENSION LINE1(80),LINE2(80)
 4            WRITE (3,99)
 5            ICOUNT=0
 6         15 SUMD=0.0
 7            READ(1,40) (LINE1(I),I=1,80 )
 8            READ(1,40) ( LINE2(I),I=1,80)
 9            DO 100 J=1,4
10            READ, D1P, D2P, DDP, D1, D2, DN
11            READ, P, Y2, T, V, R, M, C, Y1
12            ZP( J)=P
13            ZY2( J)=Y2
14            ZT(J)=T
15            ZD1( J)=D1
16            ZD2(J)=D2
17            ZDN(J)=DN
18            L=2.0
19            A=1.98
20            Y3=Y2/2.0
21            D=(P*V*R*L) / (M*T*A*C*(Y1-Y3))
22            DIFF( J)=D
23            SUMD=SUMD+D/4.0
24        100 CONTINUE
25            WRITE(3,50) (LINE1(I), I=10,80)
26            WRITE(3,60) (LINE2(I), I=1,80)
27            WRITE(3,70) D1P,D2P,DDP
28            WRITE(3,10) V,A,Y1
29            WRITE (3,80)
30            DO 120  J=1,4
31        120 WRITE(3,130)  J, ZD1( J),ZD2( J), ZDN( J), ZT( J), ZP( J),
             1ZY2( J), DIFF( J)
32            WRITE(3,140) SUMD
33            ICOUNT=ICOUNT+1
34            IF (ICOUNT.LT.2) GO TO 15
35            ICOUNT=0
36            WRITE (3,99)
37            GO TO 15
38         10 FORMAT(10X, 'V =', F6.2,  5X, 'A =', F5.2,
              1 6X,  'Y1 =',  F8.6, / )
39         40 FORMAT(80A1)
40         50 FORMAT(10X, 70A1   )
41         60 FORMAT(10X, 80A1, //)
42         70 FORMAT(10X, 'D1'' =', F6.3, 3X, 'D2'' =', F6.3,  3X,
             1'DD'' =', F6.3,  / )
43         80 FORMAT(10X, 'RUN', 7X, 'D1',  9X, 'D2',  9X, 'DN', 11X, 'T',
             113X, 'P', 10X, 'Y2', 13X, 'D', /)
44         99 FORMAT(1H1)
45        130 FORMAT(10X, I2, 6X, F6.4, 5X, F6.4, 3X, F7.2, 'E-06', 3X, F8.1,
              1 5X, F8.6, 5X, F8.6, 3X, 1PE12.3,  / )
46        140 FORMAT(10X, /, 10X, 'AVERAGE DIFFUSIVITY IS',  1PE11.3,
             1' CM*CM/SEC', //////      )
47            RETURN
**WARNING**  UNNUMBERED EXECUTABLE STATEMENT FOLLOWS A TRANSFER
48            END
```

STEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

CYCLOHEXANE-CARBON TETRACHLORIDE

D1' = 4.700 D2' = 4.780 DD' = 0.080

V = 24.10 A = 1.98 Y1 =0.043160

RUN	D1	D2	DN	T	P	Y2	D
1	4.6430	4.8370	106.02E-06	122400.0	0.005500	0.003050	1.469E-05
2	4.6400	4.8410	112.53E-06	129600.0	0.005900	0.003250	1.491E-05
3	4.6330	4.8460	123.69E-06	144000.0	0.006500	0.003730	1.487E-05
4	4.6370	4.8380	112.53E-06	126000.0	0.005900	0.003250	1.534E-05

AVERAGE DIFFUSIVITY IS 1.495E-05 CM*CM/SEC

STEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

HEXANE-DODECANE

D1' = 4.860 D2' = 4.875 DD' = 0.015

V = 24.60 A = 1.98 Y1 =0.038620

RUN	D1	D2	DN	T	P	Y2	D
1	4.7650	4.9700	176.70E-06	68400.0	0.005300	0.002800	2.670E-05
2	4.7580	4.9770	189.72E-06	72000.0	0.005700	0.002900	2.731E-05
3	4.7470	4.9870	209.25E-06	79200.0	0.006300	0.003200	2.755E-05
4	4.7400	4.9940	222.27E-06	86400.0	0.006700	0.003400	2.693E-05

AVERAGE DIFFUSIVITY IS 2.712E-05 CM*CM/SEC

STEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

HEXANE-TETRACOSANE

D1' = 4.860 D2' = 4.875 DD' = 0.015

V = 24.40 A = 1.98 Y1 =0.009620

RUN	D1	D2	DN	T	P	Y2	D
1	4.7680	4.9670	171.12E-06	90000.0	0.002700	0.000690	2.042E-05
2	4.7650	4.9710	177.63E-06	93600.0	0.002800	0.000720	2.039E-05
3	4.7590	4.9750	186.93E-06	100800.0	0.002950	0.000755	1.999E-05
4	4.7470	4.9870	209.25E-06	108000.0	0.003300	0.000850	2.098E-05

AVERAGE DIFFUSIVITY IS 2.044E-05 CM*CM/SEC

```
      $JOB   SW68118Ø S.IOAKIMIDIS                                  WATFIV JOB CARD
 1          DIMENSION ZC2(4), ZT2(4), ZD1(4), ZD2(4), ZDN(4), DIFF(4)
 2          DIMENSION LINE1(8Ø),LINE2(8Ø)
 3          WRITE (3,99)
 4          NS=4
 5          ICOUNT=Ø
 6       15 SUMD=Ø.Ø
 7          READ(1,4Ø) (LINE1(I),I=1,8Ø )
 8          READ(1,4Ø) (LINE2(I),I=1,8Ø)
 9          DO 1ØØ J=1,NS
10          READ , C1, C2, T1, T2, D1P, D2P, DDP, D1, D2, DN, V
11          ZC2( J)=C2
12          ZT2( J)=T2
13          ZD1( J)=D1
14          ZD2( J)=D2
15          ZDN( J)=DN
16          P=SQRT(3.14159)
17          A=1.98
18          C3=C2/2.Ø
19          T1=SQRT(T1)
2Ø          T2=SQRT(T2)
21          AK=(V*C2*P) / (2.Ø*A*(T1*(C1-C3)-(T2*C1)))
22          T1=T1*T1
23          D=AK*AK
24          DIFF(J)=D
25          SUMD=SUMD+D
26      1ØØ CONTINUE
27          SUMD=SUMD/NS
28          WRITE(3,5Ø) (LINE1(I), I=1Ø,8Ø)
29          WRITE(3,6Ø) (LINE2(I), I=1,8Ø)
3Ø          WRITE(3,7Ø) D1P,D2P,DDP
31          WRITE(3,1Ø) V,A,T1,C1
32          WRITE(3,8Ø)
33          DO 12Ø J=1,NS
34      12Ø WRITE(3,9Ø) J, ZD1(J), ZD2(J), ZDN(J), ZT2(J), ZC2(J), DIFF(J)
35          WRITE(3,14Ø) SUMD
36          ICOUNT=ICOUNT+1
37          IF (ICOUNT.LT.2) GO TO 15
38          ICOUNT=Ø
39          WRITE (3,99)
4Ø          GO TO 15
41       1Ø FORMAT(1ØX, 'V =', F6.2, 5X, 'A =', F5.2,
           1 6X, 'T1 =', F8.1, 1ØX, 'C1 =', F8.5, / )
42       4Ø FORMAT(8ØA1)
43       5Ø FORMAT(1ØX, 7ØA1 )
44       6Ø FORMAT(1ØX, 8ØA1, / )
45       7Ø FORMAT(1ØX, 'D1'' =', F6.3, 3X, 'D2'' =', F6.3, 3X,
           1'DD'' =', F6.3, / )
46       8Ø FORMAT(1ØX,' RUN', 6X, 'D1', 9X, 'D2', 8X, 'DN', 2X,
           113X, 'T2', 1ØX, 'C2', 12X, 'D', / )
47       9Ø FORMAT(1ØX, I3, 5X, F6.4, 5X, F6.4, 3X, F7.2, 'E-Ø6', 7X,F6.2,
           1 5X, F8.6, 3X, 1PE12.3, / )
48       99 FORMAT(1H1)
49      14Ø FORMAT(1ØX, / ,
           11ØX, 'AVERAGE DIFFUSIVITY IS ', 1PE1Ø.3,' CM*CM/SEC', / ///// )
5Ø          RETURN
**WARNING**  UNNUMBERED EXECUTABLE STATEMENT FOLLOWS A TRANSFER
51          END
```

UNSTEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

CYCLOHEXANE-CARBON TETRACHLORIDE

D1' = 4.700 D2' = 4.780 DD' = 0.080

V = 24.30 A = 1.98 T1 = 21000.0 C1 = 0.04290

RUN	D1	D2	DN	T2	C2	D
1	4.6630	4.8170	68.82E-06	83.00	0.001990	1.451E-05
2	4.6630	4.8165	68.35E-06	85.00	0.001980	1.439E-05
3	4.6655	4.8190	68.35E-06	92.00	0.001980	1.447E-05
4	4.6620	4.8150	67.89E-06	98.00	0.001970	1.438E-05

AVERAGE DIFFUSIVITY IS 1.444E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

HEXANE-DODECANE

D1' = 4.860 D2' = 4.875 DD' = 0.015

V = 24.60 A = 1.98 T1 = 14400.0 C1 = 0.03860

RUN	D1	D2	DN	T2	C2	D
1	4.7920	4.9440	127.41E-06	85.00	0.001940	2.637E-05
2	4.7895	4.9420	127.87E-06	87.00	0.001950	2.670E-05
3	4.7890	4.9400	126.48E-06	99.00	0.001930	2.645E-05
4	4.7910	4.9440	128.34E-06	78.00	0.001960	2.674E-05

AVERAGE DIFFUSIVITY IS 2.656E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 25 C WITH STIRRER

HEXANE-DODECANE

D1' = 4.860 D2' = 4.875 DD' = 0.015

V = 19.60 A = 1.98 T1 = 14400.0 C1 = 0.03860

RUN	D1	D2	DN	T2	C2	D
1	4.7740	4.9610	159.96E-06	110.00	0.002450	2.775E-05
2	4.7780	4.9620	157.20E-06	128.00	0.002420	2.748E-05
3	4.7750	4.9600	158.10E-06	124.00	0.002430	2.762E-05
4	4.7760	4.9600	157.17E-06	132.00	0.002410	2.733E-05

AVERAGE DIFFUSIVITY IS 2.754E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

HEXANE-TETRACOSANE

D1' = 4.860 D2' = 4.875 DD' = 0.015

V = 24.10 A = 1.98 T1 = 16200.0 C1 = 0.00962

RUN	D1	D2	DN	T2	C2	D
1	4.7980	4.9345	112.99E-06	87.00	0.000460	2.015E-05
2	4.8010	4.9370	112.53E-06	93.00	0.000455	1.981E-05
3	4.7980	4.9340	112.53E-06	99.00	0.000455	1.992E-05
4	4.7990	4.9360	113.46E-06	79.00	0.000465	2.044E-05

AVERAGE DIFFUSIVITY IS 2.008E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

HEXANE-DOTRIACONTANE

D1' = 4.860 D2' = 4.875 DD' = 0.015

V = 24.70 A = 1.98 T1 = 19800.0 C1 = 0.00436

RUN	D1	D2	DN	T2	C2	D
1	4.8150	4.9090	82.77E-06	80.00	0.000206	1.654E-05
2	4.8175	4.9210	82.30E-06	76.00	0.000205	1.632E-05
3	4.8180	4.9200	80.91E-06	98.00	0.000202	1.612E-05
4	4.8150	4.9180	81.84E-06	89.00	0.000204	1.633E-05

AVERAGE DIFFUSIVITY IS 1.633E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 25 C WITHOUT STIRRER

OCTANE-TETRACOSANE

D1' = 4.785 D2' = 4.830 DD' = 0.045

V = 24.50 A = 1.98 T1 = 26100.0 C1 = 0.01207

RUN	D1	D2	DN	T2	C2	D
1	4.7200	4.9010	126.48E-06	90.00	0.000550	1.134E-05
2	4.7160	4.8990	128.34E-06	77.00	0.000560	1.165E-05
3	4.7160	4.8980	127.41E-06	83.00	0.000555	1.149E-05
4	4.7210	4.9030	127.41E-06	98.00	0.000555	1.162E-05

AVERAGE DIFFUSIVITY IS 1.153E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 25 C WITH STIRRER

OCTANE-TETRACOSANE

D1' = 4.810 D2' = 4.830 DD' = 0.020

V = 18.50 A = 1.98 T1 = 26100.0 C1 = 0.01207

RUN	D1	D2	DN	T2	C2	D
1	4.7590	4.8900	103.23E-06	118.00	0.000750	1.248E-05
2	4.7500	4.8790	101.37E-06	130.00	0.000730	1.188E-05
3	4.7500	4.8850	102.30E-06	123.00	0.000740	1.217E-05
4	4.7545	4.8850	102.76E-06	127.00	0.000745	1.237E-05

AVERAGE DIFFUSIVITY IS 1.223E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 25 C WITH STIRRER

OCTANE-DOTRIACONTANE

D1' = 4.810 D2' = 4.830 DD' = 0.020

V = 17.80 A = 1.98 T1 = 32400.0 C1 = 0.00363

RUN	D1	D2	DN	T2	C2	D
1	4.7840	4.8600	52.08E-06	118.00	0.000230	9.540E-06
2	4.7895	4.8660	52.54E-06	132.00	0.000232	9.788E-06
3	4.7865	4.8620	51.61E-06	126.00	0.000229	9.496E-06
4	4.7850	4.8620	53.01E-06	113.00	0.000233	9.772E-06

AVERAGE DIFFUSIVITY IS 9.649E-06 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 75 C WITH STIRRER

OCTANE-TETRACOSANE

D1' = 4.810 D2' = 4.830 DD' = 0.020

V = 17.60 A = 1.98 T1 = 18000.0 C1 = 0.00956

RUN	D1	D2	DN	T2	C2	D
1	4.7645	4.8820	90.67E-06	119.00	0.000660	2.102E-05
2	4.7670	4.8850	91.14E-06	125.00	0.000665	2.145E-05
3	4.7630	4.8800	90.21E-06	130.00	0.000655	2.086E-05
4	4.7620	4.8780	89.28E-06	128.00	0.000650	2.050E-05

AVERAGE DIFFUSIVITY IS 2.096E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 100 C WITH STIRRER

OCTANE-TETRACOSANE

D1' = 4.810 D2' = 4.830 DD' = 0.020

V = 18.80 A = 1.98 T1 = 15300.0 C1 = 0.00956

RUN	D1	D2	DN	T2	C2	D
1	4.7650	4.8750	83.70E-06	115.00	0.000610	2.425E-05
2	4.7680	4.8780	83.70E-06	110.00	0.000610	2.415E-05
3	4.7650	4.8740	82.77E-06	129.00	0.000600	2.371E-05
4	4.7715	4.8810	83.23E-06	122.00	0.000605	2.399E-05

AVERAGE DIFFUSIVITY IS 2.403E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 75 C WITH STIRRER

OCTANE-DOTRIACONTANE

D1' = 4.810 D2' = 4.830 DD' = 0.020

V = 19.40 A = 1.98 T1 = 23400.0 C1 = 0.00451

RUN	D1	D2	DN	T2	C2	D
1	4.7795	4.8730	68.35E-06	115.00	0.000300	1.773E-05
2	4.7810	4.8750	68.82E-06	110.00	0.000305	1.829E-05
3	4.7795	4.8730	68.35E-06	145.00	0.000300	1.808E-05

AVERAGE DIFFUSIVITY IS 1.803E-05 CM*CM/SEC

UNSTEADY-STATE DIFFUSION AT 100 C WITH STIRRER

OCTANE-DOTRIACONTANE

D1' = 4.810 D2' = 4.830 DD' = 0.020

V = 19.20 A = 1.98 T1 = 18900.0 C1 = 0.00451

RUN	D1	D2	DN	T2	C2	D
1	4.7750	4.8660	66.03E-06	125.00	0.000290	2.056E-05
2	4.7790	4.8700	66.03E-06	134.00	0.000290	2.069E-05
3	4.7710	4.8630	66.96E-06	112.00	0.000295	2.109E-05
4	4.7730	4.8640	66.03E-06	129.00	0.000290	2.062E-05

AVERAGE DIFFUSIVITY IS 2.074E-05 CM*CM/SEC