ABSTRACT

The solubilities of methane in normal hexane, heptane, octane, dodecane and hexadecane at 0°C, 25°C, 50°C and 75°C and atmospheric pressure were measured with an estimated accuracy of better than ±2%. Based upon this new data and an extensive amount of data obtained from the literature, a semi-empirical method was developed for predicting the temperature coefficient of gas solubility in regular solutions. The method requires knowledge of at least one solubility measurement at any temperature, the solvent critical temperature, and solubility parameter. For a temperature range between the solvent freezing point and boiling point, the method can be used to estimate solubilities to an apparent accuracy of at least ±4%.

Diffusivities of methane in normal hexane, heptane, octane, dodecane and hexadecane at 25°C and in dodecane at 50°C (at atmospheric pressure) were measured. The results supported the hypothesis that the diffusivities of dilute solutes in liquids are determined mainly by the solvent viscosity raised to a power which is characteristic of the particular solute.

ACKNOWLEDGEMENTS

The author expresses his deep gratitude and appreciation for the helpful guidance and enlightening ideas provided by his research director, Dr. W. Hayduk. Many thanks are also extended to Mr. G. Gasperetti for his technical assistance in the construction and maintenance of the equipment. In addition, the author is grateful to the National Research Council of Canada for the financial support provided as an NRC Scholarship. Finally, the author would like to thank his dear wife for the countless number of ways in which she has helped in the evolution of this thesis.

TABLE OF CONTENTS

Page No.

INTRODUCTION 1

LITERATURE REVIEW OF GAS SOLUBILITY 1

- Experimental Methods 1
  - Saturation Methods 2
  - Extraction Methods 3
- Theoretical Aspects 4
  - Regular Solution Theory 4
  - Solubility Variation with Temperature 5
  - Theory of Solubility Measurements 6

LITERATURE REVIEW OF DIFFUSIVITY FOR GASES IN LIQUIDS 7

- Experimental Methods 7
  - Steady-State Diaphragm Cell 8
  - Steady-State Gas Absorption in Laminar Flow Systems 9
  - Unsteady-State Gas Absorption 10
  - Steady-State Capillary Cell 11
- Theoretical Aspects and Correlations 11
  - Hydrodynamic Theory 12
  - Activated Rate Theory 12
  - Semi-Empirical Correlations 12
  - Variation of Diffusivity with Temperature and Concentration 14
  - Theory of Capillary Cell Method 15

Page No.

EXPERIMENTAL EQUIPMENT AND PROCEDURE 16

Deareation of Solvent 16

Solubility Apparatus 17

Solubility Determinations 19

Diffusivity Apparatus 21

Diffusivity Determinations 23

EXPERIMENTAL RESULTS AND DISCUSSION 24

Methane Solubility 24

Methane Diffusivity 42

CONCLUSIONS 51

REFERENCES 52

APPENDICES 55

Methane Purity, Molal Volumes, and Partial Molal Volumes 55

Liquid Purities and Properties 57

Solubility Data 61

Diffusivity Data 90

LIST OF TABLES

Number	Title	Page No.
1	Solubilities of Methane in Normal Hexane, Heptane, Octane, Dodecane, Hexadecane and Benzene.	25
2	Comparison of Experimental and Calculated Methane Solubilities at 25°C.	25
3	Sources of Solubility Data	27, 28
4	Solvent Critical Temperature, Solubility Parameter and Reference Solubility	36
5	Entropies of Solution for Gases in Cyclohexane	40
6	Entropies of Solution for Methane in Normal Hexane, Heptane, Octane, Dodecane and Hexadecane	41
7	Diffusivities of Methane in Normal Hexane, Heptane, Octane, Dodecane and Hexadecane	43
8	Comparison of Experimental and Calculated Methane Diffusivities	46

LIST OF FIGURES

Number	Title	Page No.
1	Solubility Apparatus	18
2	Steady-State Capillary Cell Diffusion Apparatus	22
3	Gas Solubilities in Carbon Disulfide	29
4	Gas Solubilities in Carbon Tetrachloride	30
5	Gas Solubilities in Cyclohexane	31
6	Gas Solubilities in Octadecane	32
7	Gas Solubilities in Normal Heptane	33
8	Gas Solubilities in Perfluoroheptane	34
9	Reference Solubility vs. Solubility Parameter	38
10	Diffusivities of Methane, Ethane, Propane vs. Solvent Viscosity	45
11	Diffusivity vs. Solute Viscosity for various Solutes in n-Hexane and Carbon Tetrachloride at 25°C	48
12	Diffusivity vs. Solute Molal Volume for various Solutes in n-Hexane and Carbon Tetrachloride at 25°C	49
13	$D\,V_{wc}^{0.6}$ vs. Solute Viscosity for various Solutes in n-Hexane and Carbon Tetrachloride at 25°C	50(a)

NOMENCLATURE

Solubility

H	Henry's Law constant
L	Ostwald absorption coefficient, cc saturated gas/cc of solvent
p	partial pressure, mm Hg
P_t	barometric pressure, mm Hg
R	gas constant, 1.9872 cal/gm-mole - ^{o}K
$\bar{s}$	partial molal entropy of gas in solution, cal/gm-mole - ^{o}K
s^g	molal entropy of gas in its standard state at 1 atmosphere, cal/gm-mole - ^{o}K
T	temperature, ^{o}K
T_c	critical temperature, ^{o}K
V	molal volume at temperature of experiment and 1 atmosphere, cc/gm-mole
$\bar{V}$	partial molal volume (cc/gm-mole)
v_L	volume of solvent, cc
v_G	volume of vapor saturated gas (cc) which dissolves in v_L (cc) of solvent at a total pressure, P_t
v_G^1	volume of dry gas (cc) measured at P_t which is equivalent to that which dissolves in v_L (cc) of solvent at P_t
v_s	volume of solution, cc
x	mole fraction solubility
x^i	ideal mole fraction solubility
x_{T_1}	mole fraction solubility at temperature, T_1
x_{T_2}	mole fraction solubility at temperature, T_2

Solubility Cont'd

x_o	mole fraction solubility for which the entropy of solution is zero (reference solubility)
δ	solubility parameter at 25°C, $(cal/cc)^{1/2}$

Subscripts

1	solvent
2	solute
G	gas phase
L	liquid phase

Diffusivity

A_1	cross sectional area of small capillary, cm^2
A_2	cross sectional area of large capillary, cm^2
D	diffusion coefficient, cm^2/sec
h	rate of travel of bead down the capillary, cm/min
L	diffusion path length, cm
M	molecular weight, gm/gm-mole
$\bar{n}$	mass flux relative to stationary axes, gm/cm^2-sec
w	mass fraction
w_2^o	mass fraction of solute gas at gas-liquid interface
w_2^L	mass fraction of solute gas in bulk of liquid
T	temperature, ^oK
V	molal volume at temperature of experiment and 1 atmosphere, cc/gm-mole
V_{LB1}	Le Bas molal volume of solvent, cc/gm-mole
V_{LB2}	Le Bas molal volume of solute, cc/gm-mole
V_{wc}	molal volume of solute (cc/gm-mole) as a liquid at its normal boiling point (estimated by Le Bas molal volume for complex molecules)

Diffusivity Cont'd

μ	solvent viscosity, cp
χ	association parameter in Wilke-Chang equation
ρ	total mass concentration of solution, gm/cc

Subscripts

1	solvent
2	solute

INTRODUCTION

The measurement of both solubility and diffusivity is useful since both vapor-liquid equilibrium data (gas solubilities) and diffusion coefficients are used in designing gas-liquid mass transfer equipment. Also several methods for determining diffusivities require accurate solubility data. For these reasons, the solubilities and diffusivities of methane gas were measured in a series of normal paraffins; molecular interactions such as molecular association were not likely to occur in such solutions.

For clarity and uniformity, each subsequent section was divided into two parts; a section dealing with solubilities followed by one dealing with diffusivities.

LITERATURE REVIEW OF GAS SOLUBILITY

Experimental Methods

Methods for measuring the solubility of gases in liquids have been reviewed by Battino and Clever (1). These methods can be categorized as either physical or chemical.

The more frequently used physical methods can be further classified as saturation (equilibrium) techniques, in which a previously degassed liquid is saturated with the gas, and extraction methods, which involve stripping the dissolved gas from a previously saturated solution. Emphasis shall be placed upon the more frequently used saturation methods.

Saturation Methods

Four major sources of experimental error which must be either eliminated or minimized have been outlined by Cook and Hansen (2). These are non-attainment of equilibrium, incomplete degassing of the solvent, inaccurate measurement of the gas absorbed, and contamination of the gas.

The highly precise method of Cook and Hansen (2) (better than ±0.1% reproducibility) involved repeated contacting of the gas with degassed solvent and shaking the entire apparatus to attain equilibrium. The solubility was determined from measurements of volume of gas absorbed and solvent volume. The major advantage of the apparatus was that measurements covering a range of temperatures and pressures were obtained from a single charging of the apparatus. Disadvantages included a rather complicated procedure and the requirement of a good estimate of the solubility for design purposes.

An apparatus designed by Morrison and Billet (3) was based upon the attainment of saturation by slowly flowing a liquid film in contact with the gas through an absorption spiral. A reproducibility of ±0.5% was claimed by the authors. The procedure was relatively simple, and the authors showed that complete saturation was attained at the outlet of the spiral. Unfortunately, a single charging of the apparatus yielded only a single measurement at one temperature and pressure.

Subject to the same restriction was the Morrison and Billet-type apparatus used by Clever et al (4) in which the degassed solvent was injected drop-wise into the apparatus and contacted with gas in the absorption spiral. An overall reproducibility of ±0.2% was estimated for the solubilities.

A more recently innovated saturation method has been designed and described by Dymond and Hildebrand (5) to be better than ±1% accurate. A measured volume of degassed solvent contained in a lower bulb was rapidly pumped through a glass side arm into an upper bulb which initially contained a measured amount of dry gas. The solubility of the gas was calculated from the pressure of undissolved gas. The procedure was rapid, equilibrium being attained in 1 to 3 hours, and re-equilibration at a series of temperatures permitted the determination of several solubilities with a single charge of solvent.

A modified version of the apparatus of Morrison and Billet (3) which had been used previously by Hayduk and Cheng (6) was employed in this work. Although an estimate of the solubility was required, the apparatus was simply constructed, easy to operate, and required only a short measurement time. A reproducibility of ±0.5% was reported with a maximum error of ±2%.

Extraction Methods

Extraction methods for determining gas-liquid solubilities have been mainly restricted to quantitative analysis. Mass spectrometric and gas chromatographic techniques have been used to analyse gases desorbed from saturated liquid solutions since these methods are relatively simple and yield rapid analyses.

Theoretical Aspects

Regular Solution Theory

By far the most successful in describing the solubility of gases in liquids has been the regular solution theory developed by Hildebrand and Scott (7, 8). An extension of their earlier work appears in the most recent book by Hildebrand, Prausnitz and Scott (9).

Hildebrand and Scott have defined regular solutions as follows: "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". This regular solution concept is based upon the idea of maximum randomness and entropy. The internal pressures of the liquid (intermolecular forces and cohesive energies) are accounted for by a solubility parameter which was evaluated as the square root of the energy of vaporization per cubic centimeter. At low pressures, when the gaseous solute is so dilute that Henry's law is applicable, the validity of Raoult's law for the solvent follows directly from the Gibbs-Duhem relation.

Hildebrand and Scott (7) have derived an equation (Equation 1) from regular solution theory for the solubilities of non-polar gases in non-polar liquids.

$$\log x_2 = \log x_2^i - \frac{\bar{V}_2}{2.303RT}(\delta_1-\delta_2)^2 - \left(\log \frac{\bar{V}_2}{V_1} + 0.4343\left(1-\frac{\bar{V}_2}{V_1}\right)\right) \ldots (1)$$

Equation 1 was derived for systems in which the solute molecules differed significantly in size from the solvent molecules.

Solubility Variation with Temperature

Hildebrand and Scott (8) have advanced several significant observations concerning the temperature variation of the solubility for gases in liquids which led to a method for calculating the entropy of solution from a single solubility measurement.

For sparingly soluble gases that obey Henry's Law, the entropy of solution can be calculated from the change of gas solubility with temperature (Equation 2).

$$\bar{s}_2 - s_2^g = R\left(\frac{\partial \ln x_2}{\partial \ln T}\right)_{sat,\ P} \quad ....(2)$$

Hildebrand and Scott observed that plots of logarithm mole fraction solubility versus logarithm temperature for several gases dissolved in a single non-polar liquid were essentially linear. Such plots revealed a definite differentiation between positive and negative temperature coefficients of solubility. Also revealed was the fact that the magnitude of the solubility itself largely determined the sign and magnitude of the change of solubility with temperature. The authors summarized the main features of their observations as follows:

1) A regular system of relationships existed between entropy of solution and solubility.
2) The dividing line between positive and negative temperature coefficients of solubility is at $\bar{S}_2 - S_2^g = 0$, and there is a possibility of predicting the temperature coefficient from a single solubility value.
3) The entropy of solution becomes more negative in passing from the less soluble to the more soluble gases, i.e. gases more like the solvent in intermolecular potential energy parameter.

Theory of Solubility Measurements

Theoretical aspects of the solubility method employed in this work have been thoroughly considered by Cheng (10). The solubility was expressed both as a mole fraction at a gas partial pressure of one atmosphere, and as an Ostwald Coefficient. The latter quantity is the ratio of the volume of saturated gas absorbed to the volume of the absorbing pure liquid, each measured at the temperature and pressure of the experiment. In terms of experimentally determined quantities, the Ostwald Coefficient was calculated according to Equation 3.

$$L = \frac{v_G}{v_L} = \left(\frac{v_G^l}{v_S} \times \frac{P_t}{p_2} \right) \Big/ \left(1 - \frac{v_G^l}{v_S} \times \frac{P_t}{760} \times \frac{\bar{V}_2}{V_2} \right) \ldots\ldots \quad (3)$$

Because methane is rather insoluble in the paraffins, no distinction could be measured between the volume of pure solvent and the volume of the methane-saturated solution.

Thus the partial molal volume of methane in each solvent was estimated rather than measured.

The partial pressure of the gas, p_2, was calculated by means of Raoult's law. The conversions from solubilities measured at an experimental gas partial pressure, p_2, to ones at 1 atmosphere partial pressure were achieved by using Henry's law to describe the behaviour of the solute gas,

$$H = \left.\frac{p_2}{x_2}\right)_{p_2} = \left.\frac{p_2}{x_2}\right)_{p_2 = 760} \quad \ldots\ldots(4)$$

The mole fraction solubilities were calculated from Ostwald Coefficients, determined at a gas partial pressure of p_2, using Equation 5.

$$\left.x_2\right)_{p_2 = 760} = \frac{L/V_2}{\frac{L}{V_2} \times \frac{p_2}{760} + \frac{1}{V_1}} \quad \ldots\ldots(5)$$

LITERATURE REVIEW OF DIFFUSIVITY FOR GASES IN LIQUIDS

Experimental Methods

A relatively recent review of diffusion of dissolved gases in liquids published by Himmelblau (11), included a discussion about theories and correlations for gas-liquid diffusion in addition to experimental methods for obtaining diffusion coefficients of dissolved gases.

In general, the measurement techniques incorporated one of two procedures; either measurement of the rate of transfer into or out of a liquid phase, or measurement of the concentration gradient within a solution through which diffusion was occurring. For either method the diffusion process was described by a differential mass balance equation, and the molecular diffusion coefficient was obtained from the mathematical solution incorporating the appropriate initial and boundary conditions.

Steady-State Diaphragm Cell

Many diffusion measurements have been made using a diaphragm cell which is basically a porous glass or metal disc sealed in a reservoir. Under steady-state conditions, changes in concentration on either side of the disc are measured as the gas diffuses vertically downward through the holes from a solution of high concentration to one of lower concentration.

Typical of most cells, a cell used by Vivian and King (12) had to be calibrated using a solute of known diffusivity and forming a solution of similar viscosity to the gas-liquid system under study. For example, an aqueous solution of potassium chloride was used for measurements involving the diffusion of gases in water to arrive at a cell constant which was a function of both viscosity and concentration. Solute gas concentrations on either side of the cell were measured by chemical methods (for reactive gases) or by gas chromatography (for inert gases). Besides the inherent difficulty of loss of gas upon sampling from the solution, the problem of accurately measuring small concentration changes was encountered for slightly soluble gases. Once calibrated, the diaphragm cell apparatus has been useful for measuring diffusion coefficients in aqueous solutions.

Ross and Hildebrand (13) eliminated the calibration procedure by constructing a stainless steel disk containing drilled capillary sized holes of known diameter (about 1 mm). Thus, the area and length of diffusion path were known accurately. Previously measured gas solubilities were used to calculate the concentration of the gas in the saturated solution above the plate. The amount of gas that diffused through the holes in the plate was measured volumetrically by mercury displacement of the gas. The estimated accuracy of the method was ±5%. The minor drawback of this technique was the requirement of accurate solubility data.

Steady-State Gas Absorption in Laminar Flow Systems

Another technique for measuring gas-liquid mutual diffusion coefficients has been used by Baird and Davidson (14). The method involved the measurement of the rate for steady-state gas absorption by a stream of solvent in laminar flow. The authors employed both an annular jet apparatus and a wetted sphere absorption apparatus. In each experiment, the absorption process was considered to be diffusion controlled in the liquid phase with negligible mass transfer resistance in the gas phase and at the gas-liquid interface. Penetration theory was applied to the process to evaluate the effect of the diffusion coefficient. A similar technique employing a wetted wall column has been used by Davies et al (15).

Unsteady-State Gas Absorption

A capillary cell method **developed** by Wang (16) was later modified by Witherspoon and Saraf (17). It involved filling a known length of capillary (a 1 mm. diameter micro-syringe ground flat at one end) with a saturated solution, and immersing the capillary into a constant temperature reservoir of unstirred, degassed solvent. Initial and final gas concentrations were measured by means of a hydrogen-flame gas chromatograph. The total solution was injected for analysis into the chromatograph, and it was in this procedure that loss of gas from the very small sample was difficult to prevent.

A less accurate unsteady-state technique involved the rate of solution of small gas bubbles in a degassed liquid. The method was also restricted to slightly soluble gases since relatively long times were required to measure the rate of change of bubble size. An experiment developed by Wise and Houghton (18) involved measuring the rate of collapse of bubbles (about 0.4 mm. diameter) held by surface tension forces to a vertical wall. For these measurements, an average experimental error of ±10% was claimed.

The experimental technique of Krieger et al (19) involved trapping a bubble on a fine horizontal fibre, and photographing its projected image, as dissolution proceeded. The authors claimed an accuracy comparable to most alternate techniques.

Steady-State Capillary Cell

A steady-state capillary cell method used by Malik and Hayduk (20) and later refined by Hayduk and Cheng (21) was shown to be a reliable technique (±3% accuracy) for measuring many gas-liquid diffusion coefficients. The principle involved was similar to that of Ross and Hildebrand (13). However, diffusion occurred only in a single capillary (1 mm. diameter) and the rate of gas absorption was measured volumetrically by the movement of a liquid bead which trapped a small volume of gas in a smaller capillary. This volumetric measurement of the gas absorbed eliminated the possibility of loss of gas which was encountered in the sampling procedure of other techniques. It was also believed that convective mixing was eliminated by the use of a 1 mm. diameter capillary. These attributes enhanced the use of the method in this work even though it was limited to moderately soluble gases and depended upon knowledge of accurate solubility data.

Theoretical Aspects and Correlations

Molecular diffusion leads to an equalization of concentration within a single phase. The laws of diffusion connect the rate of flow of the diffusing substance with the concentration gradient responsible for this flow. The diffusion process has been analysed by several approaches in an attempt to arrive at a satisfactory explanation. Any model proposed for molecular diffusion should apply equally well for gas-liquid diffusion as for liquid-liquid diffusion since the gases form liquid state solutions upon dissolution.

Hydrodynamic Theory

A hydrodynamical analysis developed for the diffusion of macromolecules through a solvent uses Stoke's law to describe the frictional forces experienced by a rigid sphere moving in a gravitational field through a stationary, viscous medium. For large molecules diffusing in a low molecular weight solvent, the process is described by the Stokes-Einstein equation in which the diffusivity and solvent viscosity are inversely related. The equation also indicates an inverse relationship between the diffusion coefficient and the radius of the diffusing species.

Activated Rate Theory

An analysis of diffusion based upon an activated rate process has been instigated by Eyring (22). This theory postulates that diffusion occurs by the jumping of molecules from one equilibrium neighboring site to another under a force arising from the gradient of the chemical potential. A certain activation energy is required for the formation of "holes" in a given solvent. This energy is expressed as some fraction of the energy of vaporization. In general, this theory has not been supported by experimental results. Furthermore the existence of persisting "holes" in solution has been questioned by some workers.

Semi-Empirical Correlations

As a substitute for the theoretical approach, empirical correlations are useful in cases where experimental data are not available. A variety of correlations are available for predicting diffusivities in dilute solutions, including correlations of Arnold (23), Scheibel (24), Othmer and Thakar (25), Ibrahim and Kuloor (26), Wilke and Chang (27) and Lusis and Ratcliff (28). Also useful is an hypothesis proposed by Hayduk and Cheng (21).

The correlations of Wilke and Chang (27) and Lusis and Ratcliff (28), and the hypothesis of Hayduk and Cheng (21), were considered useful in describing diffusivities in the gas-liquid systems under study.

The equation of Wilke and Chang (27) incorporates the effects of both solute and solvent properties as follows:

$$D = 7.4 \times 10^{-8} \frac{(x M_1)^{1/2} T}{\mu V_{wc}^{0.6}} \quad \ldots\ldots\ldots(6)$$

in which x is an association parameter which is equal to unity for non-associated solvents. The authors recognized the limitations of the equation since no rigorous treatment of solute-solvent interaction was attempted in its derivation.

Lusis and Ratcliff (28) developed their correlation to describe diffusion in non-aqueous solvents at infinite dilution. They also neglected complications introduced by solute-solvent interactions. Hydrodynamic theory was employed as a basis for the derivation of the following equation:

$$\frac{D\mu}{T} = \frac{8.52 \times 10^{-8}}{V_{LB1}^{1/3}} \left[1.40 \left(\frac{V_{LB1}}{V_{LB2}} \right)^{1/3} + \frac{V_{LB1}}{V_{LB2}} \right] \ldots.(7)$$

This equation was not recommended when association of the solute and solvent molecules was likely to occur, nor for the diffusion of long straight-chain solutes in straight-chain solvents.

Hayduk and Cheng (21) reviewed the diffusivity of several solutes in many solvents. From their treatment of the available data, they confirmed their hypothesis that the diffusivity of a dilute species in any solvent depended largely upon the solvent viscosity. They also found that, for the systems they studied, the temperature dependence of diffusivity was restricted only to the temperature effect on viscosity. Their hypothesis was revealed graphically when linear relationships were obtained by plotting logarithm diffusivity versus logarithm solvent viscosity for one solute in many solvents and at various temperatures when such data were available.

Variation of Diffusivity with Temperature and Concentration

A shortage of reliable diffusivity data makes it difficult to evaluate proposed correlations or to determine the effects of temperature, pressure, and concentration on the diffusion coefficient. Theoretical and semi-theoretical equations do not clearly indicate the temperature dependence of diffusivity because they involve temperature dependent parameters or variables. Also most data cover only a moderate temperature range.

Because the concentration of dissolved gas in the liquid phase is very low under normal conditions, the viscosity of the solution should be essentially the same as that of the pure solvent. Thus, it may be expected that the diffusion coefficient does not vary significantly with concentration for gas-saturated solutions. For example, Tang and Himmelblau (29) found that the diffusivity of carbon dioxide in water was essentially independent of solute concentration (up to 0.9 mgm./cm.^{3}).

At higher concentrations where the solvent viscosity is affected the diffusivity is expected to vary with concentration.

Theory of Capillary Cell Method

The mathematical analysis for the capillary cell method has been described previously (10).

The diffusion process can be described by Fick's first law which is represented by Equation 8 for unidirectional, steady-state molecular diffusion in which the mass density of the solution is equal to that of the pure solvent.

$$\bar{n}_2 = -\rho D \frac{\partial w_2}{\partial z} + w_2 (\bar{n}_2+\bar{n}_1) \quad \ldots\ldots(8)$$

As gas absorption occurs, the column of liquid is displaced upward as a result of an increase in the solution volume. For constant density, this upward displacement is equal to the mass flux of solute gas (Equation 9) since the reservoir is of constant volume.

$$\frac{\bar{n}_1 + \bar{n}_2}{\rho} = \frac{-\bar{n}_2}{\rho} \quad \ldots\ldots\ldots(9)$$

The equation obtained by combining Equation 8 and Equation 9 is integrated to yield Equation 10.

$$D = \frac{\bar{n}_2 \; L}{e^{\ln\left(\frac{1+w_2^o}{1+w_2^L}\right)}} \quad \ldots\ldots\ldots\ldots\ldots (10)$$

When the mass flux of solute gas is expressed in terms of experimental quantities, Equation 11 is obtained which can be used to calculate the experimental diffusivities.

$$D = \frac{A_1}{A_2} \times \frac{h}{60.0} \times \frac{p_2 M_2}{V_2} \times \frac{L}{e^{\ln\left(\frac{1+w_2^o}{1+w_2^L}\right)}} \quad \ldots\ldots (11)$$

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Deaeration of Solvent

The degassing apparatus has been described by Cheng (10). This two stage apparatus was used to deaerate the solvents in both the solubility and diffusivity experiments.

The glass bottle of the first stage was filled with solvent. A vacuum was applied to both the bottle and the long, narrow glass column. After about 20% of the liquid had boiled away (boiling assisted by a heating tape for slightly volatile liquids) the liquid was sprayed through a capillary tube into the top of the accumulation column by opening the pinch cock at the bottom of the bottle. In the solubility experiments, the bottom of the long glass column was sealed by a rubber serum cap which facilitated the withdrawal of the deaerated liquid into a gas-tight syringe.

For the diffusion experiments, the rubber serum cap was replaced by a short piece of Tygon tubing closed off with a pinch cock.

After sufficient liquid had accumulated (about 70 c.c.) the pinch cock was closed and the vacuum to the whole system released. Only the top portion of deaerated solvent was exposed to the air so that the solvent near the bottom of the tube was considered to remain air-free until used.

Solubility Apparatus

The solubility apparatus was essentially the same design as described previously by Hayduk and Cheng (6). The major features are shown in Figure 1. Because the solubility of methane in the solvents was estimated to be 1 c.c. of gas/c.c. of solvent, both the gas buret (A) and the liquid buret (B) were of 10 c.c. capacity calibrated in 0.02 c.c. subdivisions. Stopcock (C) facilitated draining of the liquid buret. The degassed liquid entered the spiral gas-liquid contacting chamber (D) from a 20 c.c. gas tight syringe driven by an infusion pump which was supplied by Harvard Apparatus Company. An injection rate of 0.064 c.c./min. (1/5 rpm motor) was considered sufficient to saturate the liquid leaving the absorption spiral. The u-shaped capillary tube (E) served as a manometer to indicate any pressure differential between the gas-liquid contacting chamber and atmospheric pressure.

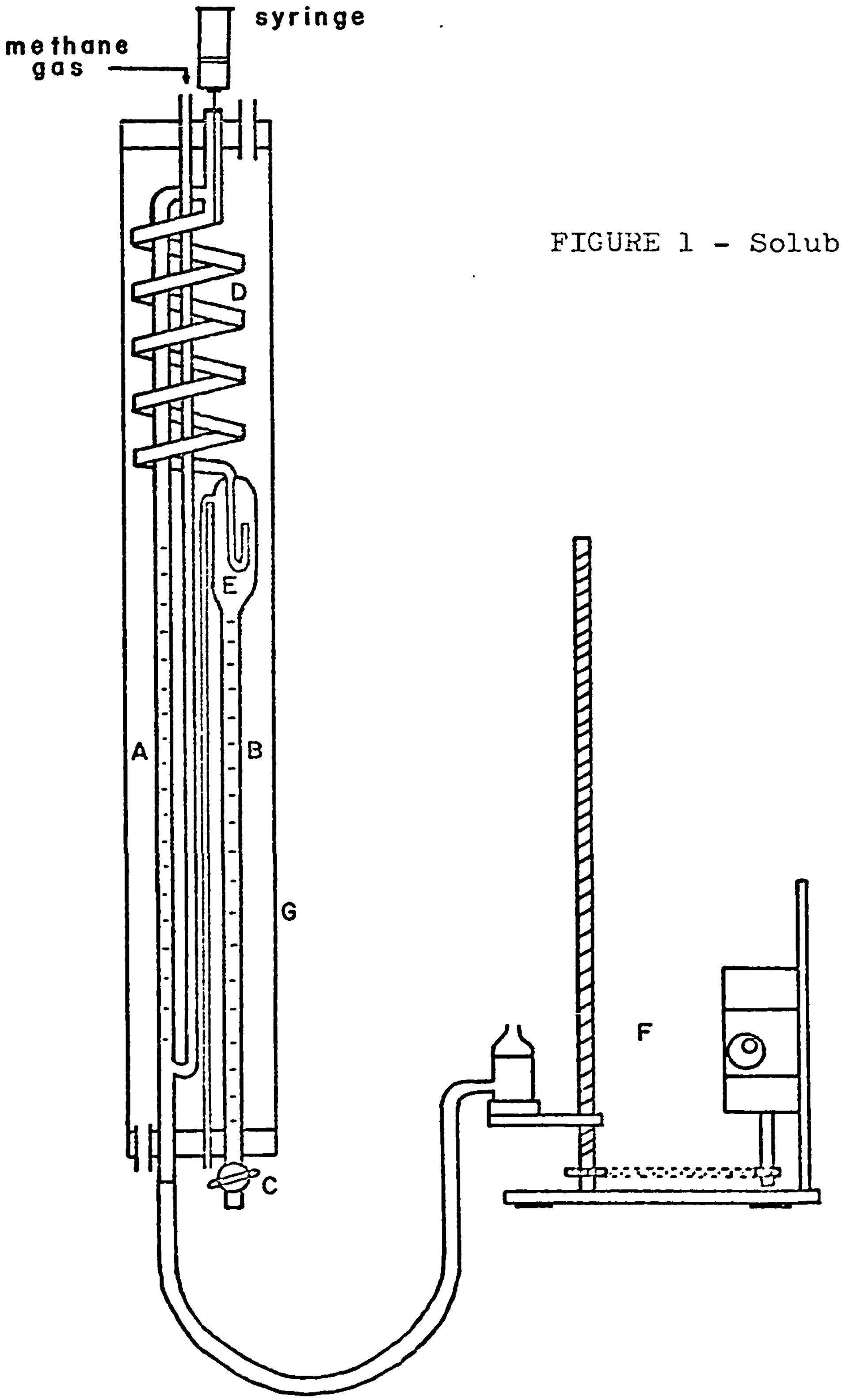


FIGURE 1 - Solubility Apparatus

The belt and pulley drive of the mercury lift (F) was replaced by a chain and sprocket drive to eliminate any possibility of slip.

The solubility apparatus was enclosed in a tubular glass jacket (G) through which a constant temperature ($\pm 0.05^{\circ}C$) water-glycol solution was circulated by means of a standard Colora circulating bath. The low temperature was obtained by means of a portable bath refrigerator supplied by Neslab Instruments Incorporated which was used in conjunction with the Colora bath.

Solubility Determinations

After the apparatus had been cleaned by flushing the contacting chamber and liquid buret with acetone or used hexane, the system was purged with a low flowrate of methane for approximately one hour with stopcock C in the open position. The gas purged from the apparatus was vented through Tygon tubing to the fumehood.

A 20 c.c. gas tight syringe was filled carefully (not to allow air contamination) with about 20 c.c. of the degassed liquid, an amount which was sufficient for two experimental determinations. After the syringe had been fitted into the infusion pump, the needle was inserted through the rubber serum cap so that the tip rested just above the gas liquid contacting chamber. Stopcock C was closed and the infusion pump started; both gas and liquid were purged simultaneously for about 20 minutes to achieve steady-state in the absorption spiral.

The mercury level was initially raised to isolate a quantity of gas in the gas buret; subsequently the lift was stopped and the methane feed line opened to the atmosphere.

When the pressure in the absorption spiral became equal to atmospheric pressure, the mercury lift was restarted and the speed maintained at a rate which kept the liquid levels in each side of the u-tube manometer equal. Readings at regular time intervals were recorded for solution volume and volume of gas absorbed.

Experiments performed using the 20 c.c. syringe and a slower 1/10 rpm motor yielded identical results as the experiments with the 1/5 rpm motor. It was concluded that the gas-liquid contact time with the 1/5 rpm motor was sufficient to achieve saturation.

For measurements at temperatures other than 25°C, a thick polyethylene sheet wrapped around the outer glass jacket served as an insulator. A 0.2°C and 0.5°C temperature drop across the column was observed at 50°C and 75°C respectively. To approximate an average temperature of 50°C and 75°C throughout the apparatus, the inlet temperature was set at 50.1°C and 75.2°C respectively.

Similarly at 0°C, the inlet temperature was set at -0.2°C to compensate for a 0.5°C temperature rise through the apparatus.

Diffusivity Apparatus

The diffusion apparatus was similar to that used by Hayduk and Cheng (21). The diffusion cells were idential in design (Figure 2).

The cell consisted of an upper, small diameter, thick-wall capillary tubing (0.03302 cm. diameter in one cell and 0.04064 cm. diameter in the other) fused to a lower, larger diameter capillary tubing (0.1016 cm. diameter in each cell). The purpose of the smaller capillary was to magnify the small changes in volume resulting from gas being absorbed. The lower capillary was sealed into a small, tubular glass reservoir of about 6 c.c. in capacity. Inlet (C1) and outlet (C2) high vacuum stopcocks permitted the filling of the cell. A column of liquid trapped in the larger diameter capillary served as the liquid through which the diffusion rate was measured.

The cell was purged with gas by means of stopcock (C3). Once filled, the cell was immersed in a constant temperature full-visibility bath supplied by Neslab Instruments Incorporated. As indicated in the experimental arrangement in Figure 2, a cathetometer (Precision Tool and Instrument Company) was used to measure the rate of travel of the saturated bead in the smaller diameter capillary.

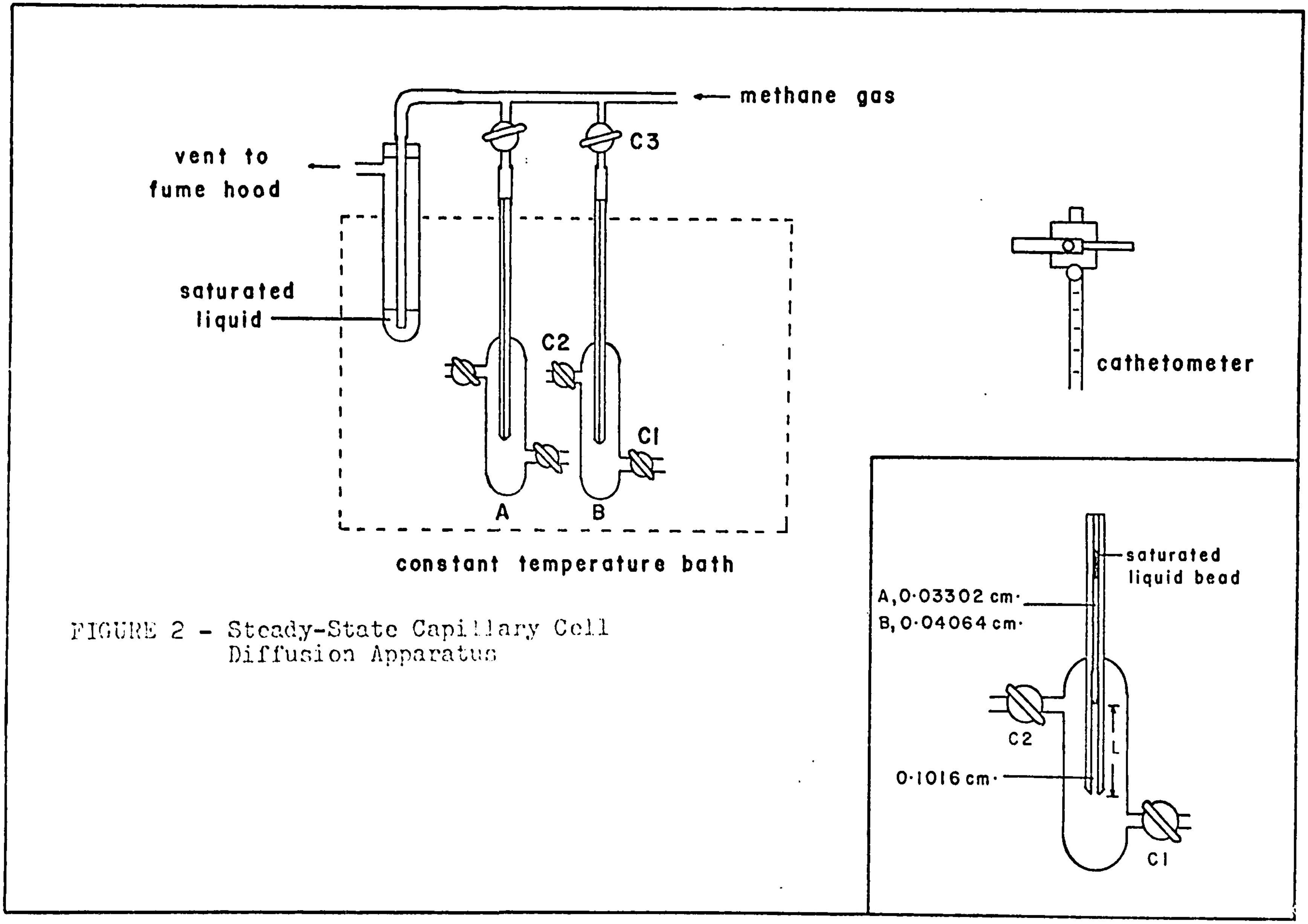


FIGURE 2 - Steady-State Capillary Cell Diffusion Apparatus

Diffusivity Determinations

The diffusion cells were cleaned prior to use. Each cell was purged first with chromic acid and then with acetone and thoroughly dried. Contaminated hexane was very effective in removing the water resistant stopcock grease.

The high vacuum stopcocks (C1 and C2) were greased with hydrocarbon resistant grease on the center portion and water resistant grease on each end to prevent leakage. For filling, the cell was connected to stopcock C3 by a 1" piece of 3/16" I.D. Tygon tubing, and C3 opened to purge the cell with methane. After 20 minutes of purging, C2, and C1 and C3 were closed in that order to maintain an atmosphere of methane within the cell.

The cell was flushed with about 30 c.c. of degassed liquid by connecting the long accumulation column of the degassing apparatus at stopcock C1. The column of liquid in the lower capillary was adjusted between 2 and 3 cm. by quickly opening C1.

After the cell had been immersed in the visibility bath for several hours, a small bead of methane-saturated liquid was injected into the upper capillary. After two hours had been allowed for complete saturation of the bead, the rate of descent of the bead was measured by means of a cathetometer.

For measurements at 50°C, the cell was filled at room temperature and slowly lowered into the bath as before.

The excess liquid due to the thermal expansion of the solvent was vented from the cell through C1 into a reservoir open to the atmosphere.

EXPERIMENTAL RESULTS AND DISCUSSION

Methane Solubility

The solubilities of methane at 0, 25, 50 and 75°C in the solvents normal hexane, heptane, octane, dodecane, and hexadecane are reported in Table 1. Also shown is the solubility of methane in benzene at 25°C. The solubilities for methane in n-hexane and benzene at 25°C compare favorably (within 2%) of those same measurements reported by Lannung and Gjaldbaek (30).

Equation 1 was used to calculate the methane solubilities at 25°C as predicted from regular solution theory. These calculated solubilities are compared with the measured solubilities in Table 2. The ideal solubility at 25°C was calculated from the integrated Clausius-Claperon equation to be 41.7×10^{-4} mole fraction rather than 39.8×10^{-4} as calculated from the same equation by Lannung and Gjaldbaek (30). A value of 6.20 was used for the solubility parameter of methane as calculated by Lannung and Gjaldbaek (30). Solvent solubility parameters were obtained from Hildebrand and Scott (8). Calculated values of the partial molal volumes of methane in the liquid paraffins were obtained from Hsi and Lu (31). At temperatures where no calculated values were available, the partial molal volume was estimated. Because

TABLE 1

Solubilities of Methane in normal hexane, heptane, octane, dodecane, hexadecane and benzene

Solvent		Temperature (^oC)				
		0	25		50	75
n-hexane	L	1.006	0.937	(0.949)(30)	0.803	
	$x_2(10^4)$	57.2	50.3	(50.8)(30)	41.3	
n-heptane	L	0.895	0.842		0.757	0.690
	$x_2(10^4)$	57.2	50.7		43.4	38.1
n-octane	L	0.827	0.768		0.697	0.655
	$x_2(10^4)$	58.7	51.2		44.2	39.8
n-dodecane	L	0.627	0.591		0.548	0.517
	$x_2(10^4)$	62.5	55.0		48.3	43.4
n-hexadecane	L		0.501		0.475	0.465
	$x_2(10^4)$		60.2		0.00537	
benzene	L		0.567	(0.571)(30)		
	$x_2(10^4)$		20.7	(20.9)(30)		

TABLE 2

Comparison of Experimental and Calculated Methane Solubilities at 25°C

Solvent	$x_2(10^4)$ (Expt.)	$x_2(10^4)$ Calculated from Equation 1
n-hexane	50.3	46.8
n-heptane	50.7	50.1
n-octane	51.2	52.9
n-dodecane	55.0	65.6
n-hexadecane	60.2	73.0
benzene	20.7	21.4

of the lack of data, the partial molal volumes in normal dodecane and hexadecane at 25°C were assumed to be equal to the calculated values for methane in normal decane (55 c.c./gm. mole) and independent of temperature. The partial molal volume of methane in benzene at 25°C was calculated to be 52 c.c./gm. mole from Horiuti's (32) measurements of the coefficient of dilation.

As seen in Table 2, the solubilities calculated from Equation 1 are a rather good estimate of the experimental values except for solubilities in normal dodecane and hexadecane. These large deviations cannot be attributed to the estimation of the partial molal volume of methane.

In addition to the new data, an extensive amount of data was obtained from the literature for the solubilities of a large number of gases in several solvents. This data and their sources are shown in Table 3.

The basis for an approach to the temperature coefficient of gas solubility for regular solutions is an application of the principle of corresponding states. It has been postulated that all gases tend to have a constant molal solubility (6) in a particular solvent as the critical temperature of the solvent is approached. Experimental evidence that such a postulate is valid is exemplified in Figures 3 to 8 in which the logarithm of mole fraction solubility is plotted as a function of logarithm temperature for the solvents indicated. The solvent freezing point, boiling point and critical temperature are also shown in each case. The data, including our

TABLE 3

Sources of Solubility Data

Solvent	Solute Gas (Data Source)
Carbon Disulfide.....	CF_4 (36); CO_2, N_2, CH_4, SF_6 (37); Ar (38); N_2O (39); H_2 (40)
Benzene..............	CF_4, SF_6 (36); N_2O (39); Ar, He, Ne (4); H_2, N_2, CO, CO_2, CH_4, C_2H_4 (32); Xe (41); C_2H_2 (42) H_2 (40); C_2H_2 (42); Ar, Xe, Ne, He (43)
Carbon Tetrachloride.	SF_6 (36); Ar (38); N_2O (39); C_2H_6, C_2H_2, C_2H_4, CH_4, O_2, CO, N_2 (32); H_2 (40, 32)
Docosane.............	C_3H_8, C_3H_6, C_2H_6, C_2H_4, CH_4 (33)
Eicosane.............	C_3H_8, C_3H_6, C_2H_6, C_2H_4, CH_4 (33)
Cyclohexane..........	CF_4, SF_6, (36); Kr, Ar, He (4); C_3H_6, C_2H_6, Xe, CO_2, N_2, H_2, Ne (34); C_3H_8, c-C_4F_8, $CClF_3$, C_3F_8, C_2F_6 (35)
Octadecane...........	C_3H_8, C_3H_6, C_2H_6, C_2H_4, CH_4 (33)
Methyl Cyclohexane...	SF_6 (36); Xe, Kr, Ne, He (44); Ar (38)
n-dodecane...........	CH_4 (this work); Kr, Ar, Ne, He (4); Xe (41)
n-octane.............	CH_4 (this work); Kr, Ar, Ne, He (4); H_2 (40)
n-heptane............	CH_4 (this work); SF_6 (36); H_2 (40); N_2O (39); Kr, Ar, Ne, He (4); C_2H_6 (6); CF_4 (45)
Freon 113............	CF_4, SF_6 (36); C_2H_6, Xe, C_2F_6, Ne, H_2 (46); CO_2, CH_4, Ar, N_2 (45)

Table 3 Cont'd

Solvent	Solute Gas (Data Source)
Iso-octane	CF_4 (36); C_2H_6, SF_6, O_2 (37); N_2O (39); H_2 (40); Xe (41); CO_2, CH_4 (45)
C_7F_{14}	Ar (38); Xe, Kr, Ne, He (44)
$(C_4F_9)_3N$	SF_6 (45); C_2H_6, CO_2, O_2, Ar, N_2 (37)
C_7F_{16}	CH_4, CO_2, SF_6, He (37); H_2 (40); N_2 (47)

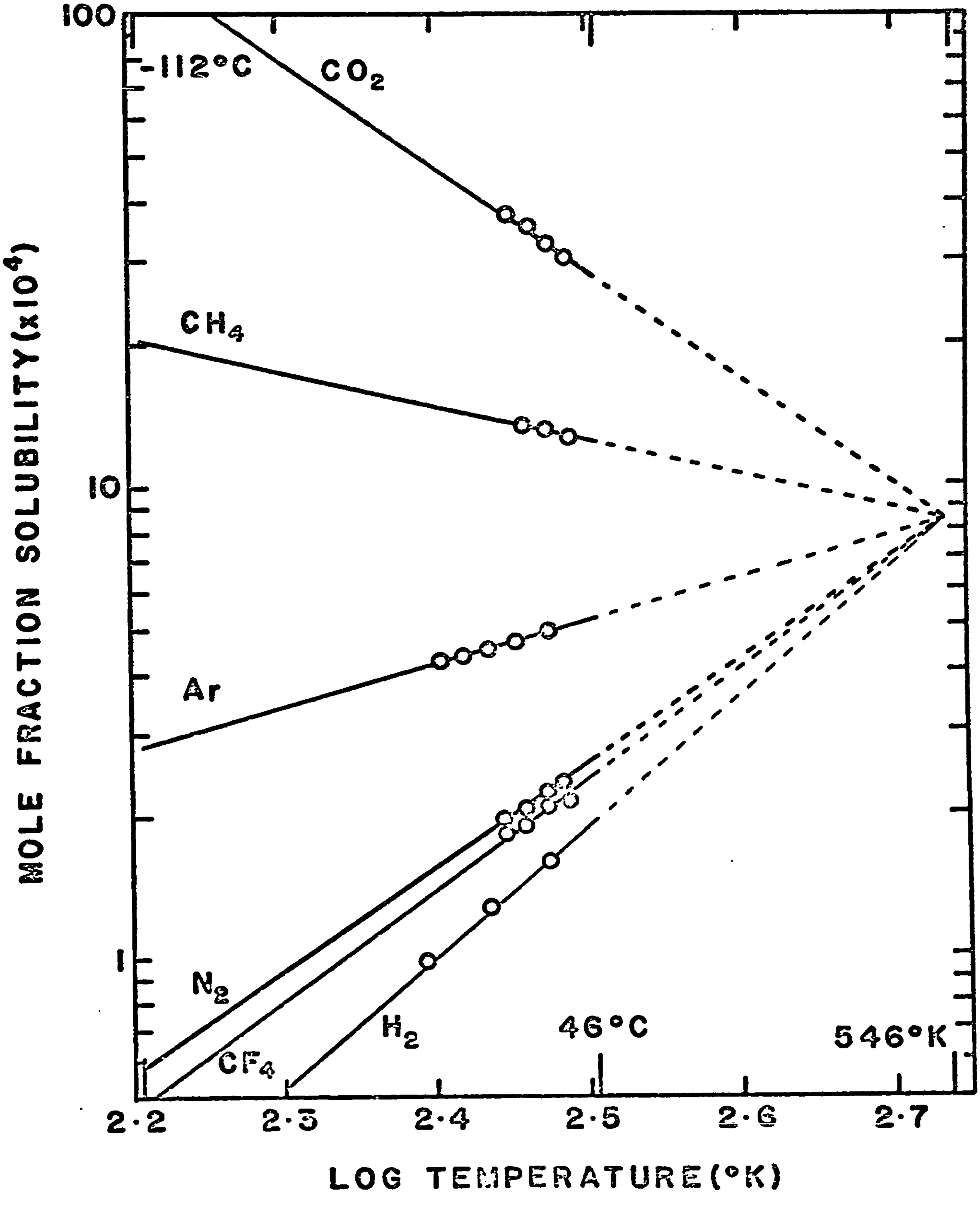


FIGURE 3 - Gas Solubilities in Carbon Disulfide

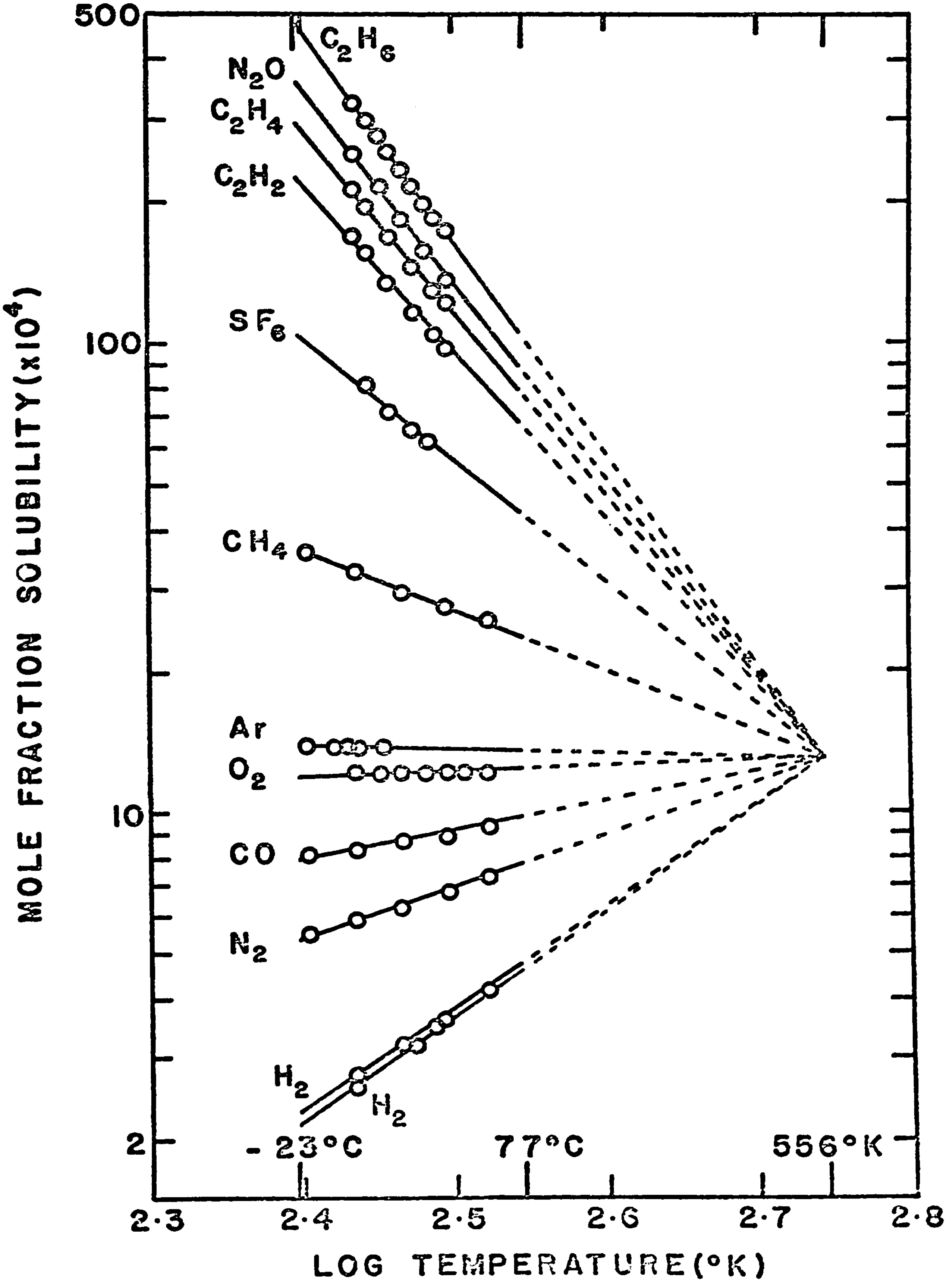


FIGURE 4 - Gas Solubilities in Carbon Tetrachloride

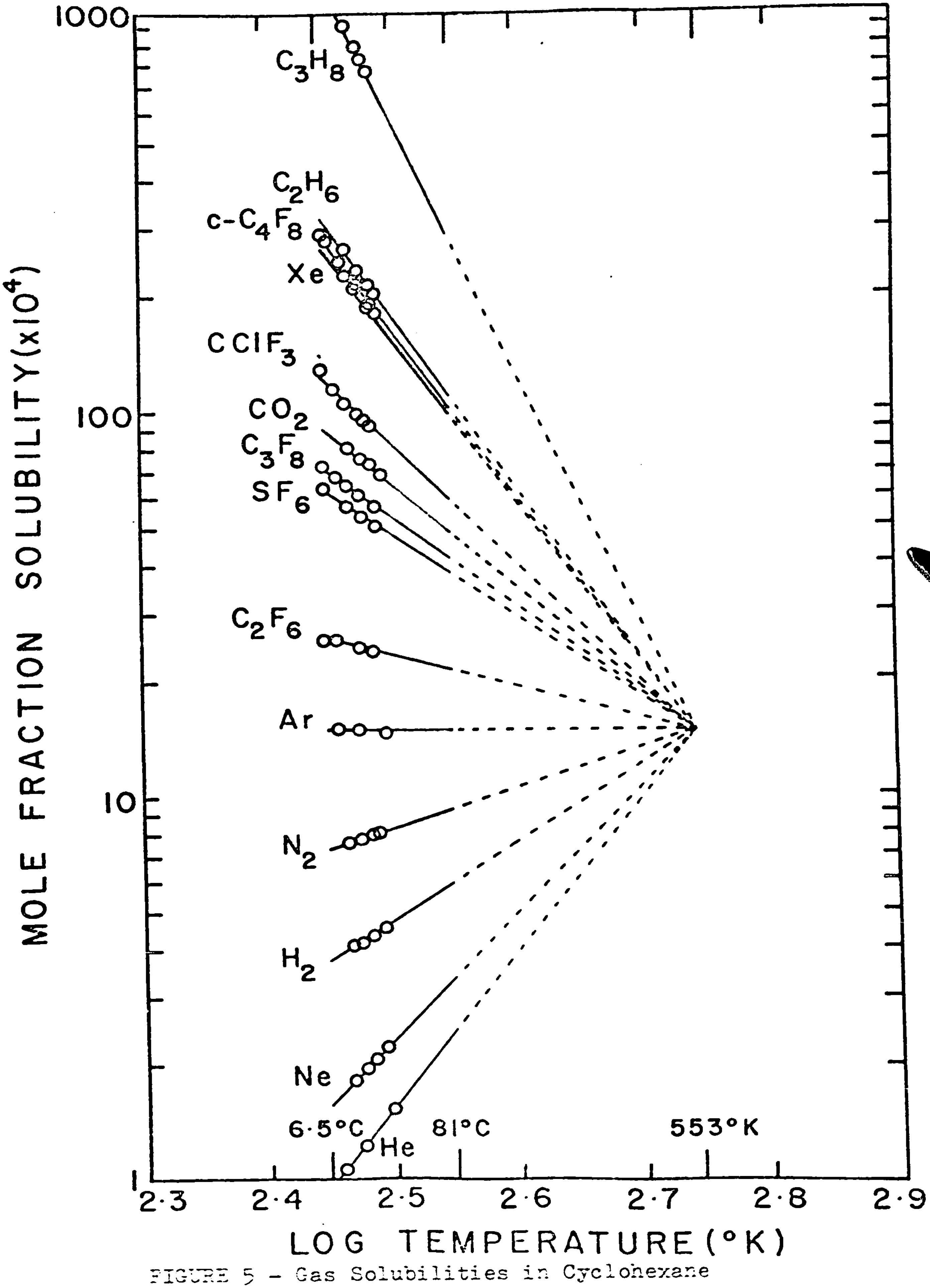


FIGURE 5 - Gas Solubilities in Cyclohexane

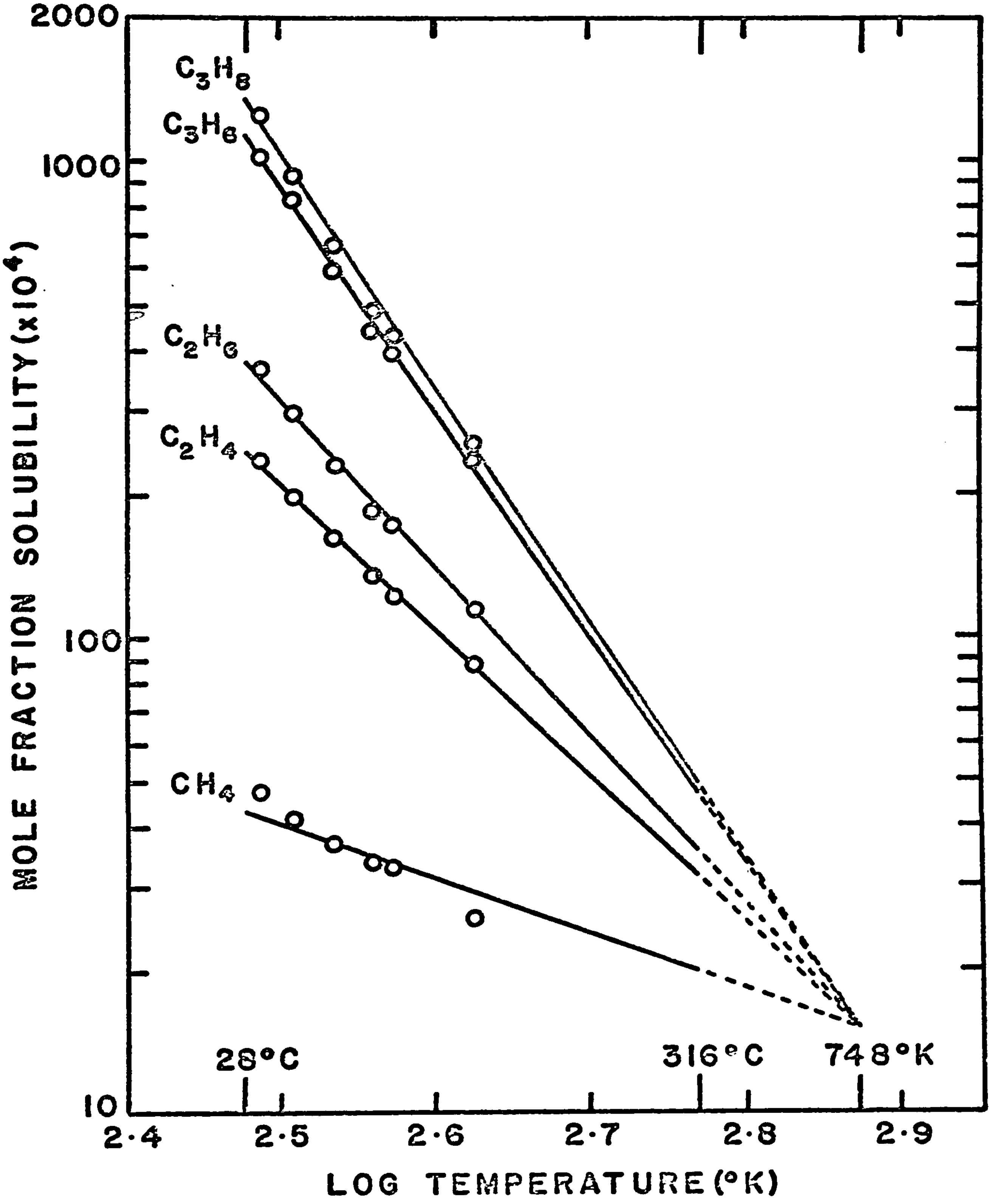


FIGURE 6 - Gas Solubilities in Octadecane

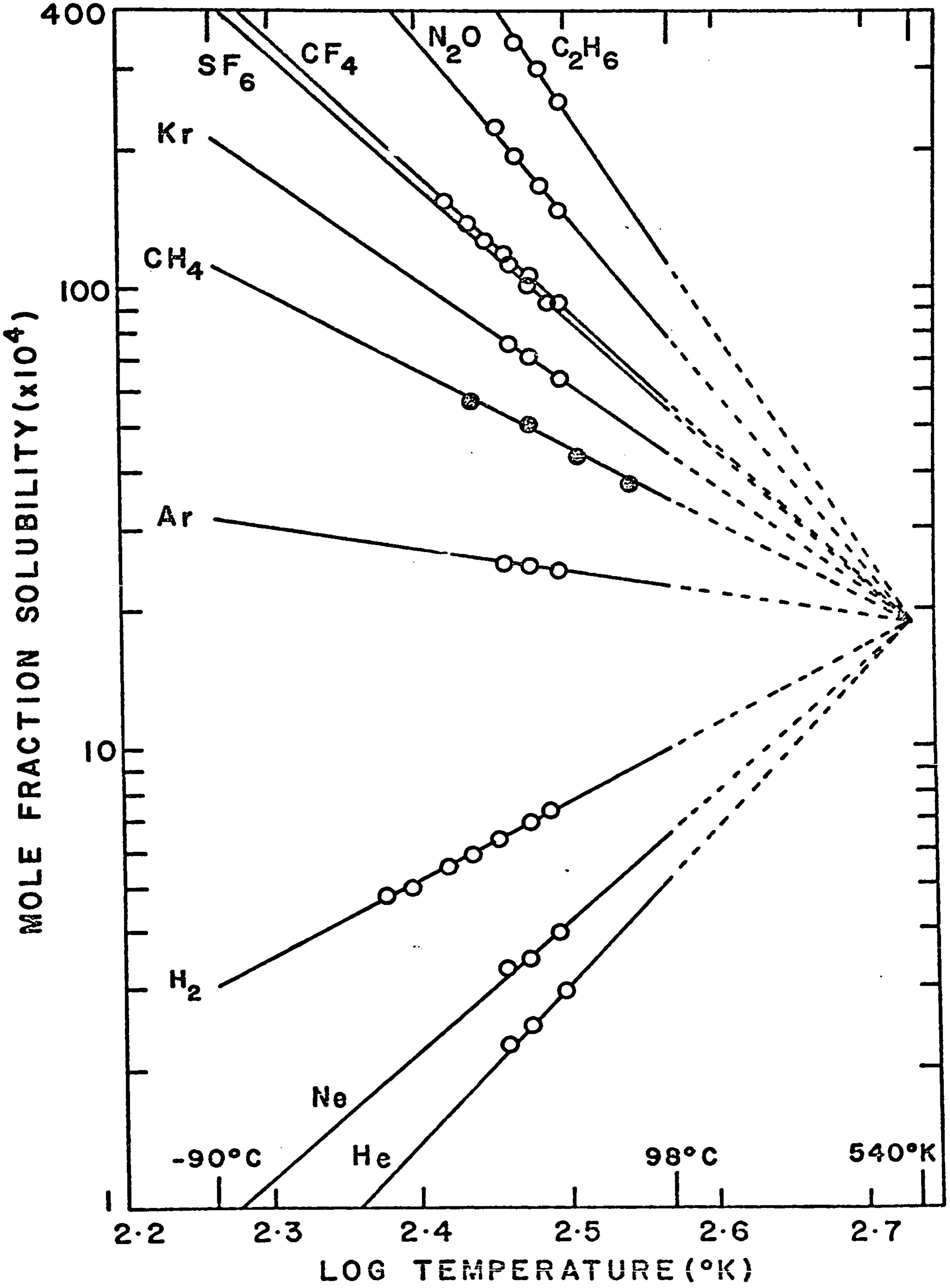


FIGURE 7 - Gas Solubilities in Normal Heptane

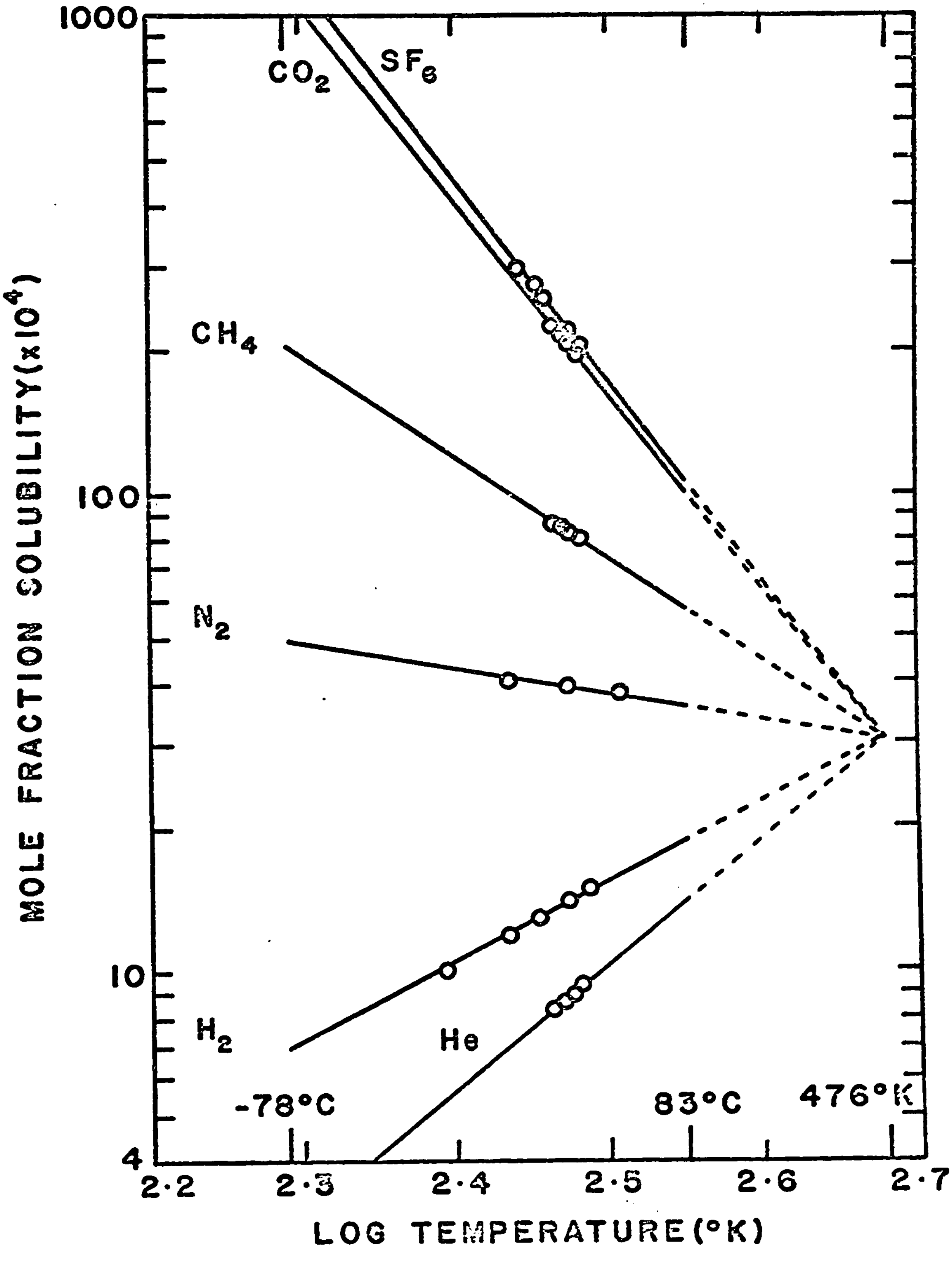


FIGURE 8 - Gas Solubilities in Perfluoroheptane

own data for methane solubility in normal heptane for example, appear to be extremely consistent. The solubility of all the gases in each solvent appears to approach a common reference value at the solvent critical temperature. Similar consistency was indicated on graphs (not shown) for the remaining solvents listed in Table 3.

From these plots of logarithm mole fraction solubility versus logarithm temperature, the solubility at any temperature can be related to that at a known temperature, by considering proportional distances of similar triangles. Such a relationship is described by Equation 12.

$$\log\left(\frac{x_{T_2}}{x_{T_1}}\right) = \log\left(\frac{x_o}{x_{T_1}}\right) \times \frac{\log\left(T_2/T_1\right)}{\log\left(T_c/T_1\right)} \quad .....(12)$$

In an attempt to describe the temperature coefficient of solubility it was useful to define a reference solubility for each solvent and to relate it to some solvent parameter. The solubility parameter of the solvent was chosen because it had been used to indicate internal pressure. Solubility parameters (Table 4) were available from Hildebrand and Scott (8).

In Figure 3 to Figure 8 a general trend for the reference solubility among the various solvents is noted. Solubilities in the solvents carbon disulfide to perfluoroheptane are presented in decreasing order of solubility

TABLE 4

Critical Temperature, Solubility Parameter and Reference Solubility

Solvent	T_c (°K)	δ_1 at 25°C (8)	$x_o \times 10^4$
Carbon Disulfide	546	10.0	7.4
Benzene	563	9.2	12.3
Toluene	594	8.9	14.5
Carbon Tetrachloride	556	8.6	11.9
Docosane	801	8.4	15.5
Eicosane	775	8.3	12.8
Cyclohexane	553	8.2	13.5
Octadecane	748	8.1	13.7
Methyl Cyclohexane	572	7.8	17.3
n-dodecane	658	7.7	19.1
n-octane	569	7.5	19.7
n-heptane	540	7.4	17.3
Freon 113	487	7.3	20.4
Iso-octane	544	6.9	16.6
C_7F_{14}	487	6.1	30.7
$(C_4F_9)_3N$	553	5.9	28.9
C_7F_{16}	476	5.8	33.0

parameter, but an increasing order of reference solubility is observed. An attempt was made to relate mathematically the reference solubility and the solvent solubility parameter.

When the solubility data for each gas were represented by a least squares regression line and extrapolated to the solvent critical temperature, the values for the reference solubility were not always identical. An arithmetic average was used to obtain an average reference solubility for each solvent (Table 4).

The logarithm of the average reference solubility for each solvent was plotted against the corresponding solubility parameter (Figure 9). A least squares regression analysis yielded the linear relationship shown by Equation 13.

$$\log (x_o \times 10^4) = 2.265 - 0.134\delta_1 \quad ....(13)$$

Equation 13 was used to calculate the average reference solubilities shown in Figure 3 to Figure 8.

In essence, the combination of Equation 12 and Equation 13 describes the temperature coefficient of gas solubility in regular solutions. It constitutes a method of predicting the solubility of a gas in a non-polar liquid at various temperatures from the knowledge of at least a single solubility measurement and solvent critical temperature and solubility parameter.

The data of Ng, Harris and Prausnitz (33) for the solubility of various hydrocarbons in octadecane (Figure 6) illustrate the effectiveness of the proposed method in determining the reliability of data. Except for the methane

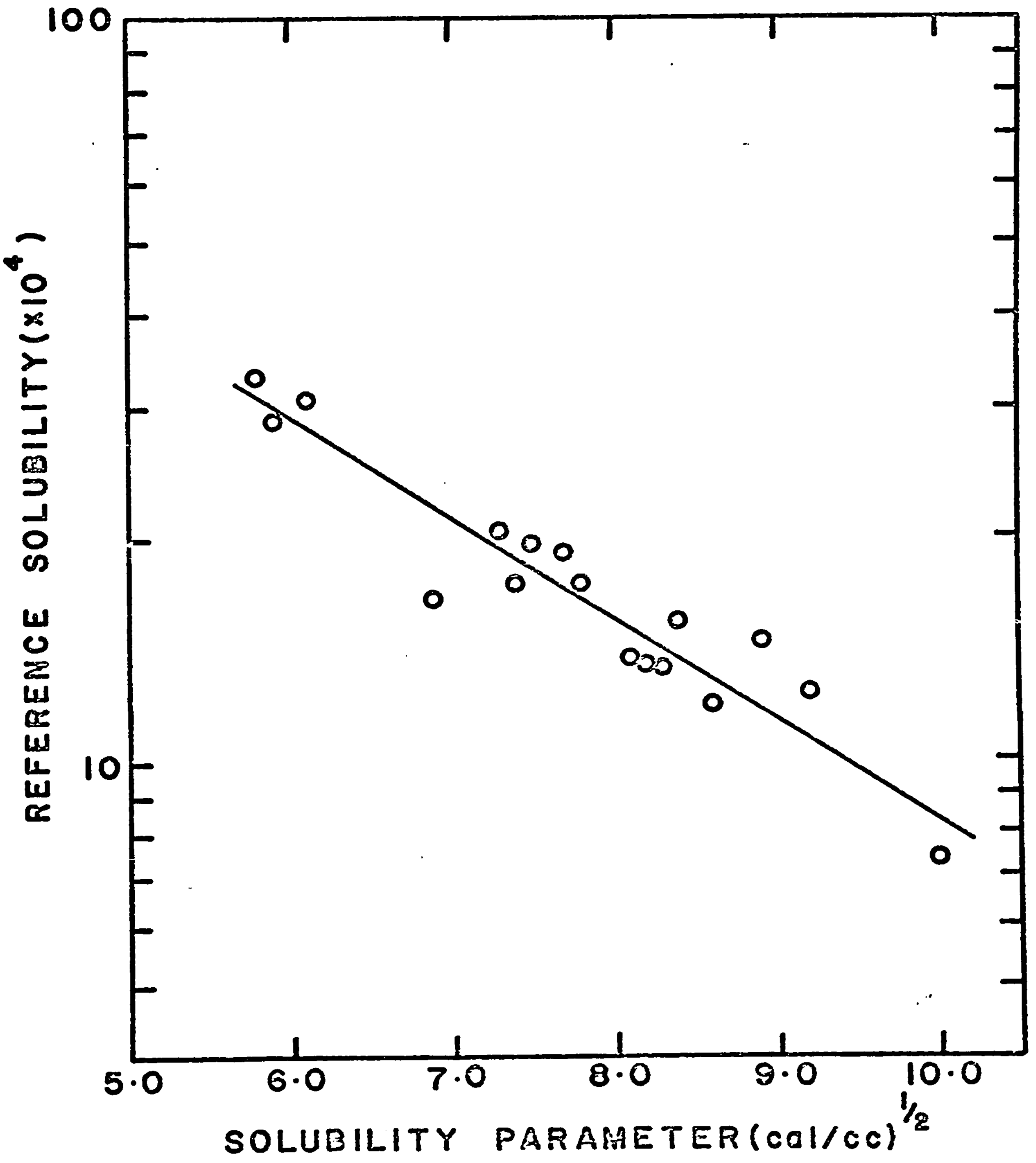


FIGURE 9 - Reference Solubility vs. Solubility Parameter

solubilities the data is well represented. This poor representation for the solubilities of methane appears consistent with the fact that the authors claimed a much lower accuracy for this gas (less than 5%).

Predicted gas-liquid solubilities using Equation 12 and Equation 13 had an estimated minimum accuracy of ±4% for the data considered. Because the extrapolation from the critical temperature to the temperature of interest spanned a large temperature range, even a relatively large variation (±10%) in the value for the average reference solubility yielded a relatively small error in the extrapolated solubility provided the original data were accurate. The method is expected to apply in the temperature range between the solvent freezing point and the boiling point.

The slope of the logarithm solubility-logarithm temperature line has been related to the entropy of solution. Since rather extensive solubility data were available for cyclohexane, the entropies of solution of various gases in this solvent were calculated using Equation 12 and 13, and compared to the corresponding literature values (34, 35). Molal entropies of solution were calculated by two slightly differing methods, and are reported in Table 5. One value was obtained from the slope of the least mean squares line through the data and the other from the slope of the line passing through the point defined by the average reference solubility and the solvent critical temperature and fitted to the solubility data so

TABLE 5

Entropies of Solution for Gases in Cyclohexane

Solute Gas	Entropy of Solution (Cal/mole-°K) Reference (35, 36)	Best Fit of Solubility Data	Best Fit of Solubility Data & (x_o,T_c)
Cyclopropane	-14.4	-13.4	-14.6
Propane	-12.2	-13.3	-13.2
cyclo-C_4F_8	- 9.0	- 9.5	- 8.7
Ethane	- 8.7	- 9.2	- 8.9
Xenon	- 8.2	- 8.4	- 8.6
Chlorotrifluoromethane	- 6.1	- 6.6	- 6.2
Perfluoropropane	- 4.7	- 5.5	- 4.6
Carbon Dioxide	- 5.2	- 5.1	- 5.3
Sulfur Hexafluoride	- 4.9	- 4.6	- 4.3
Krypton	- 3.1	- 2.8	- 3.7
Perfluorethane	- 2.2	- 2.1	- 1.7
Argon	0	- 0.8	0
Carbon Tetrafluoride	0.5	0.4	1.1
Nitrogen	2.0	2.2	2.1
Hydrogen	4.2	3.8	4.1
Neon	6.8	6.9	6.6
Helium	8.1	7.7	8.0

TABLE 6

Entropies of Solution for Methane in Normal
Hexane, Heptane, Octane, Dodecane & Hexadecane

Solvent	Entropy of Solution (Cal/mole-^{o}K)	
	Best Fit of Solubility Data	Best Fit of Solubility Data & (x_o,T_c)
n-hexane	- 3.8	- 3.5
n-heptane	- 3.4	- 3.3
n-octane	- 3.2	- 3.2
n-dodecane	- 3.0	- 2.9
n-hexadecane	- 2.4	- 3.1

that the sum of the squares of the deviations was minimum. Appearing in Table 6 are the entropies of solution calculated for each system in this work. It is apparent that the method proposed, utilizing an average reference solubility and the solvent critical temperature, provides a good estimate of the entropy of solution.

Methane Diffusivity

The diffusion coefficients of methane in the normal paraffins hexane, heptane, octane, dodecane and hexadecane at 25°C are reported in Table 7. Also included is the diffusivity of methane in normal dodecane at 50°C. Except for the diffusion of methane in normal hexane at 25°C, there are no previous literature values for comparison. Shim (48) measured the diffusion coefficient for methane in normal hexane at atmospheric pressure and 25°C by unsteady-state diffusion in a capillary. A value of 9.51×10^{-5}cm.^{2}/sec. was reported compared to the value of 8.62×10^{-5}cm.^{2}/sec. determined in this work. The value reported by Shim is suspected to be high since convective mixing may have occurred in the relatively large diameter capillary tubes (0.4 cm. I.D.).

Diffusivities of methane in other solvents can be mentioned for comparison. Witherspoon and Saraf (17) found a value of 1.88×10^{-5}cm.^{2}/sec. for the diffusion coefficient of methane in water at 24.8°C using a capillary cell method. Ross and Hildebrand (13) reported a value of 2.89×10^{-5}cm.^{2}/sec. at 25°C for methane diffusivity in carbon tetrachloride measured by a diaphragm cell. The diffusivity of methane in normal octane for example would be expected to be greater than

TABLE 7

Diffusivities of Methane (cm.^{2}/sec.) x 10^5 in Normal Hexane, Heptane, Octane, Dodecane & Hexadecane

Solvent	Temperature	
	25°C	50°C
n-hexane	8.62	
n-heptane	7.50	
n-octane	6.48	
n-dodecane	3.94	5.27
n-hexadecane	2.65	

that in both water and carbon tetrachloride because of the polarity of the first solvent and the relative high viscosity of the second solvent.

Hayduk and Cheng (21) have shown that the diffusivity is determined largely by the solvent viscosity. This linear relationship between the logarithm diffusivity and logarithm solvent viscosity is indicated in Figure 10 for the methane diffusivities. The methane diffusivity in normal dodecane at 50°C appears to obey the relationship. Figure 10 shows ethane diffusivities (10) and propane diffusivities (49) are also well represented by a linear relationship.

Experimental values were compared to the diffusion coefficients calculated from both the Wilke-Chang correlation and the Lusis and Ratcliff equation in Table 8. Similar to ethane diffusivities (10), the calculated values for methane diffusivities deviated greatly from the experimental values. Such deviations were expected to be small since no unusual interactions between solute and solvent were expected. However, the Lusis-Ratcliff equation is not strictly applicable to long-chain molecules.

The effect of solute properties such as viscosity, molal volume, and molecular shape on the diffusivity could be illustrated by considering the diffusion of several solutes in a single solvent. In particular, the data of Bidlack et al (50) for the diffusion of several solutes in hexane and carbon tetrachloride were quite revealing.

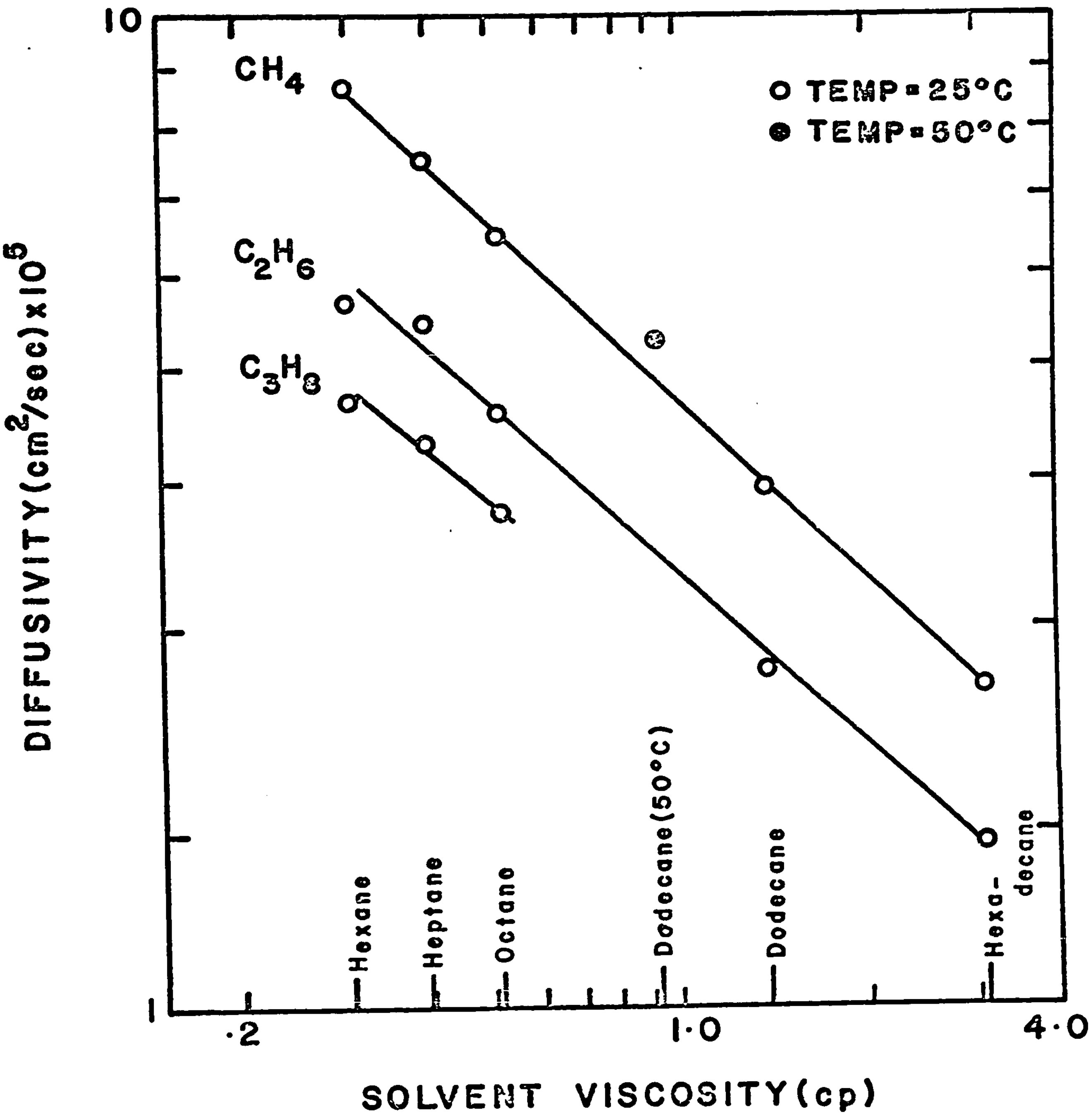


FIGURE 10 - Diffusivities of Methane, Ethane, Propane vs. Solvent Viscosity

TABLE 8

Comparison of Experimental & Calculated Methane Diffusivities

Solvent (Temp.)	Diffusivity (cm.^{2}/sec.) x 10^5		
	Expt.	Wilke-Chang	Lusis-Ratcliff
n-hexane (25)	8.64	8.92	11.5
n-heptane (25)	7.52	7.23	9.27
n-octane (25)	6.49	5.95	7.57
n-dodecane (25)	3.94	2.72	3.43
n-dodecane (50)	5.27	4.35	5.49
n-hexadecane (25)	2.66	1.39	1.77

As indicated in Figure 11, the normal paraffins showed a linear behaviour between logarithm diffusivity and logarithm solute viscosity. However, for the branched-chained solutes, 2 - methylbutane, 2, 2-dimethylbutane, and 2,2,4-trimethylpentane the diffusion coefficients fell below the line for normal paraffins. As the degree of branching increased, the diffusivity became lower than the anticipated value. Such an observation would suggest that the side-branches of the molecules actually impede the rate of diffusion. This further suggests the possibility that the solute molecules (when dealing with a long-chain molecule) diffuse in a direction parallel to the main chain.

An additional observation (Figure 11) was the upward displacement of the solutes acetone, benzene, carbon tetrachloride, cyclohexane and tetralin. Although lower diffusivities were expected for either polar or ring-type molecules, the higher values could be explained by the effect of solute molal volume. The molal volumes of these solutes are much smaller than those of the normal paraffins, and thus each of these liquids would be expected to diffuse faster than a normal paraffin of a similar viscosity (e.g. carbon tetrachloride and normal decane).

The effect of solute molal volume on the diffusivity is illustrated in Figure 12. The data of Bidlack et al (50) were plotted as logarithm diffusivity versus logarithm solute

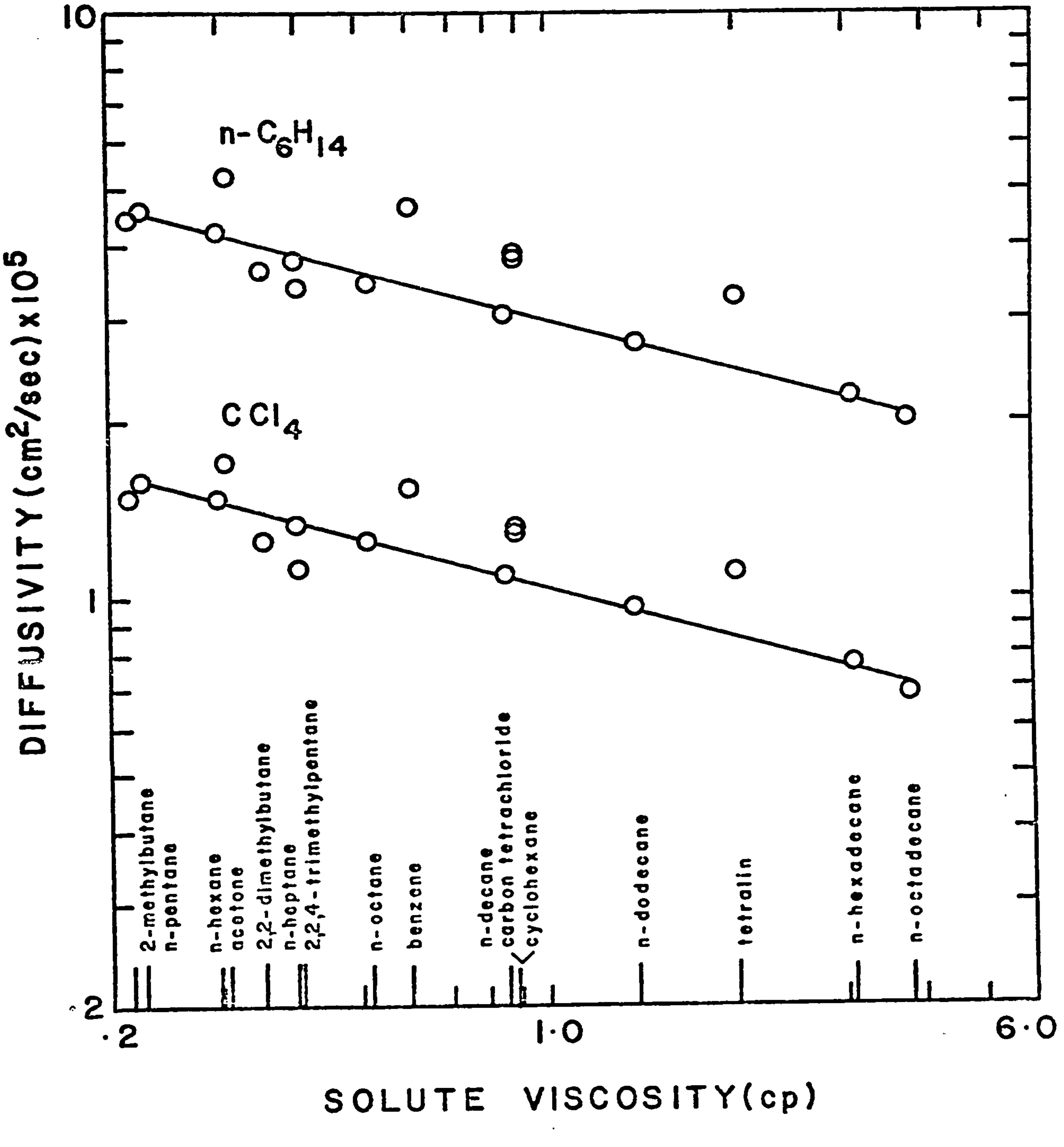


FIGURE 11 - Diffusivity vs. Solute Viscosity for various Solutes in n-Hexane and Carbon Tetrachloride at 25°C

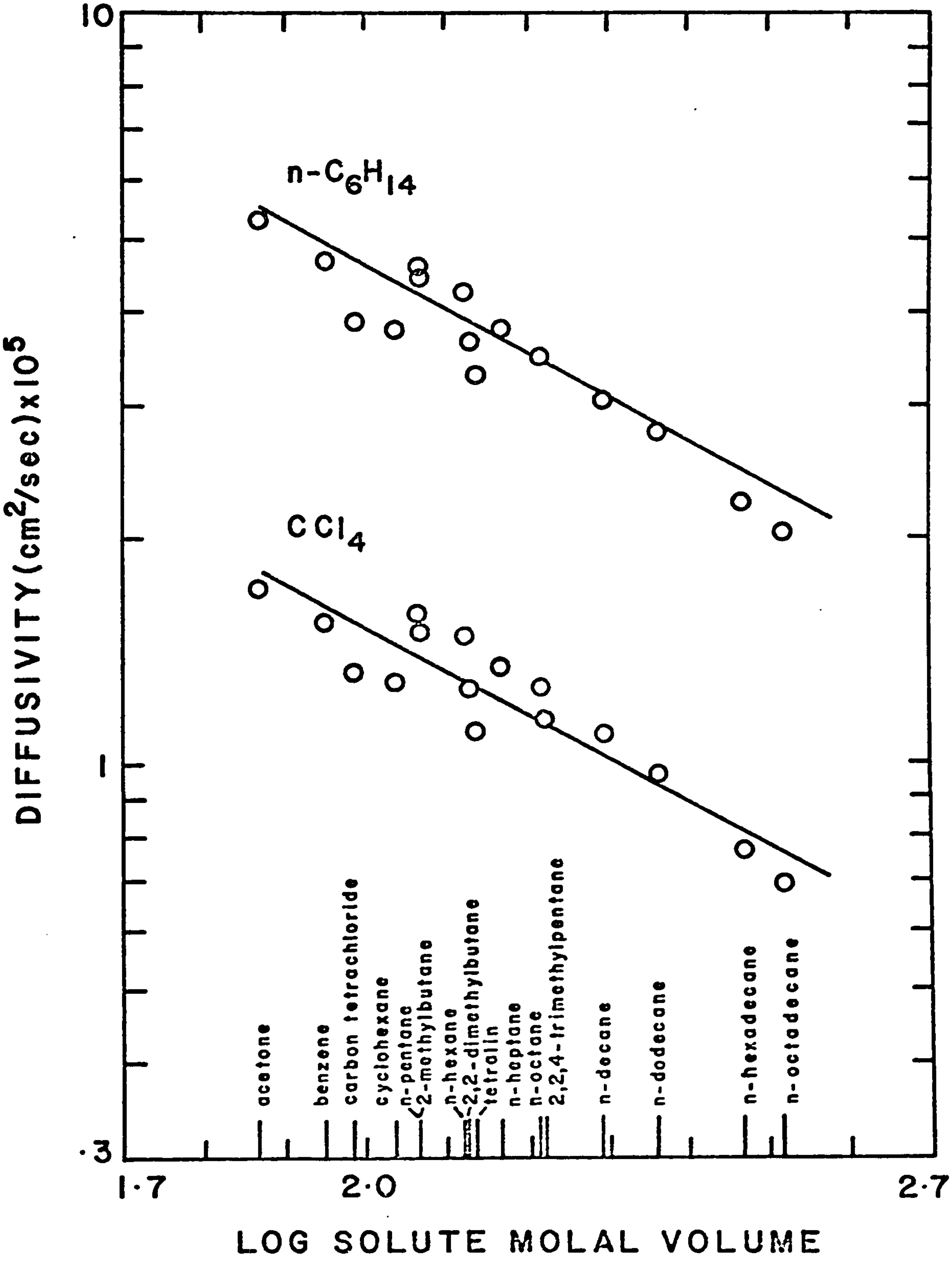
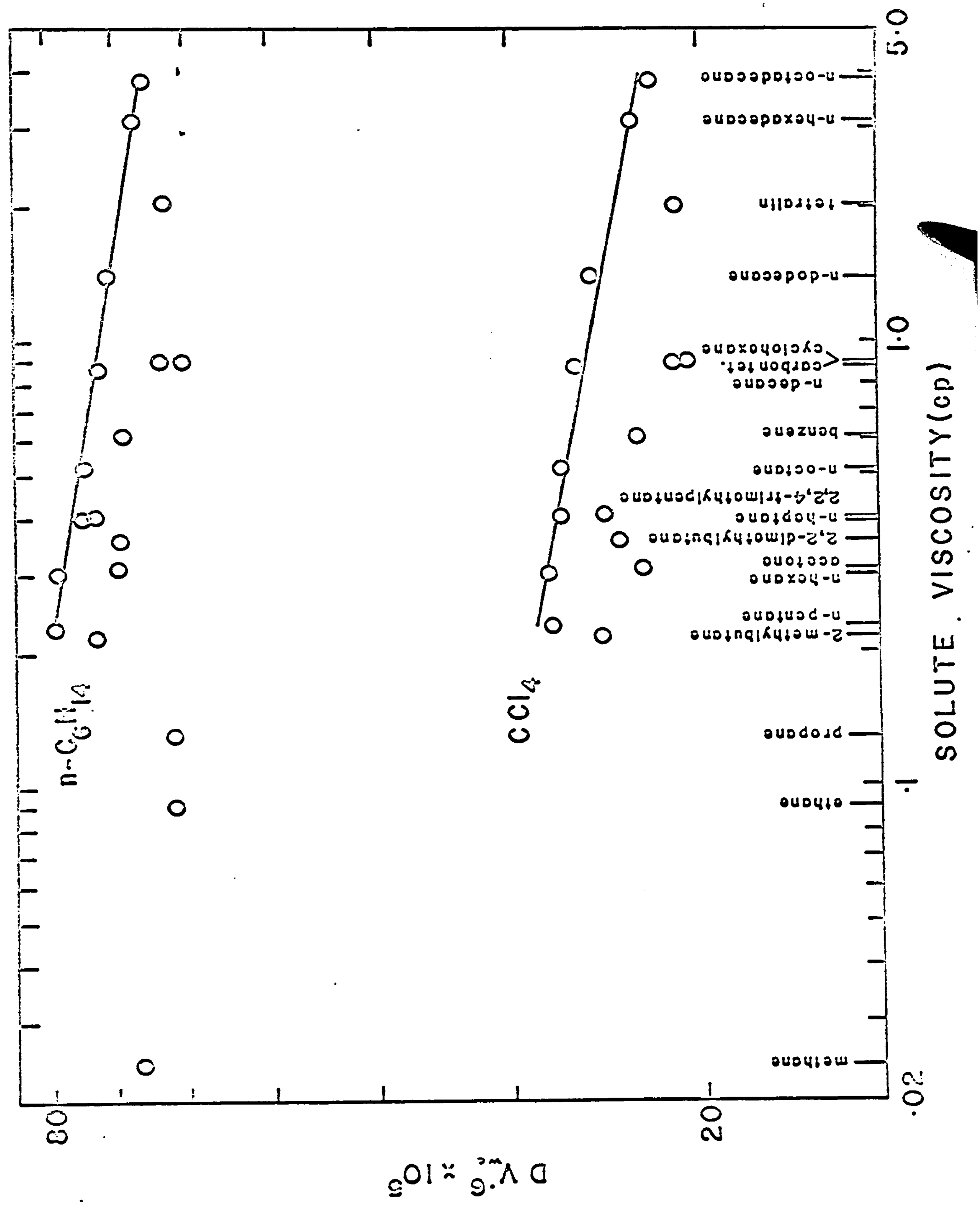


FIGURE 12 - Diffusivity vs. Solute Molal Volume for various Solutes in n-Hexane and Carbon Tetrachloride at 25°C

molal volume. As expected, the diffusivity decreased as the solute molal volume increased. A straight line of slope -0.6 (as expressed in the Wilke-Chang correlation) was drawn through the data for each solvent. Acetone and normal hexane have similar viscosities but because of its lower molal volume, acetone (a polar solvent) has a higher diffusivity. A similar observation was made for carbon tetrachloride and normal decane.

In Figure 13, the data of Bidlack et al (50) are shown as logarithm $D\ V_{wc}^{0.6}$ versus logarithm solute viscosity. The fact that $D\ V_{wc}^{0.6}$ was not constant for the diffusion of several solutes in a single solvent suggested that the solute viscosity may be a useful property in predicting diffusivities. A linear relationship was observed for the normal paraffins with the exception of the additional data (in normal hexane) for methane, ethane (10), and propane (49) which are gases at $25^{\circ}C$ and atmospheric pressure. Further investigation is necessary to determine the usefulness of the solute viscosity in predicting liquid-liquid or gas-liquid diffusivities.

FIGURE 13 - D $V_{wc}^{0.6}$ vs. Solute Viscosity



CONCLUSIONS

The semi-empirical method developed for predicting the temperature coefficient of gas solubility in regular solutions is considered capable of estimating solubilities between the solvent boiling point and freezing point to an accuracy of ±4% from at least one solubility measurement at any temperature, the solvent solubility parameter, and the solvent critical temperature. The method also appears to provide a good estimate of the entropy of solution.

The new data for the diffusivity of methane in normal hexane, heptane, octane, dodecane and hexadecane at 25°C and in dodecane at 50°C support the hypothesis that the diffusivity of a gas in a liquid is determined largely by the solvent viscosity raised to a power which is variable depending upon the solute gas.

The equations developed by Wilke and Chang and Lusis and Ratcliff were unsatisfactory in estimating the diffusivities measured in these experiments.

REFERENCES

1. Battino, R. and Clever, H.L., Chemical Reviews, 66, 395 (1966).
2. Cook, M.W. and Hansen, D.N., Rev. Sci. Instr., 28, 370 (1957).
3. Morrison, T.J. and Billet, F., J. Chem. Soc., 2033 (1948).
4. Clever, H.L., Battino, R., Saylor, J.H. and Gross, P.M., J. Phys. Chem., 61, 1078 (1957).
5. Dymond, J.H. and Hildebrand, J.H., Ind. Eng. Chem. Fundamentals, 6, 130 (1967).
6. Hayduk, W. and Cheng, S.C., Can. J. Chem. Eng., 48, 93 (1970).
7. Hildebrand, J.H. and Scott, R.L., "Solubility of Nonelectrolytes", 3rd Edition, Reinhold Pub. Co. (1950).
8. Hildebrand, J.H. and Scott, R.L., "Regular Solutions", Prentice-Hall (1962).
9. Hildebrand, J.H., Prausnitz, J.M. and Scott, R.L., "Regular and Related Solutions", Van Nostrand Reinhold Co. (1970).
10. Cheng, S.C., M.A.Sc. Thesis, Univ. of Ottawa, Ottawa (1969).
11. Himmelblau, D.M., Chemical Reviews, 64, 527 (1964).
12. Vivian, J.E. and King, C.J., A. I. Ch. E. Journal, 10, 220 (1964).
13. Ross, M. and Hildebrand, J.H., J. Chem. Phys., 40, 2397 (1964).
14. Baird, M. H. I. and Davidson, J.F., Chem. Eng. Sci., 17, 473 (1962).
15. Davies, G.A., Ponter, A.B. and Craine, K., Can. J. Chem. Eng. 45, 372 (1967).
16. Wang, J.H., J. Am. Chem. Soc., 73, 510 (1951).
17. Witherspoon, P.A. and Saraf, D.N., J. Phys. Chem., 69, 3752 (1965).
18. Wise, D.L. and Houghton, G., Chem. Eng. Sci., 21, 999 (1966).
19. Krieger, I.M., Mulholland, G.W., and Dickey, C.S., J. Phys. Chem., 71, 1123 (1967).

20. Malik, V.K. and Hayduk, W., Can. J. Chem. Eng., 46, 462 (1968).

21. Hayduk, W. and Cheng, S.C., Chem. Eng. Sci., Accepted for publication, Sept. (1970).

22. Glasstone, S., Laidler, K.J., and Eyring, H., "The Theory of Rate Processes", McGraw-Hill, New York (1962).

23. Arnold, J.H., J. Am. Chem. Soc., 52, 3937 (1930).

24. Scheibel, E.G., Ind. Eng. Chem., 46, 2007 (1954).

25. Othmer, D.F., and Thakar, M.S., Ind. Eng. Chem., 45, 589 (1953).

26. Ibrahim, S.H. and Kuloor, N.R., Brit. Chem. Eng., 5, 795 (1960).

27. Wilke, C.R. and Chang, P., A. I. Ch. E., Journal, 1, 264 (1955).

28. Lusis, M.A. and Ratcliff, G.A., Can. J. Chem. Eng., 46, 385 (1968).

29. Tang, Y.P. and Himmelblau, D.M., Chem. Eng. Sci., 20, 7 (1965).

30. Lannung, A. and Gjaldbaek, J.C., Acta. Chem. Scand., 14, 1124 (1960).

31. Hsi, C. and B.C.-Y. Lu, Manuscript of paper to be published in Can. J. Chem. Eng., February (1971).

32. Horiuti, J., Sci. Papers, Inst. Phys. Chem. Research, Tokyo, 17, 125 (1931).

33. Ng, Sai, Harris, H.G., and Prausnitz, J.M., J. Chem. Eng. Data, 14, 482 (1969).

34. Dymond, J.H., J. Phys. Chem., 71, 1829 (1967).

35. Miller, K.W., J. Phys. Chem., 72, 2248 (1968).

36. Archer, G. and Hildebrand, J.H., J. Phys. Chem., 67, 1830 (1963).

37. Kobatake, Y. and Hildebrand, J.H., J. Phys. Chem., 65, 331 (1961).

38. Reeves, L.W. and Hildebrand, J.H., J. Am. Chem. Soc., 79, 1313 (1957).

39. Yen, L.C., and McKetta, J.J., J. Chem. Eng. Data, 7, 288 (1962).

40. Cook, M.W., Hanson, D.N. and Alder, B.J., J. Chem. Phys., 26, 748 (1957).

41. Clever, H.L., J. Phys. Chem., 62, 375 (1958).

42. Vivtovec, J. and Fried, V., Coll. Czech. Chem. Commun., 25, 1552 (1960).

43. Saylor, J.H. and Battino, R., J. Phys. Chem., 62, 1334 (1958).

44. Clever, H.L., Saylor, J.H. and Gross, P.M., J. Phys. Chem., 62, 89 (1968).

45. Reeves, L.W., and Hildebrand, J.H., J. Phys. Chem., 67, 1918 (1963).

46. Linford, R.G., and Hildebrand, J.H., Trans. Far. Soc., 66, 577 (1970).

47. Gjaldbaek, J.C. and Hildebrand, J.H., J. Am. Chem. Soc., 71, 3147 (1949).

48. Shim, J., Ph.D. Thesis, University of Notre Dame, Notre Dame, Indiana (1963).

49. Bromfield, H.A., B.A.Sc. Thesis, University of Ottawa, Ottawa (1969).

50. Bidlack, D.L., Kett, T.K., Kelly, C.M. and Anderson, D.K., J. Chem. Eng. Data, 14, 342 (1969).

51. Din, F., "Thermodynamic Functions of Gases", Vol. 3, Butterworths, London (1956).

52. Reid, R.C. and Sherwood, T.K., "The Properties of Gases and Liquids", 2nd Edition, McGraw-Hill (1966).

53. Rossini, F.D., et al, Am. Petroleum Inst. Research Project 44, Circular of Natl. Bur. Standards (1947).

APPENDICES

Methane Purity, Molal Volumes & Partial Molal Volumes

The methane gas was of ultra high purity grade with a specified minimum purity of 99.9% (Matheson of Canada). The gas was used as received.

The molal volumes listed in Table 9 were obtained from Din (51). Calculated values of partial molal volumes of methane in each liquid paraffin at various temperatures were obtained from Hsi and Lu (31) as previously described and appear in Table 10. The value for methane in benzene was obtained from measurements of Horiuti (32).

A Le Bas molal volume of 30 c.c./gm-mole was obtained from reference (52).

TABLE 9

Molal Volume of Methane
at Various Temperatures (51)

Temperature (°C)	Molal Vol. (c.c./gm-mole)
0.0	22,260
25.0	24,410
50.0	26,455
75.0	28,515

TABLE 10

Partial Molal Volumes (c.c./gm-mole) of Methane in Various Liquids (31)

Solvent	Temperature			
	0	25	50	75
n-hexane	54	60	69*	
n-heptane	53*	58	65*	74*
n-octane	52*	57	63	70
n-dodecane	55*	55*	55*	55*
n-hexadecane		55*	55*	55*
benzene		52		

*Estimated from calculated values.

Liquid Purities and Properties

All liquids were of chromatographic quality supplied by Canadian Laboratory Supplies. A minimum purity of 99.0 mole per cent was specified for each solvent; normal dodecane and hexadecane were olefin free.

Various physical properties are tabulated in Table 11 to Table 14. The vapor pressures listed in Table 13 were calculated from the Antoine equation with constants obtained from reference (53). The molal volumes listed in Table 14 were calculated from the molecular weights and liquid densities obtained from reference (53).

TABLE 11

Liquid Viscosities (cp) (53)

Solvent	Temperature (°C)	
	25	50
n-hexane	0.2985	
n-heptane	0.3967	
n-octane	0.5151	
n-dodecane	1.378	0.9321
n-hexadecane	3.095	

TABLE 12

Liquid Densities (gm/cc) (53)

Solvent	Temperature (°C)			
	0	25	50	75
n-hexane	0.6769	0.6548	0.6316	-
n-heptane	0.7006	0.6795	0.6583	0.6349
n-octane	0.7189	0.6985	0.6784	0.6572
n-dodecane	0.7637	0.7452	0.7271	0.7086
n-hexadecane	-	0.7670	0.7528	0.7355
benzene		0.8737		

TABLE 13

Liquid Vapor Pressures (mm Hg) (53)

Solvent	Temperature (°C)			
	0	25	50	75
n-hexane	45.3	151.3	405.3	-
n-heptane	11.4	45.7	141.6	361.5
n-octane	2.9	14.0	50.4	144.8
n-dodecane	0.01	0.12	0.83	4.09
n-hexadecane	-	0.00	0.01	0.11
benzene		95.2		

TABLE 14

Liquid Molal Volumes (cc/gm-mole)

Solvent	Temperature (°C)			
	0	25	50	75
n-hexane	127.3	131.6	136.4	-
n-heptane	143.0	147.5	152.2	157.8
n-octane	158.9	163.5	168.4	173.8
n-dodecane	223.0	228.6	234.3	240.4
n-hexadecane	-	294.1	300.8	307.9
benzene		89.4		

TABLE 15

Le Bas Molal Volumes (cc/gm-mole)

Solvent	Le Bas Molal Vol. (cc/gm-mole)
n-hexane	141
n-heptane	163
n-octane	185
n-dodecane	274
n-hexadecane	363

Solubility Data

```
     RUN #  3-N-HEXANE
     TEMPERATURE=  0.0  DEG CENT.
     BAROMETRIC PRESS.= 758.4 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

     1.000                            0.945
     2.000                            1.890
     3.000                            2.835
     5.000                            4.750
     6.000                            5.692
     7.000                            6.632

             X2 = .00575

             L = 1.012
```

```
     RUN #  4-N-HEXANE
     TEMPERATURE=  0.0  DEG CENT.
     BAROMETRIC PRESS.= 758.6 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

     1.000                            0.952
     3.000                            2.832
     4.200                            3.941
     5.000                            4.702
     6.000                            5.644
     7.000                            6.602

             X2 = .00570

             L = 1.002
```

```
        RUN #  5-N-HEXANE
        TEMPERATURE=  0.0  DEG CENT.
        BAROMETRIC PRESS.= 758.4 MM HG


  SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

        1.000                            0.954
        2.000                            1.902
        3.000                            2.842
        4.000                            3.780
        5.000                            4.727
        6.000                            5.669
        7.000                            6.614

                  X2 = .00572

                  L = 1.005
```

```
        RUN #  1-N-HEPTANE
        TEMPERATURE=  0.0  DEG CENT.
        BAROMETRIC PRESS.= 758.2 MM HG


  SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

        1.000                            0.870
        2.000                            1.725
        4.000                            3.484
        5.000                            4.345
        6.000                            5.220
        7.000                            6.085

                  X2 = .00566

                  L = 0.886
```

```
     RUN #  4-N-HEPTANE
     TEMPERATURE=  0.0  DEG CENT.
     BAROMETRIC PRESS.= 760.6 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

     1.000                         0.874
     3.000                         2.652
     4.000                         3.540
     5.000                         4.424
     6.000                         5.304
     7.000                         6.185

               X2 = .00575

               L = 0.900
```

```
     RUN #  5-N-HEPTANE
     TEMPERATURE=  0.0  DEG CENT.
     BAROMETRIC PRESS.= 760.7 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

     1.000                         0.884
     2.000                         1.761
     3.000                         2.641
     4.000                         3.529
     5.000                         4.414
     6.000                         5.304
     7.000                         6.184

               X2 = .00575

               L = 0.900
```

```
        RUN #  1-N-OCTANE
        TEMPERATURE=  0.0  DEG CENT.
        BAROMETRIC PRESS.= 760.0 MM HG


  SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                              0.855
        2.000                              1.693
        4.000                              3.336
        5.000                              4.160
        6.000                              4.989
        7.000                              5.823

                  X2 = .00590

                  L = 0.831




        RUN #  4-N-OCTANE
        TEMPERATURE=  0.0  DEG CENT.
        BAROMETRIC PRESS.= 765.4 MM HG


  SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                              0.818
        2.000                              1.639
        4.000                              3.271
        5.000                              4.087
        6.000                              4.911
        7.000                              5.726

                  X2 = .00584

                  L = 0.823
```

```
          RUN #  5-N-OCTANE
          TEMPERATURE=  0.0  DEG CENT.
          BAROMETRIC PRESS.= 765.2 MM HG


     SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

          1.000                          0.822
          2.000                          1.648
          4.000                          3.280
          5.000                          4.201
          6.000                          4.926
          7.000                          5.744

                 X2 = .00587

                 L = 0.828



          RUN #  1-DODECANE
          TEMPERATURE=  0.0  DEG CENT.
          BAROMETRIC PRESS.= 766.4 MM HG


     SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

          2.000                          1.245
          3.000                          1.878
          4.300                          2.683
          5.000                          3.124
          6.000                          3.757
          7.000                          4.395

                 X2 = .00627

                 L = 0.630
```

```
      RUN #  2-DODECANE
      TEMPERATURE=  0.0  DEG CENT.
      BAROMETRIC PRESS.= 766.2 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

      1.000                          0.623
      2.000                          1.252
      3.000                          1.882
      4.000                          2.509
      5.000                          3.140
      6.000                          3.764

              X2 = .00627

              L = 0.629




      RUN #  3-DODECANE
      TEMPERATURE=  0.0  DEG CENT.
      BAROMETRIC PRESS.= 762.8 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

      1.000                          0.619
      2.000                          1.239
      3.000                          1.865
      4.000                          2.489
      5.000                          3.110
      6.000                          3.735
      7.000                          4.355

              X2 = .00621

              L = 0.624
```

```
      RUN #  4-N-HEXANE
      TEMPERATURE= 25.00 DEG CENT.
      BAROMETRIC PRESS.= 753.5 MM HG


SOLUTION VOL.(CC)          ABSORBED GAS VOL.(CC)

      1.000                       0.750
      3.000                       2.232
      4.000                       2.980
      5.000                       3.735
      6.000                       4.475
      7.000                       5.225

               X2 = .00502

               L = 0.935



      RUN #  7-N-HEXANE
      TEMPERATURE= 25.00 DEG CENT.
      BAROMETRIC PRESS.= 759.3 MM HG


SOLUTION VOL.(CC)          ABSORBED GAS VOL.(CC)

      2.000                       1.510
      3.000                       2.253
      4.000                       2.980
      5.000                       3.744
      6.000                       4.496
      7.000                       5.240

               X2 = .00501

               L = 0.934
```

```
        RUN #  8-N-HEXANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 753.3 MM HG


SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        2.000                           1.494
        3.000                           2.255
        4.000                           2.996
        5.000                           3.751
        6.000                           4.503
        7.000                           5.260

                  X2 = .00506

                  L = 0.942
```

```
        RUN #  4-N-HEPTANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 756.2 MM HG


SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                           0.775
        2.000                           1.548
        3.000                           2.328
        4.000                           3.114
        6.000                           4.660
        7.000                           5.438

                  X2 = .00499

                  L = 0.829
```

```
        RUN #  5-N-HEPTANE
        TEMPERATURE= 25.00 DEG CENT.
        BARDMETRIC PRESS.= 755.8 MM HG


SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

        2.000                         1.590
        3.000                         2.384
        4.000                         3.184
        5.000                         3.968
        6.000                         4.752
        7.000                         5.540

                  X2 = .00506

                  L = 0.842




        RUN #  6-N-HEPTANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 755.7 MM HG


SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

        1.000                         0.790
        2.000                         1.589
        4.000                         3.203
        5.000                         4.008
        6.000                         4.802
        7.000                         5.601

                  X2 = .00515

                  L = 0.856
```

```
        RUN #  4-N-OCTANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 757.3 MM HG


SOLUTION VOL.(CC)                ABSORBED GAS VOL.(CC)

        1.000                              0.759
        2.000                              1.519
        3.000                              2.264
        5.000                              3.763
        6.000                              4.519
        7.000                              5.267

                  X2 = .00511

                  L = 0.766
```

```
        RUN #  6-N-OCTANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 757.4 MM HG


SOLUTION VOL.(CC)                ABSORBED GAS VOL.(CC)

        1.000                              0.755
        2.000                              1.527
        3.000                              2.284
        4.000                              3.032
        5.000                              3.792
        7.000                              5.299

                  X2 = .00514

                  L = 0.772
```

```
          RUN #  8-N-OCTANE
          TEMPERATURE= 25.00 DEG CENT.
          BAROMETRIC PRESS.= 762.3 MM HG


      SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

          1.000                              0.752
          2.000                              1.501
          3.000                              2.247
          4.000                              2.998
          5.000                              3.752
          6.000                              4.501
          7.000                              5.253

                    X2 = .00510

                    L = 0.766



          RUN #  1-DODECANE
          TEMPERATURE= 25.00 DEG CENT.
          BAROMETRIC PRESS.= 760.1 MM HG


      SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

          2.000                              1.193
          3.000                              1.781
          4.000                              2.372
          5.000                              2.977
          6.000                              3.565
          7.000                              4.160

                    X2 = .00554

                    L = 0.595
```

```
        RUN #  2-DODECANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 763.3 MM HG


   SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                               0.593
        2.000                               1.179
        3.000                               1.763
        5.000                               2.933
        6.000                               3.523
        7.000                               4.114

                  X2 = .00547

                  L = 0.587



        RUN #  4-DODECANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 760.7 MM HG


   SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                               0.590
        2.000                               1.181
        3.000                               1.775
        4.000                               2.362
        5.000                               2.952
        7.000                               4.127

                  X2 = .00550

                  L = 0.590
```

```
      RUN #  2-HEXADECANE
      TEMPERATURE= 25.00 DEG CENT.
      BAROMETRIC PRESS.= 748.9 MM HG


SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

      2.000                               1.009
      3.000                               1.509
      4.000                               2.010
      5.000                               2.509
      6.000                               3.005
      7.000                               3.507

                 X2 = .00601

                 L = 0.500



      RUN #  3-HEXADECANE
      TEMPERATURE= 25.00 DEG CENT.
      BAROMETRIC PRESS.= 748.2 MM HG


SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

      1.000                               0.499
      2.000                               0.999
      3.000                               1.500
      4.000                               2.001
      6.000                               3.001
      7.000                               3.502

                 X2 = .00602

                 L = 0.501
```

```
        RUN #  4-HEXADECANE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 748.4 MM HG


 SOLUTION VOL.(CC)               ABSORBED GAS VOL.(CC)

        1.000                              0.502
        2.000                              1.002
        4.000                              2.005
        5.000                              2.504
        6.000                              3.008
        7.000                              3.512

                 X2 = .00604

                 L = 0.502
```

```
        RUN #  2-BENZENE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 749.5 MM HG


 SOLUTION VOL.(CC)               ABSORBED GAS VOL.(CC)

        2.000                              1.053
        3.000                              1.572
        4.000                              2.037
        5.000                              2.536
        6.000                              3.004
        7.000                              3.497

                 X2 = .00203

                 L = 0.557
```

```
        RUN #  3-BENZENE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 758.0 MM HG


  SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

        2.000                          1.074
        3.000                          1.569
        4.000                          2.066
        5.000                          2.574
        6.000                          3.098
        7.000                          3.596

              X2 =  .00212

              L =  0.579



        RUN #  6-BENZENE
        TEMPERATURE= 25.00 DEG CENT.
        BAROMETRIC PRESS.= 766.0 MM HG


  SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

        1.000                          0.517
        2.000                          1.032
        3.000                          1.530
        5.000                          2.495
        6.000                          2.981
        7.000                          3.491

              X2 =  .00205

              L =  0.581
```

```
          RUN #   1-R-N-HEXANE
          TEMPERATURE= 50.00 DEG CENT.
          BAROMETRIC PRESS.= 769.5 MM HG


      SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

          2.000                           0.777
          3.000                           1.163
          4.000                           1.547
          5.000                           1.922
          6.000                           2.300
          7.000                           2.688

                     X2 = .00413

                     L = 0.803


          RUN #   2-R-N-HEXANE
          TEMPERATURE= 50.00 DEG CENT.
          BAROMETRIC PRESS.= 762.1 MM HG


      SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

          1.000                           0.394
          2.000                           0.776
          3.000                           1.156
          4.000                           1.530
          5.000                           1.918
          6.000                           2.294
          7.000                           2.666

                     X2 = .00416

                     L = 0.808
```

```
          RUN #   3-R-N-HEXANE
          TEMPERATURE= 50.00 DEG CENT.
          BAROMETRIC PRESS.= 761.2 MM HG


     SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

          1.000                           0.362
          2.000                           0.737
          3.000                           1.120
          4.000                           1.504
          6.000                           2.232
          7.000                           2.608

                    X2 = .00411

                    L = 0.798



          RUN #   2-N-HEPTANE
          TEMPERATURE= 50.00 DEG CENT.
          BAROMETRIC PRESS.= 757.8 MM HG


     SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

          2.000                           1.261
          3.000                           1.875
          4.000                           2.486
          5.000                           3.101
          6.000                           3.724
          7.000                           4.342

                    X2 = .00435

                    L = 0.758
```

```
        RUN #  1-R-N-HEPTANE
        TEMPERATURE= 50.00 DEG CENT.
        BARCMETRIC PRESS.= 771.2 MM HG


  SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

        1.000                          0.620
        2.000                          1.241
        3.000                          1.918
        4.000                          2.492
        5.000                          3.103
        6.000                          3.720

               X2 = .00435

               L = 0.759



        RUN #  3-R-N-HEPTANE
        TEMPERATURE= 50.00 DEG CENT.
        BARCMETRIC PRESS.= 769.6 MM HG


  SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

        1.000                          0.612
        2.000                          1.217
        3.000                          1.835
        4.000                          2.449
        5.000                          3.059
        6.000                          3.679
        7.000                          4.291

               X2 = .00432

               L = 0.753
```

```
        RUN #  1-R-N-OCTANE
        TEMPERATURE= 50.00 DEG CENT.
        BARCMETRIC PRESS.= 751.0 MM HG


SOLUTION VOL.(CC)                ABSORBED GAS VOL.(CC)

        1.000                              0.660
        2.000                              1.303
        3.000                              1.962
        4.000                              2.622
        5.000                              3.280
        6.000                              3.939

                  X2 = .00447

                  L = 0.705




        RUN #  2-R-N-OCTANE
        TEMPERATURE= 50.00 DEG CENT.
        BARCMETRIC PRESS.= 748.4 MM HG


SOLUTION VOL.(CC)                ABSORBED GAS VOL.(CC)

        1.000                              0.654
        2.000                              1.290
        4.000                              2.568
        5.000                              3.219
        6.000                              3.858
        7.000                              4.500

                  X2 = .00437

                  L = 0.689
```

```
        RUN #  4-R-N-OCTANE
        TEMPERATURE= 50.00 DEG CENT.
        BARCMETRIC PRESS.= 749.8 MM HG


SOLUTICN VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                            0.639
        2.000                            1.294
        3.000                            1.941
        4.000                            2.587
        5.000                            3.239
        7.000                            4.528

                  X2 = .00441

                  L = 0.696




        RUN #  1-DODECANE
        TEMPERATURE= 50.00 DEG CENT.
        BARCMETRIC PRESS.= 759.6 MM HG


SOLUTICN VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                            0.548
        2.000                            1.100
        3.000                            1.647
        4.000                            2.196
        5.000                            2.740
        6.000                            3.283
        7.000                            3.829

                  X2 = .00483

                  L = 0.548
```

```
     RUN #  2-DODECANE
     TEMPERATURE= 50.00 DEG CENT.
     BAROMETRIC PRESS.= 759.8 MM HG


SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

     1.000                            0.539
     2.000                            1.079
     4.000                            2.153
     5.000                            2.698
     6.000                            3.242
     7.000                            3.790

             X2 = .00478

             L = 0.543
```

```
     RUN #  3-DODECANE
     TEMPERATURE= 50.00 DEG CENT.
     BAROMETRIC PRESS.= 761.7 MM HG


SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

     2.000                            1.118
     4.000                            2.241
     5.000                            2.793
     6.000                            3.340
     7.000                            3.884
     8.000                            4.435

             X2 = .00488

             L = 0.553
```

```
      RUN #   1-R-HEXADECANE
      TEMPERATURE= 50.00 DEG CENT.
      BAROMETRIC PRESS.= 761.8 MM HG


SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

      1.000                            0.477
      2.000                            0.959
      3.000                            1.432
      4.000                            1.902
      5.000                            2.380
      6.000                            2.848
      7.000                            3.328

                 X2 = .00537

                 L = 0.475
```

```
      RUN #   2-R-HEXADECANE
      TEMPERATURE= 50.00 DEG CENT.
      BAROMETRIC PRESS.= 761.6 MM HG


SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

      1.000                            0.474
      2.000                            0.940
      3.000                            1.412
      4.000                            1.882
      5.000                            2.355
      6.000                            2.831
      7.000                            3.319

                 X2 = .00536

                 L = 0.474
```

```
        RUN #  3-R-HEXADECANE
        TEMPERATURE= 50.00 DEG CENT.
        BAROMETRIC PRESS.= 761.2 MM HG


  SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

        1.000                             0.478
        2.000                             0.952
        3.000                             1.432
        4.000                             1.914
        5.000                             2.387
        7.000                             3.331

                  X2 = .00539

                  L = 0.477
```

```
        RUN #  2-R-N-HEPTANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 761.2 MM HG


  SOLUTION VOL.(CC)             ABSORBED GAS VOL.(CC)

        1.000                             0.367
        3.000                             1.097
        4.000                             1.455
        5.000                             1.807
        6.000                             2.169
        7.000                             2.525

                  X2 = .00377

                  L = 0.683
```

```
        RUN #  3-R-N-HEPTANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 754.9 MM HG


  SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

        1.000                           0.361
        2.000                           0.727
        3.000                           1.086
        4.000                           1.453
        5.000                           1.810
        7.000                           2.547

                 X2 = .00385

                 L = 0.697



        RUN #  4-R-N-HEPTANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 756.3 MM HG


  SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

        1.000                           0.365
        3.000                           1.080
        4.000                           1.442
        5.000                           1.802
        6.000                           2.166
        7.000                           2.523

                 X2 = .00380

                 L = 0.689
```

```
        RUN #  2-R-N-OCTANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 765.7 MM HG


   SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        1.000                              0.530
        3.000                              1.601
        4.000                              2.126
        6.000                              3.190
        7.000                              3.711

                 X2 = .00398

                 L = 0.654



        RUN #  3-R-N-OCTANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 764.7 MM HG


   SOLUTION VOL.(CC)              ABSORBED GAS VOL.(CC)

        2.000                              1.068
        3.000                              1.595
        4.000                              2.125
        5.000                              2.647
        6.000                              3.173
        7.000                              3.705

                 X2 = .00395

                 L = 0.650
```

```
        RUN #  4-R-N-OCTANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 761.5 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

      1.000                          0.531
      3.000                          1.584
      4.000                          2.117
      5.000                          2.656
      7.000                          3.732

                  X2 = .00401

                  L = 0.660
```

```
        RUN #  1-DODECANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 761.7 MM HG


SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

      1.000                          0.513
      2.000                          1.033
      3.000                          1.543
      4.000                          2.063
      5.000                          2.573
      6.000                          3.088

                  X2 = .00435

                  L = 0.518
```

```
        RUN #  2-DODECANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 761.2 MM HG


   SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

        1.000                           0.508
        2.000                           1.020
        3.000                           1.540
        4.000                           2.050
        6.000                           3.060
        7.000                           3.571

                   X2 = .00431

                   L = 0.513




        RUN #  4-DODECANE
        TEMPERATURE= 75.00 DEG CENT.
        BAROMETRIC PRESS.= 760.0 MM HG


   SOLUTION VOL.(CC)            ABSORBED GAS VOL.(CC)

        1.000                           0.510
        2.000                           1.025
        3.000                           1.543
        4.000                           2.065
        5.000                           2.577
        6.000                           3.091
        7.000                           3.611

                   X2 = .00437

                   L = 0.520
```

```
      RUN #  1-HEXADECANE
      TEMPERATURE= 75.00 DEG CENT.
      BAROMETRIC PRESS.= 751.8 MM HG


SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

      1.000                             0.470
      2.000                             0.934
      3.000                             1.406
      5.000                             2.334
      6.000                             2.808

                X2 = .00503

                L = 0.468



      RUN #  2-HEXADECANE
      TEMPERATURE= 75.00 DEG CENT.
      BAROMETRIC PRESS.= 750.0 MM HG


SOLUTION VOL.(CC)           ABSORBED GAS VOL.(CC)

      1.000                             0.462
      2.000                             0.920
      3.000                             1.385
      4.000                             1.845
      5.000                             2.301
      6.000                             2.764

                X2 = .00495

                L = 0.461
```

```
      RUN #  4-HEXADECANE
      TEMPERATURE= 75.00 DEG CENT.
      BAROMETRIC PRESS.= 758.4 MM HG


SOLUTION VOL.(CC)               ABSORBED GAS VOL.(CC)

      1.000                            0.468
      3.000                            1.400
      4.000                            1.865
      5.000                            2.333
      6.000                            2.797

             X2 = .00501

             L = 0.466
```

Diffusivity Data

Temperature = 25.0°C

```
RUN #  1-METHANE-N-HEXANE-25
BAROMETRIC PRESS.= 755.4 MM HG
DIFF. PATH LENGTH= 2.373 CM
DIA. SMALL CAPILLARY=  0.03302 CM

TIME(MIN)              BEAD POS(CM)
   16.00                  0.260
   38.00                  0.711
   64.00                  1.212
   86.00                  1.644
  117.00                  2.265
  149.00                  2.884
  176.00                  3.398
  205.00                  4.000
  230.00                  4.481
  244.00                  4.770

              D =    8.80E-05
```

```
RUN #  3-METHANE-N-HEXANE-25
BAROMETRIC PRESS.= 760.5 MM HG
DIFF. PATH LENGTH= 2.418 CM
DIA. SMALL CAPILLARY=  0.03302 CM

TIME(MIN)              BEAD POS(CM)
   16.00                  0.306
   44.00                  0.818
   70.00                  1.288
   98.00                  1.812
  127.00                  2.362
  156.00                  2.918
  185.00                  3.461
  219.00                  4.109

              D =    8.53E-05
```

```
RUN #  6-METHANE-N-HEXANE-25
BAROMETRIC PRESS.= 749.0 MM HG
DIFF. PATH LENGTH= 1.200 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)              BEAD POS(CM)
   15.00                 0.358
   35.00                 0.851
   56.00                 1.358
   76.00                 1.836
  105.00                 2.546
  134.00                 3.283
  166.00                 4.115
  192.00                 4.808
  220.00                 5.573

          D =    8.66E-05
```

```
RUN #  8-METHANE-N-HEXANE-25
BAROMETRIC PRESS.= 767.3 MM HG
DIFF. PATH LENGTH= 1.955 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)              BEAD POS(CM)
   18.00                 0.280
   45.00                 0.708
   63.00                 0.979
   94.00                 1.437
  130.00                 1.978
  163.00                 2.509

          D =    8.50E-05
```

```
RUN #  14-METHANE-N-HEPTANE-25
BAROMETRIC PRESS.= 766.3 MM HG
DIFF. PATH LENGTH= 2.434 CM
DIA. SMALL CAPILLARY=  0.03302 CM

TIME(MIN)              BEAD POS(CM)
   15.00                  0.226
   32.00                  0.488
   78.00                  1.123
  108.00                  1.563
  144.00                  2.063
  175.00                  2.563
  213.00                  3.119
  246.00                  3.660

          D =     7.51E-05
```

```
RUN #  15-METHANE-N-HEPTANE-25
BAROMETRIC PRESS.= 763.6 MM HG
DIFF. PATH LENGTH= 2.096 CM
DIA. SMALL CAPILLARY=  0.03302 CM

TIME(MIN)              BEAD POS(CM)
   18.00                  0.250
   61.00                  1.016
   88.00                  1.446
  109.00                  1.852
  131.00                  2.196
  157.00                  2.603
  186.00                  3.189

          D =     7.57E-05
```

```
RUN #  17-METHANE-N-HEPTANE-25
BAROMETRIC PRESS.= 759.1 MM HG
DIFF. PATH LENGTH= 1.940 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)             BEAD POS(CM)
   35.00                0.384
   65.00                0.756
   99.00                1.158
  126.00                1.475
  154.00                1.840
  194.00                2.321
  211.00                2.531

          D =    7.50E-05
```

```
RUN #  20-METHANE-N-HEPTANE-25
BAROMETRIC PRESS.= 759.1 MM HG
DIFF. PATH LENGTH= 3.030 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)             BEAD POS(CM)
   75.00                0.545
  101.00                0.738
  132.00                0.993
  162.00                1.232
  182.00                1.377
  213.00                1.597

          D =    7.40E-05
```

```
RUN #  3-METHANE-N-OCTANE-25
BAROMETRIC PRESS.= 755.4 MM HG
DIFF. PATH LENGTH= 2.158 CM
DIA. SMALL CAPILLARY=  0.03302 CM

TIME(MIN)          BEAD POS(CM)
   19.00              0.303
   80.00              1.057
  115.00              1.553
  145.00              1.951
  177.00              2.365
  206.00              2.770

         D =    6.55E-05
```

```
RUN #  4-METHANE-N-OCTANE-25
BAROMETRIC PRESS.= 755.4 MM HG
DIFF. PATH LENGTH= 1.920 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)          BEAD POS(CM)
   17.00              0.201
   46.00              0.483
   80.00              0.789
  113.00              1.112
  145.00              1.449
  175.00              1.718
  206.00              2.049

         D =    6.50E-05
```

```
RUN #  5-METHANE-N-OCTANE-25
BAROMETRIC PRESS.= 754.2 MM HG
DIFF. PATH LENGTH= 2.450 CM
DIA. SMALL CAPILLARY=  0.04064 CM


TIME(MIN)           BEAD POS(CM)
   20.00               0.123
   45.00               0.316
   81.00               0.582
  112.00               0.803
  140.00               1.039
  169.00               1.252
  191.00               1.403


          D =    6.40E-05
```

```
RUN #  1-METHANE-DODECANE-25
BAROMETRIC PRESS.= 754.1 MM HG
DIFF. PATH LENGTH= 1.835 CM
DIA. SMALL CAPILLARY=  0.03302 CM


TIME(MIN)           BEAD POS(CM)
   17.00               0.120
   53.00               0.396
   82.00               0.607
  107.00               0.795
  139.00               1.018
  167.00               1.209
  199.00               1.458
  232.00               1.701
  256.00               1.881
  318.00               2.336


          D =    4.01E-05
```

```
RUN #  2-METHANE-DODECANE-25
BAROMETRIC PRESS.= 754.1 MM HG
DIFF. PATH LENGTH= 2.542 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)              BEAD POS(CM)
   29.00                  0.114
   55.00                  0.214
  115.00                  0.424
  165.00                  0.577
  220.00                  0.763
  276.00                  0.944

          D =    3.83E-05
```

```
RUN #  3-METHANE-DODECANE-25
BAROMETRIC PRESS.= 759.0 MM HG
DIFF. PATH LENGTH= 1.750 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)              BEAD POS(CM)
   22.00                  0.100
   52.00                  0.276
   86.00                  0.431
  128.00                  0.646
  192.00                  0.987
  270.00                  1.390
  349.00                  1.740

          D =    3.99E-05
```

```
RUN #  1-METHANE-N-HEXADECANE-25
BAROMETRIC PRESS.= 753.4 MM HG
DIFF. PATH LENGTH= 1.749 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)             BEAD POS(CM)
   53.00                 0.204
  119.00                 0.433
  184.00                 0.608
  244.00                 0.759
  304.00                 0.957
  420.00                 1.280

         D =    2.70E-05
```

```
RUN #  2-METHANE-N-HEXADECANE-25
BAROMETRIC PRESS.= 753.4 MM HG
DIFF. PATH LENGTH= 2.238 CM
DIA. SMALL CAPILLARY=  0.03302 CM

TIME(MIN)             BEAD POS(CM)
   57.00                 0.251
  186.00                 0.695
  244.00                 0.869
  306.00                 1.071
  362.00                 1.261
  420.00                 1.448

         D =    2.58E-05
```

```
RUN #  3-METHANE-N-HEXADECANE-25
BAROMETRIC PRESS.= 758.9 MM HG
DIFF. PATH LENGTH= 2.102 CM
DIA. SMALL CAPILLARY=  0.04064 CM

TIME(MIN)             BEAD POS(CM)
   59.00                 0.152
  116.00                 0.284
  181.00                 0.447
  234.00                 0.579
  305.00                 0.744
  362.00                 0.880
  418.00                 1.002


          D =    2.67E-05
```

Temperature = 50.0°C

```
RUN #  8-METHANE-N-DODECANE-50
BAROMETRIC PRESS.= 755.9 MM HG
DIFF. PATH LENGTH= 2.648 CM
DIA. SMALL CAPILLARY=  0.03302 CM

TIME(MIN)             BEAD POS(CM)
   33.00                 0.261
   49.00                 0.385
  105.00                 0.735
  136.00                 0.933
  182.00                 1.165
  212.00                 1.371
  234.00                 1.530
  362.00                 2.298


          D =    5.24E-05
```

```
RUN #  9-METHANE-N-DODECANE-50
BAROMETRIC PRESS.= 774.5 MM HG
DIFF. PATH LENGTH= 1.882 CM
DIA. SMALL CAPILLARY=  0.03302 CM


TIME(MIN)            BEAD POS(CM)
   19.00                0.166
   50.00                0.431
   84.00                0.707
  124.00                1.038
  157.00                1.300
  179.00                1.485
  210.00                1.759
  242.00                2.044
  310.00                2.600
  336.00                2.817
  379.00                3.190

          D =     5.08E-05
```

```
RUN #  10-METHANE-N-DODECANE-50
BAROMETRIC PRESS.= 774.5 MM HG
DIFF. PATH LENGTH= 1.981 CM
DIA. SMALL CAPILLARY=  0.04064 CM


TIME(MIN)            BEAD POS(CM)
   17.00                0.091
   47.00                0.254
   80.00                0.446
  108.00                0.615
  178.00                0.998
  202.00                1.131
  247.00                1.400

          D =     5.48E-05
```