ABSTRACT

New data are reported for the solubilities of butane in normal hexane, heptane, octane, dodecane and hexadecane over the temperature range from 5° to 50°C, and in normal butanol between 5° and 75°C. Solubilities of propane in normal hexane and hexadecane at 25°C, and in normal butanol, chlorobenzene and acetone, at 0°, 25° and 50°C, are also reported. Statistical analyses, based on some of these results, along with a large number of literature data, were made to compare the linearity of the plots log x vs log T, and log x vs 1/T, for polar solvents; the first mentioned plot was found to be slightly more linear. A correlation relating log x and log T was found to describe the data appreciably better than the one relating log x and 1/T, for both polar and non-polar solvents. Based on the chosen correlation, a method involving the solvent solubility parameter and the critical temperature, was found to successfully describe the temperature coefficient of gas solubility in both non-polar and slightly polar solvents.

Diffusion coefficients for propane in normal hexane, hexadecane and butanol, as well as chlorobenzene, were measured at 25°C using the capillary-cell method. A linear relationship between the logarithm of the solvent viscosity and the logarithm of the diffusion coefficient was obtained for non-associated solvents. The constancy of the product

$D\sigma^2$, where D is the diffusion coefficient and σ the molecular diameter of the solute, was confirmed for the systems involving methane, ethane and propane, this result being consistent with the concept that diffusion is controlled by molecular size.

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NOMENCLATURE

A_1, A_2	Cross sectional areas for the upper and lower diffusion capillaries, respectively.
a_2	Activity of solute 2.
B	Slope, log D/logμ .
c	Solute concentration.
D_{21}	Diffusivity of solute 2 in solvent 1.
D^o	Diffusivity at infinite dilution, cm^2/sec.
$\bar{D}$	Integral diffusivity, cm^2/sec.
ΔE_1	Energy of vaporization, cal/gmole.
e	Percentage maximum absolute error.
G	Solubility, ml solute/gm solvent.
ΔH	Enthalphy of vaporization, cal/gmole.
ΔH_w	Enthalphy of vaporization of water, cal/gmole.
h	Slope: bead position/time, cm/min.
L	Ostwald coefficient.
l	Diffusion path length, cm.
M_1	Molecular weight of solvent.
M_2	Molecular weight of solute.
m	Slope, ml gas absorbed/ml solution.
N	Number of solubility data points for a certain system.
n	Number of gas-liquid systems for a certain liquid.
p	Total pressure, mm Hg.
p_2	Partial pressure of solute 2 in vapor phase, mm Hg.
p_1^o	Vapor pressure of solvent 1 at the experimental temperature, mm Hg.

NOMENCLATURE

R	Gas constant.
S	Standard deviation.
S_r	Watson heat of vaporization factor.
T	Absolute temperature, ^oK.
T_b	Normal boiling temperature of the solvent, ^oK.
T_c	Critical temperature of the solvent, ^oK.
T'_c	Critical temperature of water, ^oK.
V_1, V_2	Molar volumes for solvent 1 and solute 2, respectively, ml/gmole.
V_1	Volume of solution accumulated, ml.
$\overline{V}_2$	Partial molar volume of component 2, ml/gmole.
V_b	Molar volume at the normal boiling point, ml/gmole.
ΔV	Change in total volume of a solution caused by the addition of n_2 moles of solute, the solution being initially pure solvent, ml.
W	Weight percentage of solute.
w_{20}	Mass fraction of solute at the gas-liquid interface.
w_{21}	Mass fraction of solute at the end of the capillary.
X	Wilke-Chang association parameter.
x_2	Mole fraction solubility of solute 2.
x_2^i	Ideal mole fraction solubility of solute 2.
x_{oi}	Reference solubility for solute i (theoretical solubility for $T = T_c$, from the log x_2-$1/T$ plot).
x'_{oi}	Reference solubility for solute $\underline{i}$ (theoretical solubility for $T = T_c$, from the log x_2-$1/T$ plot).
$\overline{x}_o$, $\overline{x}'_o$	Average reference solubilities as obtained from the log x_2-log T and log x_2-$1/T$ plots, respectively.
z	Rate of flow of degassed solvent, ml/min.
1, 2	Solvent and solute, respectively.

NOMENCLATURE

Greek symbols

α	Bunsen coefficient.
α'	d log a_2/d log x_2.
α_g	Polarizability of the gas.
δ_1, δ_2	Hildebrand solubility parameters for solvent and solute, respectively.
ε	Dielectric constant of the solvent.
δ	Molecular diameter for solute, Å.
μ, μ_1, μ_2	Viscocity of solution, solvent, and solute, respectively, centipoises.
ρ_1	Density of the solvent, gm/ml.
θ	Time, minutes.

CHAPTER 1

INTRODUCTION

Gas-liquid solubilities and diffusivities have become increasingly more important for both the theoretical understanding of the liquid state and solutions, and for practical applications, such as the design of gas-liquid mass transfer equipment.

In the write-up of this thesis solubilities and diffusivities were treated separately for the sake of convenience and clarity in presentation.

Solubility

Much work has been done, particularly by Hildebrand and Scott (2, 3) to present a satisfactory theory of solutions for regular systems, from experimental results for the solubilities of light gases in normal liquids. Some useful relations have been discovered, based either on empirical evidence or on theoretical derivations in some simplifying assumptions:

1. The entropy of solution is directly related to the slope of the logarithm solubility - logarithm temperature line.
2. For a number of gases in a particular solvent, the entropies of solution are linearly related to the logarithm of the gas solubilities themselves, i.e., the higher the solubilities, the higher the coefficient of solubility.

3. There is a linear relationship between logarithm solubility and both logarithm temperature and inverse temperature.
4. For a certain gas, logarithm solubility varies linearly with the number of carbon atoms in the solvent.

Some of these relations, along with the observation that it appeared that as the solution temperature was increased toward the critical temperature of the solvent (or solution), the solubilities of all gases in that solvent approached a constant molar concentration, constitute the basis of an empirical method proposed recently from this laboratory (11) for determining the temperature coefficient of solubility for regular solutions in liquids.

There are a large number of systems involving either highly soluble gases or polar solvents for which the extent of applicability of the above mentioned relations is either unknown (highly soluble gases) or not sufficiently studied (polar solvents). One of the purposes of this work was to give some indications about the behavior of these systems and to suggest a way to predict solubilities of gases in polar solvents.

For the experimental part, butane was chosen as an example of a gas of particularly high solubilities in normal hydrocarbons; due to the high solubilities involved, a transition between gas solubility and vapor-liquid equilibrium behavior was expected. Also, some experiements for propane in the polar solvents acetone, chlorobenzene and normal butanol were performed to analyze the solubility behavior in polar solvents. These results, together with the literature data for gas solubilities in 17 polar solvents, ranging from slightly polar, such as toluene and bromobenzene, to highly polar, such as acetone and methanol, were used to select the more appropriate solubility plot for polar solvents.

An empirical method relating logarithm solubility and logarithm temperature have been proposed recently for non-polar solvents.(11). This method was tested to find its limits of applicability to polar solvents. A similar method relating logarithm solubility and inverse temperature was also tested for both polar and non-polar solvents.

In conjunction with solubilities, partial molar volumes were measured and some observations briefly discussed.

Diffusion

The development of empirical equations to predict diffusivities has been hindered by the lack of experimental data and the uncertainty in measuring accurate diffusion coefficients for gas-liquid and liquid-liquid systems. Most of these equations, notably those by Wilke-Chang (42) and Scheibel (43), can be used to predict diffusivities at infinite dilution for the systems discussed here, even though large deviations sometimes appear, particularly for dissolved gases in viscous solvents.

The relationship between molecular diffusivity and solvent viscocity in dilute solutions was recently reviewed (58) for various substances in a number of non-associating solvents. In general, a linear relationship was obtained between logarithm diffusivity and logarithm solvent viscocity. Gases, such as propane for which diffusivity data were not available at that time, were not included in the review. It was considered interesting to experimentally verify this relationship for propane. With this purpose, diffusion coefficients for this gas in normal hexane, hexadecane and butanol, as well as in chlorobenzene, were measured at 25°C by use of the capillary cell technique previously utilized in this laboratory (11, 12, 60). Solvents were chosen so as to have a wide range of viscosities, from 0.2969 cp for hexane to 3.0909 for hexadecane.

In general, diffusion coefficients are functions of the concentration of the diffusing substance. Most of the experimental techniques give only integrated values over the concentration range of the experiment. For slightly soluble gases in liquids, integrated and differential diffusivities are very close due to the small concentration gradients involved. This argument however, is not valid for a highly soluble gas, such as butane in normal hydrocarbons; for these systems, a complicated relationship between diffusivity and concentration appears. A brief account of the progress in this area is presented in this work.

CHAPTER 2

SOLUBILITIES AND PARTIAL MOLAR VOLUMES

2-1. Theory

Solubility

For any gas-liquid system, solubility is defined as the amount of gas dissolved per unit mass of volume of liquid at equilibrium at a constant pressure and temperature. According to the units and conditions utilized to express these amounts of gas and liquid, various ways to express solubilities appear.

As a part of this thesis, literature values of mole fraction solubilities in polar solvents were obtained either directly or by use of the appropriate conversions. A list of these units and conversions are presented:

1. Mole Fraction Solubility (x_2): Moles of gas dissolved per mole of solution.
2. Ostwald Coefficient (L): Milliliters of gas dissolved (at the temperature and pressure of the experiement) per milliliter of solvent (1).

$$x_2 = \frac{L/V_2}{L/V_2 + 1/M_1} \qquad (2\text{-}1)$$

3. Bunsen Coefficient (α): mls of gas dissolved (at $0^\circ C$ and 1 atm) per ml of solvent (1).

$$L = \alpha T/273.15 \qquad (2\text{-}2)$$

4. Milliliters solute per gram solvent (G):

$$L = \frac{G \rho_1 T}{273.15} \tag{2-3}$$

5. Weight percentage of solute in the solution (W)

$$x_2 = \frac{W/100\ M_2}{(W/100\ M_2) + 1/M_1} \tag{2-4}$$

The experimental results from this work are presented as mole fraction solubilities.

A great deal of work has been done particularly by Hildebrand and co-workers (2, 3, 4, 5, 6) to obtain and test equations to predict solubilities in gas-liquid systems. These equations apply fairly well for the so called 'Regular Solutions', defined by Hildebrand as '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'. These equations are:

$$-\log x_2 = -\log x_2^i + \log \frac{\overline{V}_2}{V_1} + 0.4343\left(1 - \frac{\overline{V}_2}{V_1}\right) + \frac{\overline{V}_2}{2.303RT} (\delta_1 - \delta_2)^2 \tag{2-5}$$

$$-\log x_2 = -\log x_2^i + \frac{\overline{V}_2}{2.303RT} (\delta_1 - \delta_2)^2 \tag{2-6}$$

Where:

$$\delta_1 = \sqrt{\Delta E_1 / V_1} \tag{2-7}$$

$$\log x_2^i = \frac{\Delta H}{2.303R} \left(\frac{1}{T} - \frac{1}{T_b}\right) \tag{2-8}$$

These equations are not applicable to the systems studied in this work, for two reasons:

1. They are useful for dilute solutions of dissolved gases in liquids, and cannot be applied with confidence when $x_2 > 0.1$.
2. They were derived on the assumption that the molecules in solution were non-polar (polar molecules present solvation and association complexes) and hence cannot be applied to solutions of polar solvents.

Gjaldbaeck and Andersen (7) tried to use equation (2-6) to calculate the solubilities of carbon dioxide, oxygen, carbon monoxide and nitrogen in various polar solvents. They found that the differences between calculated and experimental values of $-\log x_2$ were approximately proportional to the dipole moments of the solvents (μ') as well as the electronic polarization of the gas (α_g).

In 1958, Gjaldbaeck and Niemann (9) showed that equation (2-5) can roughly account for the solubility at 25 C of nitrogen, argon and ethane in alcohols, if δ_1 is substituted by δ_1^0 calculated from

$$\delta_1^0 = \delta_1 - (\varepsilon - 1)(0.165 - 0.00143\alpha_g \cdot 10^{25}) \qquad (2\text{-}9)$$

Later on, Lannung and Gjaldbaeck (8) followed the same procedure to calculate the solubilities of methane in various alcohols and other polar solvents. In general, serious deviations were found (29% in acetone, 17% in methyl acetate, etc.).

It can be concluded that for calculations of solubilities of gases in polar solvents, only qualitative considerations are so far available, and application of Equations (2-5) and (2-6) to these systems may lead to values which are considerably lower than the corresponding experimental results.

Partial Molar Volumes

In dealing with extensive properties of solutions, it is convenient to consider separately the contribution attributable to each component present. For example, the total volume of solution represents the sum of the contributions of all components present. For a two components gas-liquid system, that portion of the total volume of a solution which is attributable to the presence of the solute is termed the partial volume of that solute. Similarly, the partial molar volume represents the volume occupied by the dissolved solute per mole of gas in the solution, while the composition of the solution remains the same.

In ideal liquid solutions, the contributions of the two components are the same as the properties of the two components existing separately in the solution. However, for the systems considered here, intermolecular forces between unlike molecules causing all factors involved in deviations from ideal behavior (dipoles, hydrogen bonds and weak complexes, among others) play an important role; for that reason additivity of properties does not exist, and the volume of the solution is not exactly equal to the sum of the pure component volumes.

Mathematically, the partial molar volume of a component of a solution may be defined (10) as:

$$\bar{V}_2 = \frac{(\partial V)}{\partial n_2}_{p,T,n_1} \tag{2-10}$$

If the assumption that $\bar{V}_2$ is constant with composition is made (a small addition of component 2 does not affect the concentration enough to vary $\bar{V}_2$), equation (2-10) becomes:

$$\bar{V}_2 = \frac{(\partial V)}{\partial n_2}_{p,T,n_1} = \frac{(\Delta V)}{n_2}_{p,T,n_1} \tag{2-11}$$

In Equation (2-11) ΔV is the change in total volume of the solution, caused by the addition of n_2 moles of solute, the solution being initially pure solvent.

2-2. Apparatus and Procedure

Refer to Figure 2-1. Basically the solubility apparatus utilized here was the same as the one described previously by Buckley (11). Because of the high solubilities of the gases involved, a number of changes were required to guarantee good accuracy for the experiments. The solubility was measured by observing the rate of absorption of a gas by a continuus stream of degassed solvent.

As a result of the very high and variable solubilities expected (Ostwald Coefficients ranging from about 5 to 600 ml gas per ml solvent), the gas burette utilized (100 ml,

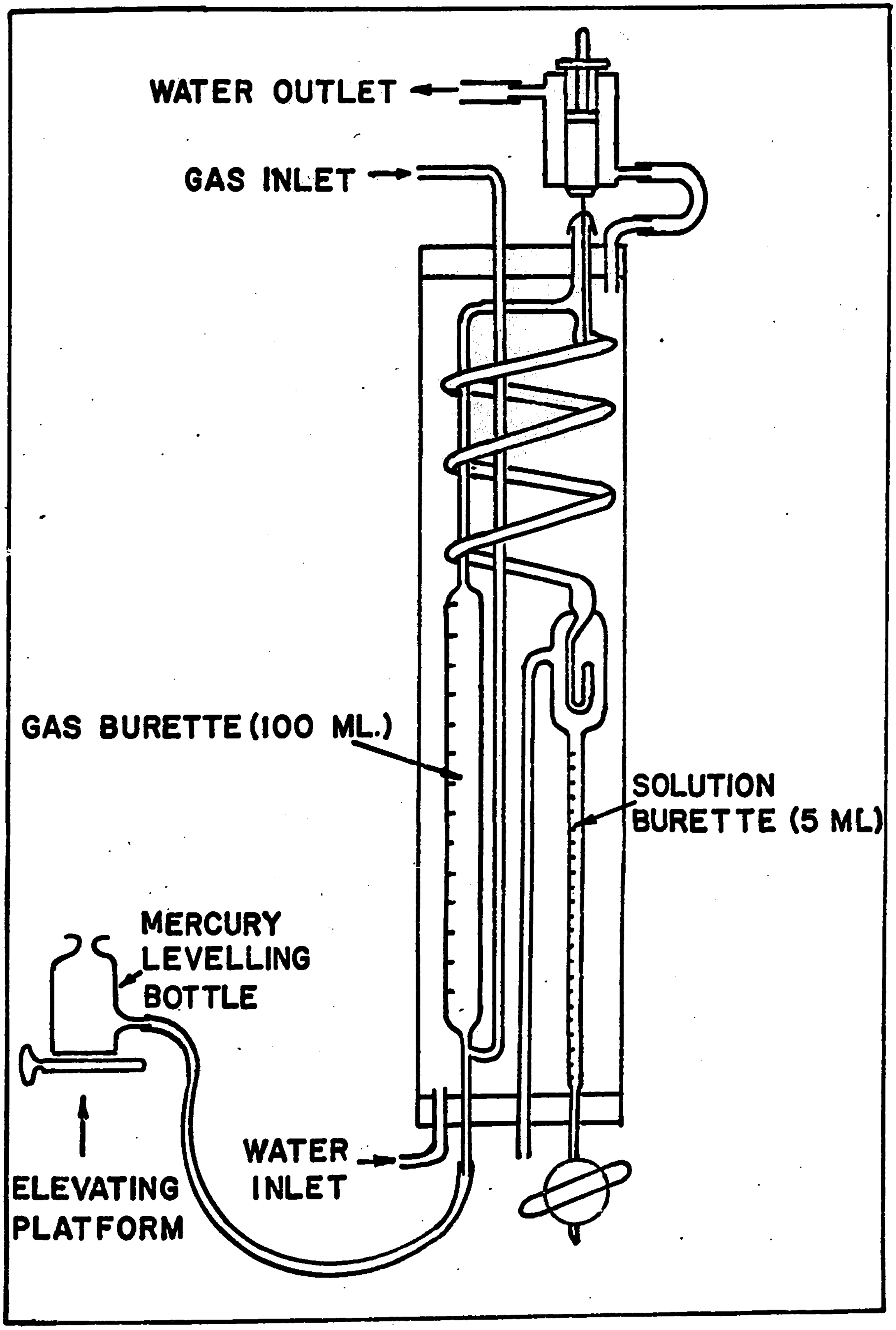

FIGURE 2-1. Solubility apparatus.

graduated in 0.1 ml subdivisions) was substantially bigger than the liquid burette (5 ml, graduated in 0.01 ml subdivisions). For the same reason, the rate of flow of deaerated solvent was adjusted to have enough time (about two hours) to enable the volume of the gas burette to be accurately read and to ensure saturation in the absorption spiral. The deaerated solvent was fed into the apparatus by means of a syringe pump supplied by the Harvard Apparatus Company, using a 10 ml gas-tight Hamilton syringe and motor speeds of 1/3, 1/5, 1/10, 1/20 and 1/30 r.p.m., the one being used depending on the temperature and the system under consideration. The rate of flow corresponding to a given motor speed was obtained by weighing the amount of distilled water collected from the syringe for a certain period of time and then converting to volume units from the density of water at the temperature of the calibration.

The required temperature was obtained by circulating a constant temperature (± 0.05°C) glycol-water solution, by means of a Standard Colora bath, through the jacket of the solubility apparatus and then through a jacket surrounding the syringe pump in order that the degassed liquid entered the solubility apparatus at the temperature of the experiment.

In some cases, especially at 0°C and 5°C, some leakage of solvent from around the piston of the syringe occured, in which case the flow of cooling fluid through the syringe jacket was stopped. Necessary corrections for the change in the density of the liquid were made in determining the right solvent flowrate.

The lowest temperatures (0 and 5°C) were obtained by using a refrigerating unit provided by Neslab Instruments. The temperature rise through the apparatus was observed by comparing the readings of two thermometers, one located at the entrance and the other at the exit of the jacket of the solubility apparatus. Adjustment of the heater setpoint in the temperature bath was made so that the desired temperature was the arithmetic mean of the input and output values. This difference in temperature was minimized by wrapping a transparent plastic film around the solubility apparatus thus decreasing the heat interchange with the surroundings.

In every case it was verified at the beginning of each run that the end of the syringe needle was touching the walls of the spiral so as to have a constant flowrate of liquid down the tube. If this was not done the pressure in the gas buret was not constant and tended to vary in a cycle equivalent to that for drop formation.

Volumes of solution accumulated along with volumes of gas absorbed were recorded for various periods of time and, since partial molar volumes were computed, the total time for each run was also registered.

Full details concerning the different steps followed in these experiments are presented by Cheng (13) and Buckley (11).

2-3. Properties of test fluids

The gases used here, n-propane and n-butane, were supplied by Matheson of Canada and had a specified minimum purity of 99.5% (instrument grade). The gas molar volumes for n-butane and n-propane at one atmosphere and the experimental temperature used in the calculation of solubility and their sources are presented in Table 2-1. Molar volumes for the compressed liquids at the same temperatures, utilized in the analysis of partial molar volumes, are also presented.

The normal hydrocarbons were supplied by Canadian Laboratory Supplies (Canlab). The hexane, heptane and octane were of the chromatoquality grade (99.0 mole % min.) and had lot analyses all above the minimum specification. The dodecane and hexadecane were specified olefin-free with a minimum purity of 99%.

The polar hydrocarbons were obtained from Fisher Scientific Company. The acetone and n-butane were of a certified 99% minimum purity. The chlorobenzene had lot analyses indicating a 0.2% of water and 0.1% of volatile matter.

Due to some uncertainty in the available results for densities of acetone and chlorobenzene, these values were measured in this laboratory with the help of a 50 ml pycnometer. These results seem to agree fairly well with the literature values as shown in Table 2-2.

TABLE 2-1

Gas name	Temp. (°C)	Normal Molar Volume ml/gmole	Liquid Molar Volume ml/gmole
n-butane	5	21981(15)	97.19(23)
	25	23757	100.55
	50	25908	106.06
	75	28026	113.74
n-propane	0	22000(16)	83.05
	25	23950	89.27
	50	26190	98.22

TABLE 2-2. Comparison of densities (gms/ml)

Temp. (°C)	Acetone			Chlorobenzene		
	expt.	lit.(19)	%dev.	expt.	lit.(20)	%dev.
0	0.81372	0.81392	0.0024	1.12798	1.12780	0.0590
25	0.78572	0.78612	0.0051	1.10163	1.10100	0.0572
50	0.75652	0.75820*	0.2090	1.07463	1.07380	0.0772

*Extrapolated

TABLE 2-3

liquid name	Temp. (°C)	density (gm/ml)	vapor pressure (mm Hg)
n-Hexane	5	0.6724(16)	58.894(16)
	25	0.6548	151.261
	50	0.6316	405.328
n-Heptane	5	0.6964	15.411
	25	0.6795	45.718
	50	0.6583	141.620
n-Octane	5	0.7148	4.043
	25	0.6985	13.976
	50	0.6784	50.355
n-Dodecane	5	0.7600	0.0162
	25	0.7452	0.1551
	50	0.7271	0.8334
n-Hexadecane	25	0.7670	0.00068
	50	0.7528	0.00119
n-Butanol	0	0.8242	1.117(19)
	5	0.8206	1.680
	25	0.8060	6.780
	50	0.7867	34.450
	75	0.7699	128.00
Acetone	0	0.8137*	70.80(17)
	25	0.7857	228.10
	50	0.7565	600.20
Chlorobenzene	0	1.1280	2.66 (18)
	25	1.1016	11.68
	50	1.0746	40.40

*Measured in this laboratory.

Densities and vapor pressures for all of these solvents as used in the calculations of solubilities are presented in Table 2-3.

2-4. Treatment of data

Solubility

In the determination of the Ostwald coefficient L, the different data points for volumes of vapor-free gas dissolved vs volumes of solution accumulated were fitted by least squares to obtain the best linear relation between them.

It was assumed that the liquid adjacent to the interface was readily saturated with the contacting gas, and that the gas adjacent to the interface was likewise saturated with vapor. For these conditions, Raoult's law was applied in estimating the solvent vapor pressure. The volume of the gas was measured at its partial pressure $p - p_1^o(1 - x_2)$, and upon application of the ideal gas law the corresponding volume for a total pressure p was found. With these considerations in mind, L was given by:

$$L = \frac{m \cdot V_1 \cdot p}{\theta z \{p - p_1(1 - x_2)\}} \qquad (2\text{-}12)$$

The calculations for L from (2-12) implied a trial-and-error procedure: initially x_2 was assumed equal to zero and a first estimate for L was obtained. With this value of L, x_2 was calculated and a new estimate for L was made. This was repeated until the difference between two successive values for L was sufficiently small.

Partial Molar Volumes

The Partial Molar Volumes were calculated from

$$\overline{V}_2 = \frac{\Delta V}{n_2} = \frac{(V_1 - \theta z)}{m \cdot V_1} \cdot \frac{760}{p} \cdot V_2 \qquad \text{(ml/g mole)} \qquad (2\text{-}13)$$

2-5. Experimental Results

The solubilities of n-butane at 5°C, 25°C and 50°C in hexane, heptane, octane, dodecane, hexadecane and n-butanol (also at 75°C for this liquid) are reported in Table 2-4 A both as Ostwald coefficients and mole fractions. In the same way, the solubilities of n-propane at 25°C in hexane and hexadecane, and at 0°C, 25°C and 50°C for n-butanol, acetone and chlorobenzene are presented in Table 2-4 B.

Experimental results for propane in hexane and hexadecane at 25°C were compared with literature values. For hexane, the comparison was very favorable, 0.5% higher than the result by Thompson and Gjaldbaeck (22) and 0.9% higher than the result by other workers in this laboratory (21). For hexadecane, the result was 2.9% higher than one presented earlier from this laboratory (21).

The partial molar volumes for butane and propane in the above mentioned solvents are presented in Table 2-5.

TABLE 2-4. Solubilities for butane and propane

liquid name	Temp. (°C)	Mole Fraction solubilities				L
		run #1	run #2	run #3	mean	mean
A. Gas in n-butane						
Hexane	5	0.7311	0.7299	0.7325	0.7312	466.70
	25	0.3784	0.3839	0.3845	0.3823	111.73
	50	0.2014	0.1997	0.2008	0.2006	47.67
Heptane	5	0.7926	0.8041	0.7864	0.7944	590.97
	25	0.4256	0.4278	0.4162	0.4232	118.21
	50	0.2143	0.2143	0.2135	0.2140	46.36
Octane	5	0.7988	0.8004	0.7966	0.7986	545.44
	25	0.4314	0.4330	0.4303	0.4316	110.32
	50	0.2196	0.2206	0.2195	0.2199	43.36
Dodecane	5	0.8162	0.8120	0.7987	0.8090	416.07
	25	0.4455	0.4413	0.4413	0.4427	83.30
	50	0.2369	0.2347	0.2351	0.2356	34.08
Hexadecane	25	0.4626	0.4581	0.4594	0.4600	68.82
	50	0.2448	0.2513	0.2494	0.2485	28.48
n-Butanol	5	0.3936	0.3985	0.3860	0.3927	157.38
	25	0.1420	0.1385	0.1424	0.1410	42.39
	50	0.0689	0.0684		0.0686	20.26
	75	0.0600	0.0600	0.0601	0.0600	18.59

TABLE 2-4. (cont'd)

liquid name	Temp. (°C)	Mole Fraction solubilities				L
		run #1	run #2	run #3	mean	mean
B. Gas is n-propane						
Hexane	25	0.1160	0.1168	0.1169	0.1166	24.01
Hexadecane	25	0.1358	0.1378	0.1374	0.1370	12.93
n-Butanol	0	0.0739	0.0735	0.0739	0.0738	18.60
	25	0.0372	0.0372	0.0372	0.0372	10.07
	50	0.0227	0.0225	0.0226	0.0226	6.43
Acetone	0	0.0538	0.0528	0.0530	0.0532	17.33
	25	0.0302	0.0304	0.0301	0.0302	10.09
	50	0.0207	0.0207	0.0201	0.0205	6.33
Chlorobenzene	0	0.1036	0.1032	0.1034	0.1034	25.43
	25	0.0573	0.0574	0.0563	0.0570	14.16
	50	0.0392	0.0401	0.0394	0.0396	9.12

TABLE 2-5. Partial Molar Volumes for butane and propane

liquid name	Temp. (^{o}C)	Partial Molar Volumes (ml/gmole)			
		run #1	run #2	run #3	mean
A. Gas is n-butane					
Hexane	5	89.8	83.1	84.4	85.8
	25	80.2	73.3	79.0	77.5
	50	96.1	98.3	75.1	89.8
Heptane	5	102.5	102.5	87.1	97.3
	25	106.5	105.8	96.3	102.9
	50	116.7	106.3	97.8	106.9
Octane	5	101.0	104.4	101.5	102.3
	25	103.1	103.0	97.7	101.2
	50	111.1	114.1	112.0	112.4
Dodecane	5	101.4	103.1	98.2	100.9
	25	99.5	94.9	96.7	97.0
	50	135.7	128.9	124.3	129.7
Hexadecane	25	116.0	111.8	109.4	112.4
	50	117.2	134.2	139.3	130.2
n-Butanol	5	99.3	111.6	100.8	103.9
	25	131.5	120.3	122.9	124.9
	50	179.1	179.5		178.8
	75	183.0	188.0	184.4	185.1

TABLE 2-5. (cont'd)

liquid name	Temp. (^oC)	Partial Molar Volumes (ml/gmole)			
		run #1	run #2	run #3	mean
B. Gas is n-propane					
Hexane	25	122.7	141.5	144.1	136.1
Hexadecane	25	179.8	195.2	188.2	187.7
n-Butanol	0	153.6	133.1	135.7	140.8
	25	220.4	238.7	222.9	227.3
	50	374.7	365.7	327.7	356.0
Acetone	0	137.2	127.1	125.8	130.0
	25	240.8	252.5	221.0	238.1
	50	582.6	602.6		592.3
Chlorobenzene	0	115.4	104.5	118.7	112.9
	25	148.1	172.2	152.9	157.7
	50	157.7	179.1		168.4

In some cases (propane-acetone and propane-chlorobenzene, at 50°C) high differences in the results for duplicate runs were found and abnormally high values discarded. The reason for these deviations is the result of the small volume expansion of the solution $(V_1 - \theta z)$ so that a small error in the determination of V_1, resulted in a significant difference in partial molar volumes.

2-6. Discussion

Analysis of experimental results

a. At the temperatures considered, butane is so soluble in the n-paraffins that in many cases it constitutes the major component of the solution. Hence, the normal considerations for gas solubilities in which the dissolved gas is dilute with respect to the solvent are not found in these particular butane solutions.

Hayduk and Cheng (12) showed that for a considerable number of dilute gases in n-hydrocarbons, the mole fraction solubility varies linearly with the number of carbon atoms of the solvent. This kind of plot was intended for butane as well as propane at 25°C (data for propane were obtained from this work as well as from reference 21) as shown by Figure 2-2. For comparison, ideal solubilities based on Raoult's law were also displayed (dotted lines in Figure 2-2). For propane at 25°C, $x^{i}_{C3} = 0.120$ as given by Thompson and Gjaldbaeck (22). For butane, x^{i}_{C4} was calculated from:

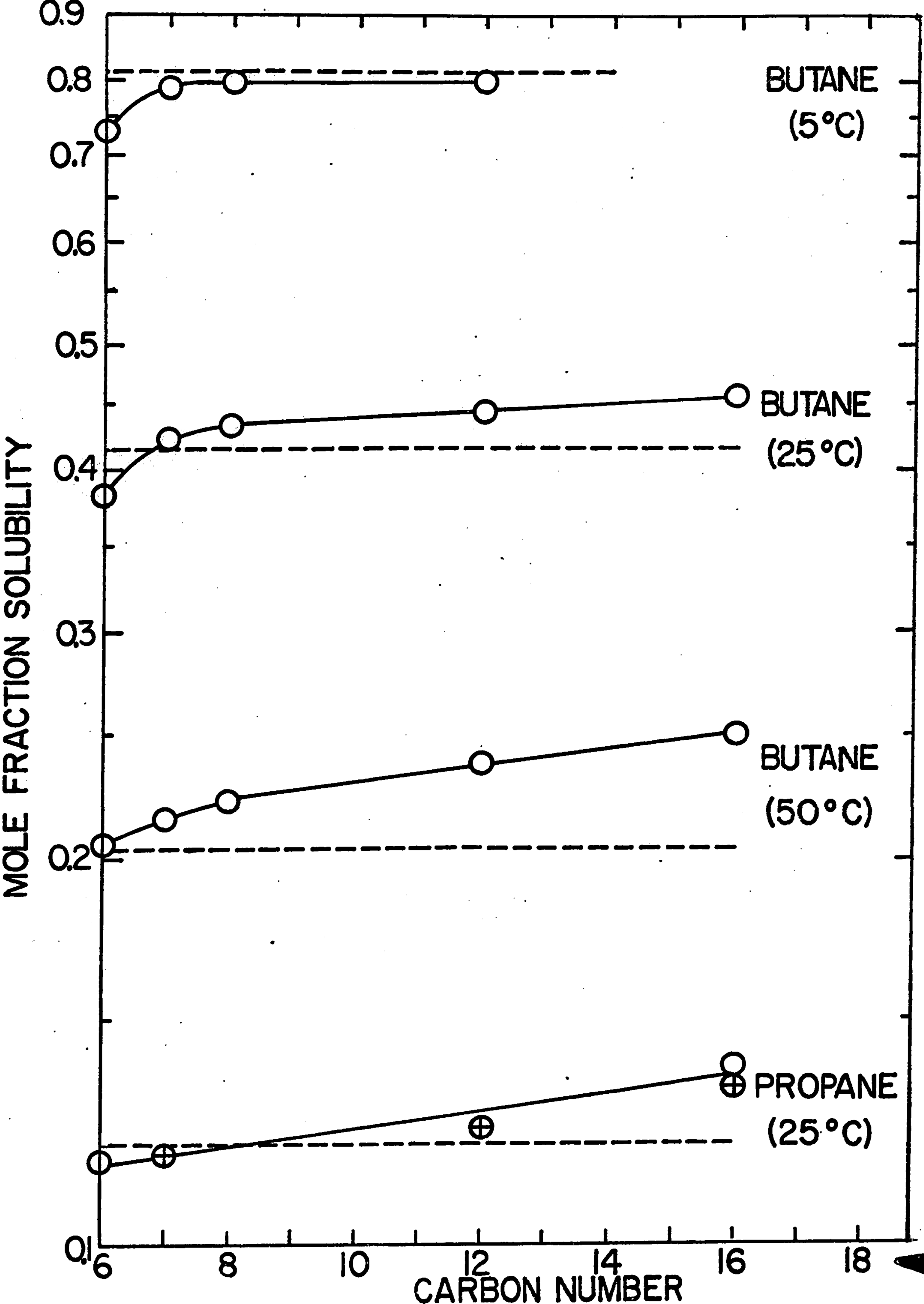

FIGURE 2-2. Mole fraction solubility vs number of carbon atoms of the solvent

$$p_{C4} = p^{0}_{C4} \cdot x^{i}_{C4} \longrightarrow x^{i}_{C4} = 1/p^{0}_{C4} \qquad (2\text{-}14)$$

Giving the results, $x^{i}_{C4} = 0.813$ at 5°C, $x^{i}_{C4} = 0.417$ at 25°C, and $x^{i}_{C4} = 0.204$ at 50°C. Data for vapor pressures of butane as used in Equation (2-14) were obtained from Jordan (24).

It can be observed that for C_8, C_{12} and C_{16} a linear relationship is observed but for C_7 and C_6 the slope changes. As the experimental temperature is increased, this behavior becomes less evident, as can be noticed by comparing the plots for 5°, 25°, and 50°C in Figure 2-2. This last result is not surprising since as the temperature increases, x_2 decreases and the system tends to follow the same patterns as the dilute gases.

Comparison between experimental and ideal solubilities indicate that they are of the same order of magnitude. In fact, specially for low temperatures (around 5°C), application of Equation (2-14) gives values of solubility which (C_6 excepted) are very close to the real ones, this being an indication that systems, such as C_4-C_8 and C_4-C_{12} are essentially ideal at these temperatures.

b. According to Hildebrand (2), when the mole fraction solubilities are plotted against the logaritms of the absolute temperatures, a linear plot is obtained. Similarly, for the solubility of n-butane in normal hydrocarbons, a linear relationship is obtained as shown by Figure 2-3. In this

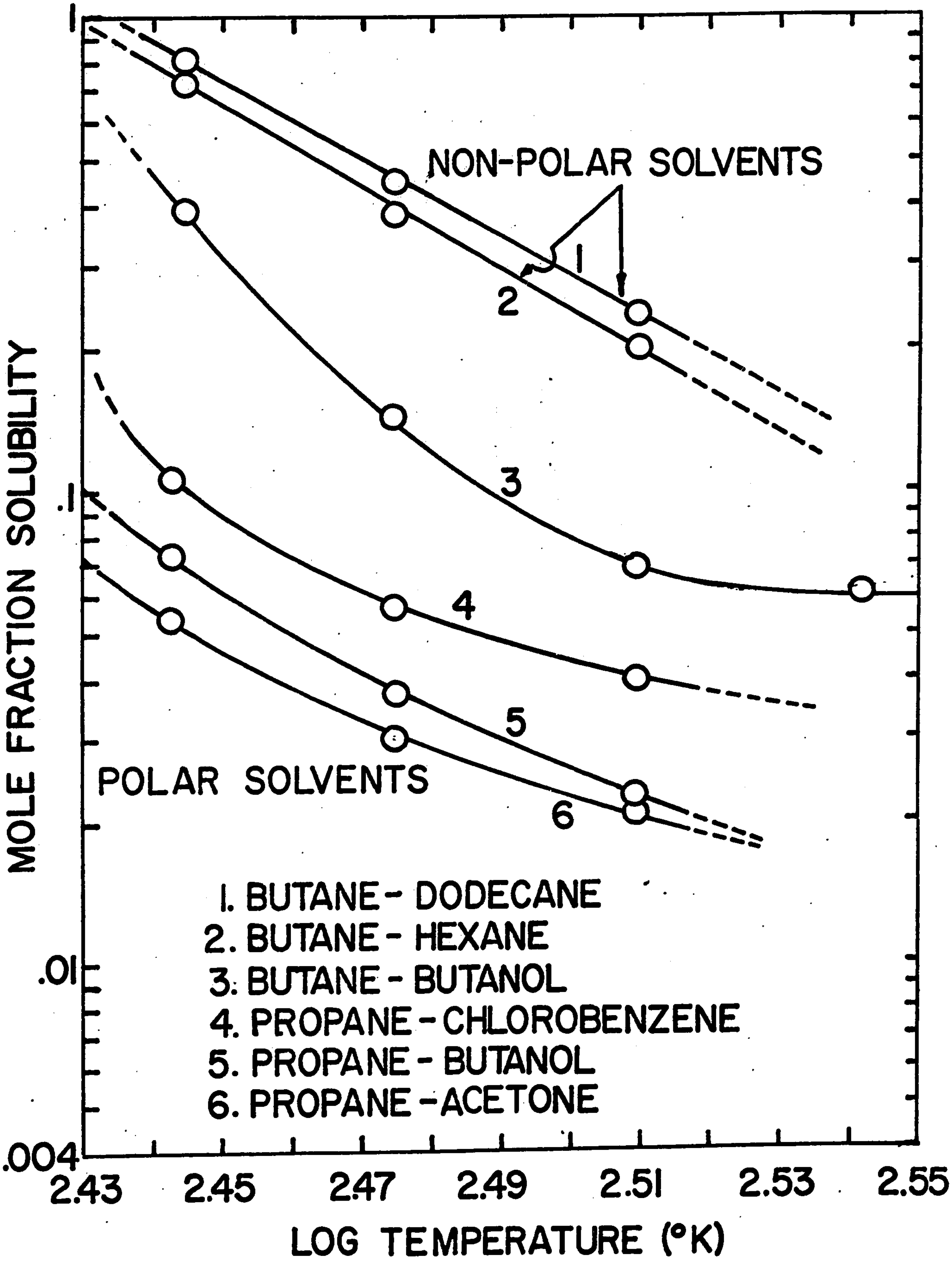

FIGURE 2-3. Mole fraction solubility vs logarithm absolute temperature (°K).

graph only data for C_4-C_6 and C_4-C_{12} are presented, but all the others follow the same pattern.

For butane dissolved in n-butanol, however, a curve is obtained which looks similar to those for inert gases dissolved in water, as obtained by Miller and Hildebrand (26), who tried to explain them in terms of hydrogen bondings and observed changes in the heat capacity of these solutions with respect to pure water. The influence of similar parameters in butanol solutions can only be speculated upon.

Finally, for propane dissolved in polar solvents a certain curvature is obtained, which might as well be somehow related to hydrogen bondings and solvent-solute associations. Curves for propane in acetone, n-butanol and chlorobenzene are shown in Figure 2-3.

c. Figure 2-4 represents a plot for the partial molar volumes of butane and propane in various polar and non-polar solvents. As a result of the high errors encountered in the determination of $\bar{V}_2$ it is just qualitative. For comparison, partial molar volumes for acetylene-chlorobenzene and acetylene-acetone, as obtained from Horiuti (27), are also presented (dotted lines in Figure 2-4). A few comments can be drawn from this graph:

1. $\bar{V}_2$ is nearly proportional to the temperature;
2. $\bar{V}_2$ increases with the number of carbon atoms, in normal hydrocarbons.

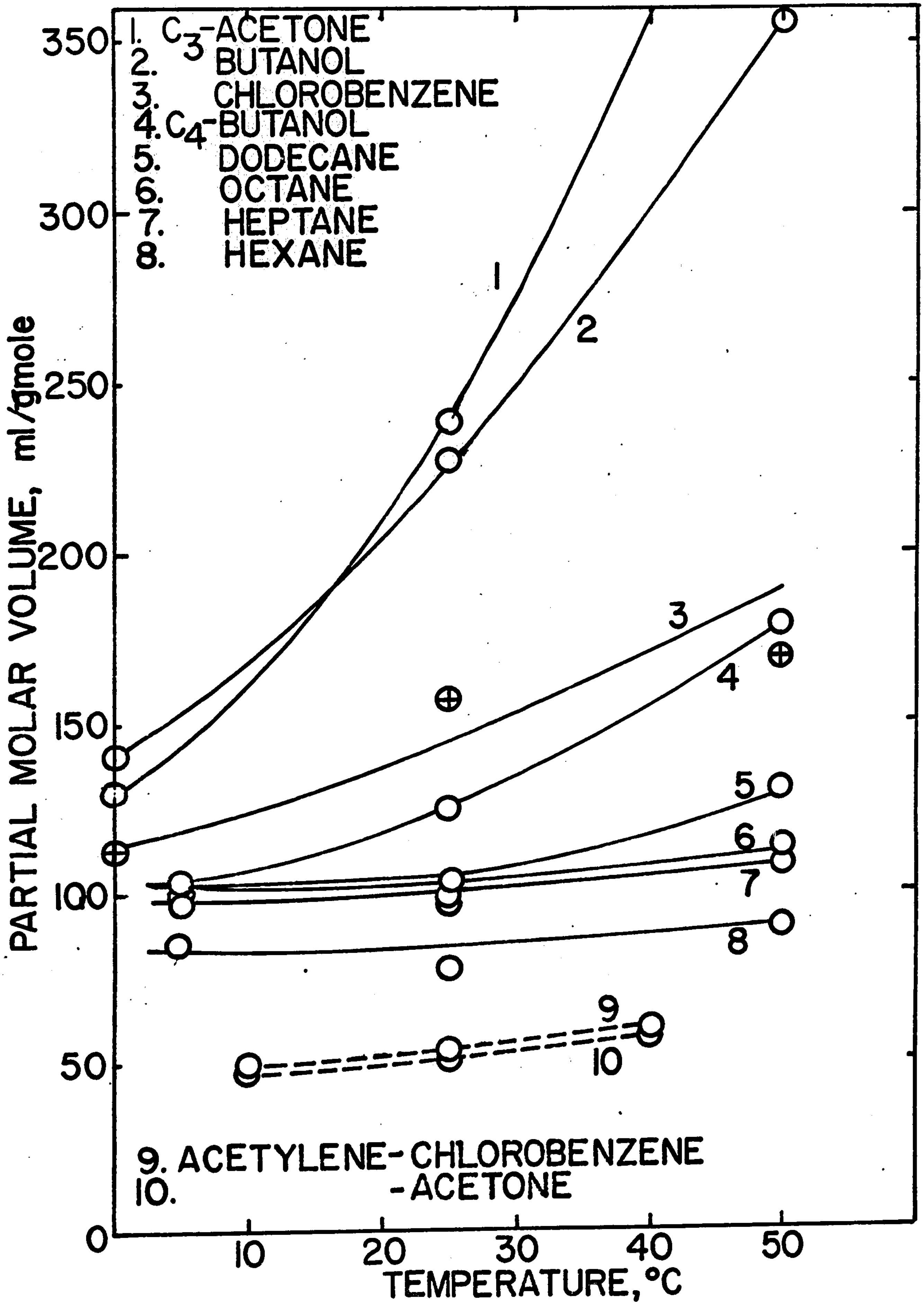

FIGURE 2-4. Partial molar volume of the solute vs Absolute Temperature (°K).

3. In general, values of $\overline{V}_2$ for both butane and propane are higher than the corresponding molar volumes at the normal boiling point (V_{b2}), i.e., 96.3 ml/gmole for butane (From Gallant (23)) and 74.5 ml/gmole for propane (from Reid and Sherwood (28)), this result being in agreement with that obtained earlier by Hildebrand and Scott (2) for various gas-liquid systems.

Values for $\overline{V}_2$ are also generally higher than the corresponding molar volumes of the compressed liquid at the experimental temperature (V_{21}) as given in Table 2-1.

The last mentioned authors try to interpret these volume expansions as the combined result of the kinetic energy of the solute and the smaller attraction which one of these solute molecules exerts upon the surrounding solvent molecules.

Exceptions for these expansions are presented by the systems butane-hexane, for which $\overline{V}_2$ is less than both V_{b2} and V_{21}, and butane-heptane, for which $\overline{V}_2$ is approximately equal to the corresponding V_{21} for the temperatures studied here. If this behavior is explained in terms of Hildebrand's interpretation, the intermolecular attractions butane-butane in the liquid phase, should be less than those for butane-hexane and approximately equal to those for butane-heptane. This result might in fact have some relation with the abnormally low solubilities observed for these two systems (Figure 2-2).

Selection of the best solubility plot

Two types of plots have been commonly used for linearly extrapolating gas solubilities to other temperatures: log x vs log T and log x vs 1/T. There appears to be no strong theoretical reason for choosing one or the other. It was therefore considered useful to statistically test these two methods of extrapolation using solubility data available in the literature. A list of the references used for this purpose is presented in Table 2-6. Densities of liquids and densities of gases as utilized in the convertion of data to mole fractions were obtained from references (20) and (29) respectively.

In Appendix I, the condensed results for the linearity test for the above mentioned data, is presented. The criteria for comparison are the percentage maximum absolute error, e,

$$e = 100\left| \{ (x_{exp} - x_{calc})/x_{calc} \} \right|_{max} \qquad (2\text{-}15)$$

And standard deviation, s ,

$$s = \sqrt{\sum (\log x_{exp} - \log x_{calc})^2/(N-1)} \qquad (2\text{-}16)$$

A few comments, based on the results from Appendix I and the considerable deviations encountered for some of the systems studied, should be made here:

a. For slightly polar solvents, such as fluorobenzene, bromobenzene, and toluene, values of e and s are relatively low for both log x vs log T and log x vs 1/T. Besides,

TABLE 2-6. Literature of the solubility data used in this work*

Solvent	gas, source of data
Acetone	CH_4(8,33)-CO_2(7,33)-O_2(7,33)-CO(7,33)-N_2(7,32,33)-He(33)-H_2(33)-C_2H_6(33)-Ne(33)-Ar(32,33)-Rn(33)-C_2H_4(33)-N_2O(33)-C_2H_2(27)-SO_2(27)
Aniline	CO_2(7,32,33)-CO(7,32)-Xe(33)-Rn(33)-N_2O(33)-H_2(32).
Bromobenzene	He(27)-Ne(27)-Ar(27)-Kr(27)-Xe(27).
n-Butanol	Ar(9,33)-N_2(9,33,34,35)-O_2(33,35)-C_2H_6(32)-CO(32).
Chlorobenzene	CO_2(32,7)-O_2(27)-CO(27)-N_2(27)-SO_2(33)-H_2(27)-CH_4(27)-C_2H_6(27)-C_2H_4(27)-N_2O(27)-C_2H_2(27)-He(30)-Ne(30)-Ar(30)-Kr(30)-Xe(30).
Chloroform	CO_2(7,32,33)-CO(7,32)-Rn(32)-H_2(33)-N_2O(33).
Cyclohexanol	CH_4(8)-He(33)-Ne(32)-Ar(33).
n-Ethanol	CH_4(8,33,34)-CO_2(38,33,36)-SO_2(33)-He(33)-Ne(33)-Ar(33)-Rn(33)-H_2(33)-N_2(8,32,33)-O_2(33)-C_2H_4(33)-N_2O(33)-NO(33).
Ethylene Glycol	Ar(9)-C_2H_6(9).
Fluorobenzene	He(30)-Ne(30)-Ar(30)-Kr(30)-Xe(30).
Iodobenzene	He(30)-Ne(30)-Ar(30)-Kr(30)-Xe(30).
Methanol	CH_4(8,33)-CO_2(32,33,36)-SO_2(33)-He(33)-Ne(33)-Ar(33), H_2(33)-N_2(33,34)-CO(32)-O_2(33)-N_2O(33)-NO(32).

TABLE 2-6. (cont'd)

Solvent	gas, source of data
Methyl Acetate	CO(33)-N_2(33)-H_2(33)-N_2O(33)-CH_4(33)-C_2H_2 (33)-C_2H_4(33)-C_2H_6(33)
Nitrobenzene	CO_2(7,32)-H_2(32)-NO(32)-He(32)-Ne(32)-Ar (32)-Kr(32), Xe(32)
i-Propanol	C_3H_8(36)-N_2(35)-O_2(35)-CO(32)
n-Propanol	Ar(9,32)-C_2H_6(9,32)-CO(9,32)
Toluene	He(30)-Ne(30)-Ar(30)-Kr(30)-Xe(30)-H_2(31)

*Data conversion carried out by using Equations (2-1) to (2-4).

when the respective graphs are made, it is found that the behavior of these solvents can be compared with that for non-polar solvents in that the solubilities can be extrapolated to a common point at the solvent critical temperature as found by Hayduk and Buckley (38).

b. There are (at least) three kinds of molecular interactions which might occur in gas-liquid solutions to complicate correlation and prediction of solubilities. These are:

   1. Polarity of the solvent. For example, nitrobenzene ($\mathcal{E}$ = 34.9, as compared with $\mathcal{E}$ = 2.37 for toluene) is a very polar solvent and chemical reactions are likely to occur.
   2. Hydrogen bonding or association of like solvent molecules. It occurs in solvents such as acetone and alcohols, with solutes such as C_2H_6 and CH_4 which act as weak proton acceptors (25).
   3. Hydrogen bonding or solvation of solvent-solute molecules. According to Prausnitz (25) it is present in solvents such as those mentioned in case 2 for solutes such as C_2H_4 and C_2H_2 (strong proton acceptors).

The above mentioned interactions being functions of temperature originate changes in the slopes of the solubility plots and decrease the tendency for the extrapolated lines to meet at the solvent critical temperature, as shown for n-ethanol in Figures 2-5 and 2-6.

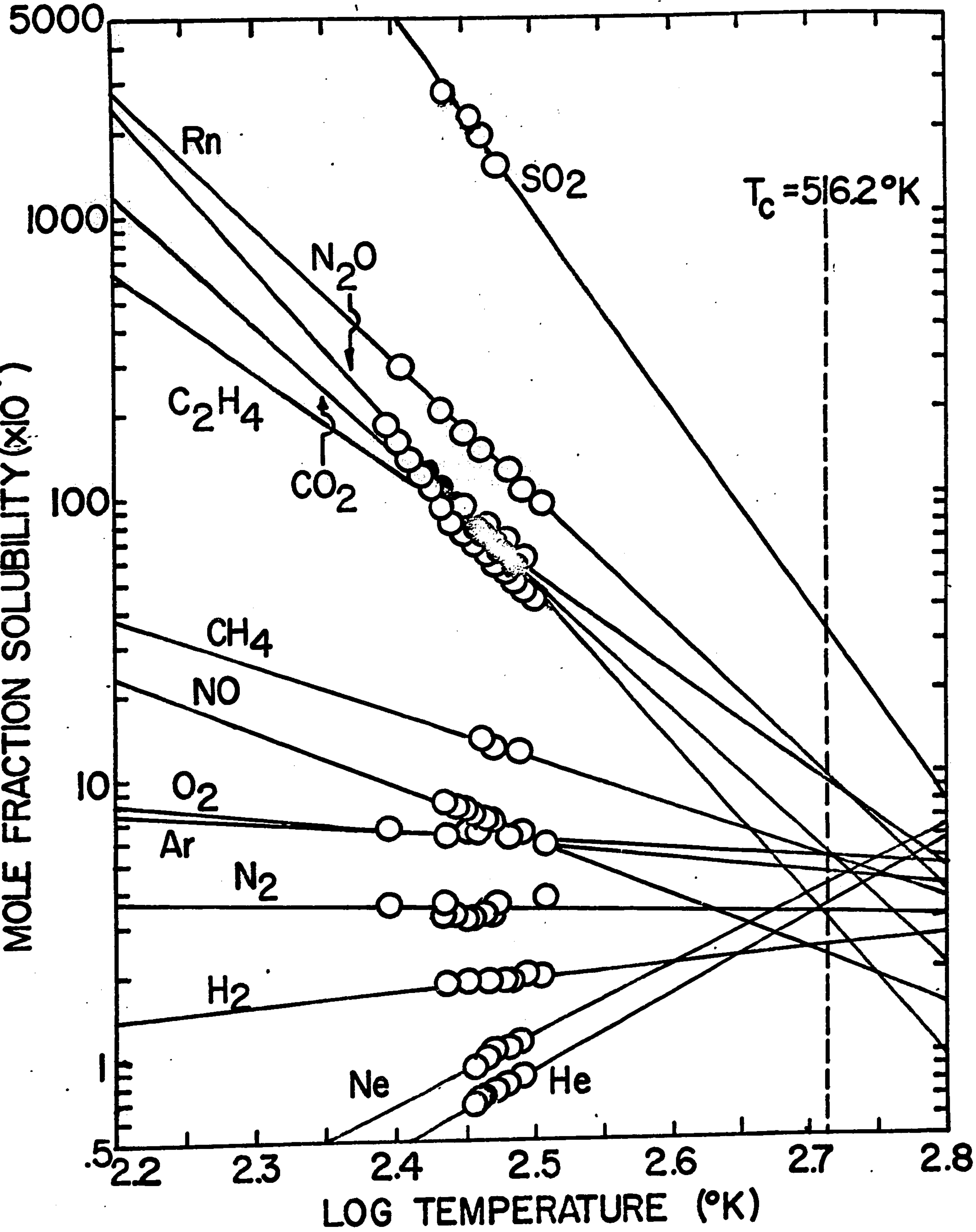

FIGURE 2-5. Mole Fraction Solubility for gases in n-ethanol vs log. Absolute Temperature (°K).

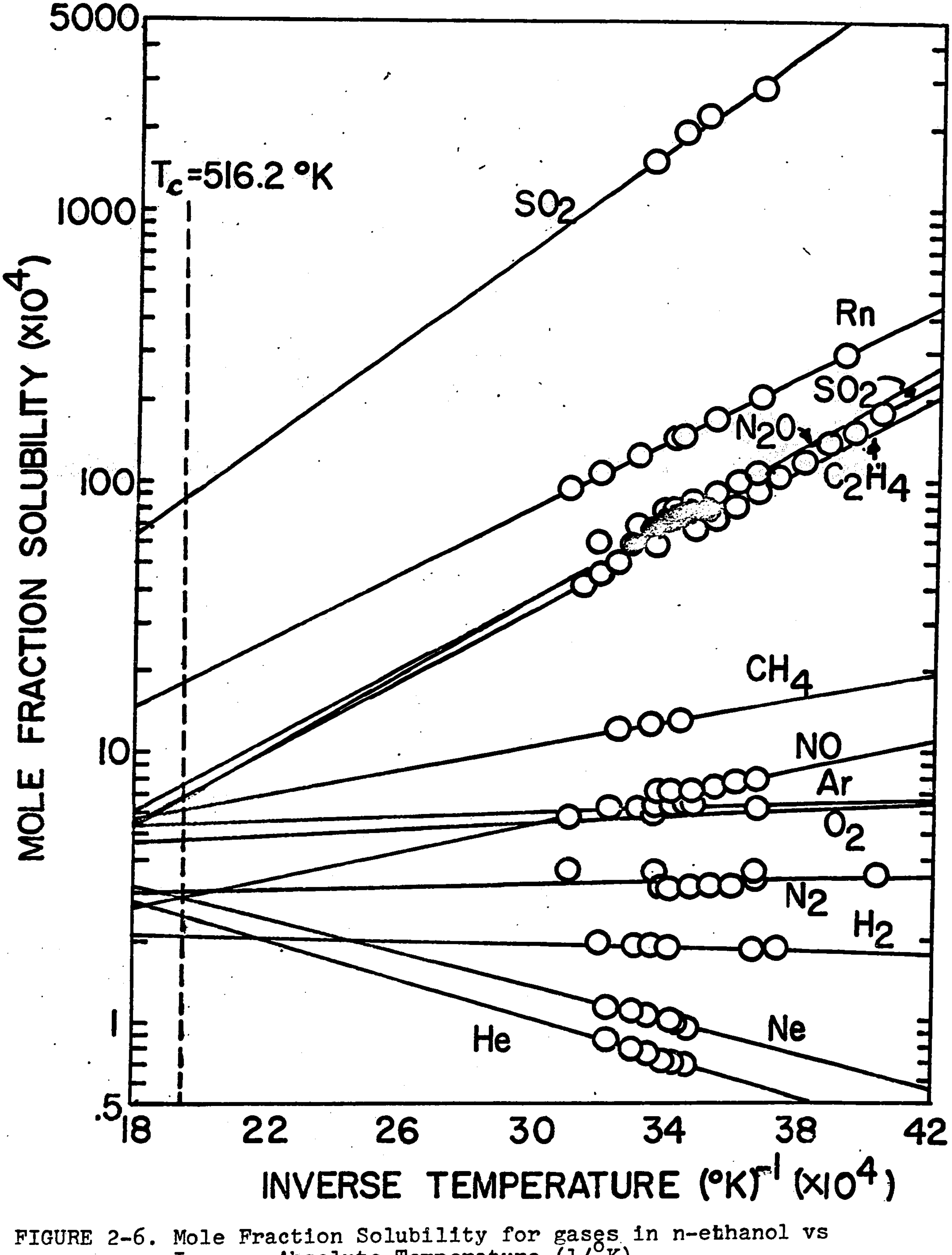

FIGURE 2-6. Mole Fraction Solubility for gases in n-ethanol vs Inverse Absolute Temperature (1/°K).

In general, analysis of the results in Appendix I suggests that the plots log x vs log T are only slightly more linear than those for log x vs 1/T; the different maximum errors and standard deviations are similar in both cases.

Selection of the best solubility correlation

Recently a correlation was developed by Hayduk and Buckley (38) to relate log x_2 with log T for non-polar solvents. It was based on the fact that the solubilities of all gases in a single solvent appeared to approach a constant value x_o (the reference solubility) as the solution temperature was increased towards the critical temperature of the solvent. A linear relationship was obtained between the solubility parameter for the solvent (δ_1) and the reference solubility x_o. One solubility point (x_1) at a temperature T_1 would permit calculation of the solubility (x_2) at a different temperature T_2:

$$\log \frac{x_2}{x_1} = \left(\log \frac{x_o}{x_1}\right) . \left(\frac{\log \frac{T_2}{T_1}}{\log \frac{T_c}{T_1}}\right) \qquad (2\text{-}17)$$

and

$$\log_{10} (10^4 x_o) = 2.265 - 0.134\delta_1 \qquad (2\text{-}18)$$

For polar solvents the tendency for the extrapolated lines to meet at the critical temperature was not as conclusive as it was for non-polar solvents. However, a correlation based on Equation (2-17) was attempted for polar solvents. At the same time, a correlation relating log x_2 and the inverse absolute temperature was also attempted for both polar and non polar solvents and its results compared with those obtained from the first mentioned correlation. The equation describing the second correlation is given by:

$$\log \frac{x_2}{x_1} = \left(\log \frac{x_o}{x_1}\right) \left(\frac{T_1/T_2}{T_1/T_c}\right) \tag{2-19}$$

The procedure followed for analysing the abilities of Equations (2-18) and (2-19) was as follows:

For a certain solvent, lines were fitted by the least squares technique to the data points for each gas and the different values for x_{oi} and x'_{oi} (theoretical solubilities for $\log T = \log T_c$ and for $1/T = 1/T_c$) calculated. The averages $\bar{x}_o$ and $\bar{x}'_o$ were obtained from:

$$\bar{x}_o = \sum_1^n x_{oi}/n \tag{2-20}$$

$$\bar{x}'_o = \sum_1^n x'_{oi}/n \tag{2-21}$$

The average reference solubilities for each solvent were used to calculate the least-mean-squares line through the solubility data for each gas. Maximum differences and standard deviations were calculated for each gas. Table 2-7 presents a list of these average reference solubilities for both polar and non-polar solvents.

For non-polar solvents, plots of log x vs log T tended to give somewhat smaller deviations from experimental solubilities than those for log x vs 1/T. The actual values are listed in Appendix II.

For butane, whose solubility was found to be extremely high in the non-polar (paraffin) solvents, a linear extrapolation to a common reference solubility at the solvent critical temperature was unsuccessful. The log x vs log T plot was essentially linear, however.

For polar solvents, in general, the consistency of solubility data for either log x - log T or log x - 1/T plots was not as good as for non-polar solvents. Between the two methods of plotting, however, using the appropriate average reference solubility, a log x - log T plot described the data appreciably better than the log x - 1/T plots, as can be observed from the tabulated values in Appendix III. Gross deviations were observed for the highly polar solvents, acetone and aniline. For these solvents, comparisons of solubility behavior with non-polar or moderately polar solvents were unsuccessful.

TABLE 2-7. Average reference solubilities for various solvents

Non Polar Solvents			Polar Solvents		
Solvent	$x_0(*10^4)$	$x_0'(*10^4)$	Solvent	$x_0(*10^4)$	$x_0'(*10^4)$
Perfluoroheptane	33.02	39.84	Acetone	14.04	23.91
Perfluorotributylamine	26.41	40.66	Aniline	2.64	6.68
Perfluoromethylcyclohexane	28.40	31.49	Bromobenzene	10.31	8.46
Isooctane	16.56	25.45	n-Butanol	7.30	8.78
$C-Cl_2-F-C-Cl-F_2$	21.82	30.48	Chlorobenzene	9.34	13.24
n-Hexane	16.98	18.03	Chloroform	13.02	19.95
n-Heptane	17.30	22.88	Cyclohexanol	9.51	6.15
n-Octane	19.68	18.21	n-Ethanol	7.21	13.99
n-Dodecane	20.85	23.25	Ethylene Glycol	5.29	1.09
n-Hexadecane	20.80	28.00	Fluorobenzene	11.02	12.49
Cyclohexane	17.31	18.80	Iodobenzene	17.59	10.55
Octadecane	12.62	29.06	Methanol	6.92	12.66
Cyclohexane	14.34	22.41	Methyl Acetate	12.52	19.54
Eicosane	12.23	28.28	Nitrobenzene	17.10	9.92
Docosane	14.58	28.68	i-Propanol	6.32	9.45
Carbon Tetrachloride	11.94	16.52	n-Propanol	5.95	8.02
Benzene	12.44	13.92	Toluene	11.43	8.74
Carbon Disulfide	8.35	8.38			

Correlation of average reference solubilities

For non-polar solvents, a linear relationship was obtained between the solubility parameter δ_1 and associated average reference solubility. The same correlation was tested for polar solvents.

Solubility parameters have been evaluated for many non-polar solvents. For polar solvents, however, only a few are available (3, 39) and for that reason they were evaluated from available information about the solvents, based on the definition:

$$\delta_1 = \frac{\Delta E}{V_1} = \sqrt{\frac{\Delta H - RT}{V_1}} \qquad (2\text{-}22)$$

If the heat of vaporization was not directly available, it was estimated in one of two ways:

1. From the method suggested by Hougen, Watson and Ragatz (10), based on the heats of vaporization of water at the reduced temperature considered. As an illustration, the calculations of ΔH at 25°C for chlorobenzene were as follows:

$$Sr\ T_c/T'_c = 0.905$$

with $T_c = 1138^\circ R$ for chlorobenzene

Where Sr is the slope of the vapor pressure plot of $\log p_1^o$ (water) and T'_c is the critical temperature of water. The factors Sr and Sr T_c/T_c' are tabulated in reference (10) for various solvents.

Finally, ΔH for chlorobenzene is given by:

$$\Delta H = \Delta H_w \cdot S_r \frac{T_c}{T_c'} \tag{2-23}$$

For $H_w = 18{,}800$ BTU/lb mole, the calculated heat of vaporization was 9,440 cal/gm mole.

2. For those solvents for which the Watson's heat of vaporization facter were not available, ΔH was calculated from the Clapeyron equation:

$$\Delta H = \frac{RT^2}{p_1^o} \frac{dp_1^o}{dT} \tag{2-24}$$

Values for p_1^o and dp_1^o/dT were obtained from the tabulations and graphs by Jordan (24).

Table 2-8 presents a list of these polar solubility parameters, along with some intermediate variables involved in the calculations.

A graph relating the reference solubilities (x_o) and the solubility parameters is presented in Figure 2-7, in which the slope of the straight line is the same as that for non-polar solvents.

The points for slightly polar solvents, such as toluene, chloroform, chlorobenzene, propanol and butanol seem to be very close to the line for non-polar solvents,

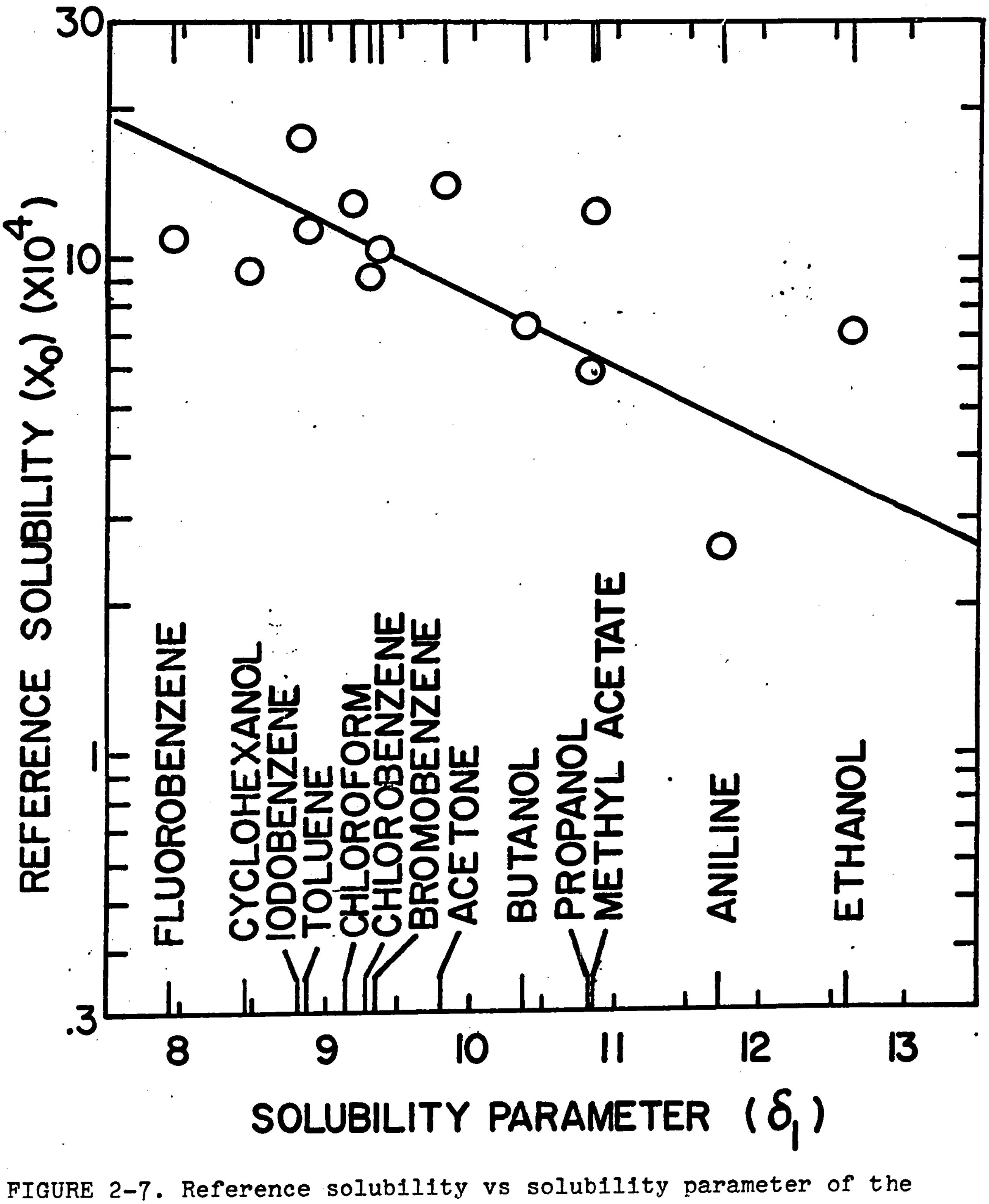

FIGURE 2-7. Reference solubility vs solubility parameter of the liquid.

TABLE 2-8. Solubility parameters for polar solvents at 25°C

liquid	p_1^o	dp/dT	ΔH	V_1	δ_1
Acetone					9.82
Aniline					11.73
Bromobenzene	4.4	0.245	9835	105.5	9.36
n-Butanol			10500	91.9	10.38
Chlorobenzene			9440	102.2	9.50
Chloroform			7410	80.7	9.19
Cyclohexanol	1.36	0.063	8180	106.1	8.46
n-Ethanol			9920	58.7	12.61
Fluorobenzene	77.0	2.86	6560	94.5	7.95
Iodobenzene	1.03	0.054	9260	111.9	8.80
Methanol			9050	40.7	14.41
Methyl Acetate	210.0	11.88	9990	79.9	10.85
Nitrobenzene					10.86
n-Propanol			9380	75.1	10.82
Toluene			9000	107.0	8.87

but points for solvents such as methanol, ethanol, acetone, aniline and methyl acetate are far from it.

Equation (2-18) seems to be useful for obtaining the reference solubilities of non-polar and slightly polar solvents as a function of the solubility parameter. When used for extrapolation of solubilities in moderately polar solvents, errors of up to 25% may be encountered.

CHAPTER 3

DIFFUSION

3-1. Theory

Diffusion is the transfer of a substance through any substance (gas, liquid or solid) resulting from a difference in concentration (or, more generally, chemical potential) at two regions in the substance (28).

For the case of diffusion in liquids, two different models have been proposed, one in which the molecules are arranged in a quasilattice (Eyring theory), the other in which they are in a state of maximum disorder (Hildebrand theory) (3, 40). According to the first, diffusion occurs by jumps of the length of the molecular diameter into 'lattice vacancies' or 'holes'; according to the other, diffusion consists of small irregular 'random walk' displacements.

Not enough evidence is as yet available to compare the validity of these two rival models; however, some observations from experimental results have been obtained (3, 41):

a. Experiments on the effect of temperature upon the rate of diffusion of I_2 in CCl_4 at constant volume and substitution of the resulting data into the equation derived from rate theory, gave jump lengths much smaller than the molecular diameters.

b. The factor $D\sigma^2$, D being the diffusion coefficient, and σ the molecular diameter, is virtually constant for CH_4, N_2, O_2, Ar, CF_4 and (isotopic) CCl_4. This observation, which has been found true only for relatively small molecules, indicates that $D \propto 1/\sigma^2$.

It can be said that the mechanism of diffusion in liquids is still unknown and only semiempirical correlations, based on known physical properties of the substances under consideration, are available to predict diffusion coefficients for gas-liquid and liquid-liquid systems.

Except for electrolytes, few experimental data are available on the effect of solute concentration on D, and most are for binary systems at low concentrations of the diffusing substance. The available empirical correlations are likewise restricted to dilute solutions. Some of these correlations are presented here:

a. Arnold correlation

Arnold (41) applied the classical kinetic theory for gas diffusivity to liquid systems. He presented an empirical correlation for diffusion as a function of molar volumes, molecular weights and abnormality factors for both solvent and solute, along with the viscocity of the solvent. Arnold's equation is, generally, not found useful in predicting diffusivities since the abnormality factors are usually not known in advance.

b. Wilke-Chang equation

Based on absolute reaction theory (molecules arranged in a quasilattice), Wilke and Chang (42) proposed the equation

$$D_{21} = 7.4 \cdot 10^{-8} \frac{(XM_1)^{1/2}T}{\mu V_2^{0.6}} \qquad (3\text{-}1)$$

Equation (3-1) gives reasonable prediction for many systems.

c. Scheibel correlation

Unless the association factors are known in advance (from experimental data), Equation (3-1) is not especially useful in predicting diffusivities of dissolved gases. Scheibel tried to eliminate the parameter X from the Wilke-Chang equation and came up with the expression (43):

$$D_{21} = 8.2 \cdot 10^{-8} \left\{ \frac{1 + (3V_2/V_1)^{2/3}}{\mu \cdot (V_2)^{1/3}} \right\} T \qquad (3\text{-}2)$$

The average absolute error with this correlation has been found to be less than 20% within the temperature range of 10 to 30°C (13).

d. Reddy equation

Reddy et al (44) replaced the association parameter of Wilke-Chang equation by retaining the exponent 1/3 for the solute molar volume, as done before by

Scheibel, and introducing the solvent molar volume, also raised to the same power:

$$D_{21} = K \frac{M_1^{\frac{1}{2}}\, T}{\mu\, (V_2)^{1/3} (V_1)^{1/3}} \qquad (3\text{-}3)$$

The value for the constant K in equation (3-3) depends on the ratio V_1/V_2 as follows:

when $V_1/V_2 \leqq 1.5$ $\quad K = 10 \cdot 10^{-8}$

when $V_1/V_2 > 1.5$ $\quad K = 8.5 \cdot 10^{-8}$

e. Lusis and Ratcliff equation

One more modification to Wilke-Chang equation was presented by Lusis and Ratcliff (45). It also eliminated the need for an association parameter:

$$D_{21} = 8.52 \cdot 10^{-8} \frac{T}{\mu_1} (V_1)^{-1/3} \left\{ 1.40 \left(\frac{V_1}{V_2}\right)^{1/3} + \left(\frac{V_2}{V_1}\right) \right\} \qquad (3\text{-}4)$$

This equation has also been tested mainly for liquid-liquid systems.

Effect of concentration on the diffusion coefficient

Available correlations for gas-liquid and liquid-liquid diffusivities are mainly restricted to dilute solutions. The diffusion coefficients in liquids, however, are functions of the concentration of the diffusing substance.

Most of the experimental techniques give only integrated values of the diffusion coefficients over the concentration range of the experiment. When this concentration range is small, and the solution is approximately ideal, those integral coefficients ($\bar{D}_{21}$) are approximately equal to the differential coefficients (D_{21}) or, mathematically:

$$D_{21} = \lim_{\Delta C \to 0} \bar{D}_{21} \qquad (3\text{-}5)$$

In general, however, since D_{21} is a function of concentration:

$$D_{21}\Big\}_{C=C_1} \neq D_{21}\Big\}_{C=C_2} \neq D_{21}\Big\}_{C=0} \qquad (3\text{-}6)$$

Since this work deals with liquid solutions, it is necessary to review the work done so far in regards to the relations between diffusion coefficients and concentrations of the diffusing substances.

Roseveare, Powell and Eyring (46) suggested that the quantity $D\mu/T$ should vary linearly with mole fraction for an ideal system:

$$\left.\frac{D_{21}\mu}{T}\right|_{x=x} = \left.\frac{D_{21}\mu}{T}\right|_{x=0} + x\left\{\left.\frac{D_{21}\mu}{T}\right|_{x=1} - \left.\frac{D_{21}\mu}{T}\right|_{x=0}\right\} \qquad (3\text{-}7)$$

If viscosity data are not available, then as an approximation, the diffusion coefficient at a given temperature, may be assumed to be linear with mole fraction (47):

$$D_{21}\Big|_{x=x} = D_{21}\Big|_{x=0} + x\left\{D_{21}\Big|_{x=1} - D_{21}\Big|_{x=0}\right\} \qquad (3\text{-}8)$$

Equations (3-7) and (3-8) have been tested by Caldwell and Babb (47) for the systems chlorobenzene-bromobenzene, toluene-chlorobenzene, and benzene-carbon tetrachloride, with excellent agreement. The same authors suggested that $D_{21}\big|_{x=0}$ and $D_{21}\big|_{x=1}$, in the absence of experimental values, could be calculated from the available semiempirical correlations. When dealing with gas-liquid systems, the error incurred by the use of these empirical equations could be higher than 20%.

Diffusivity was found to be an approximately linear function of concentration for many other systems, such as hexadecane-hexane, hexadecane-heptane, dodecane-hexane, and diphenyl-benzene, as shown in the paper by Dullien (48). For many other systems, such as hydrogen bonding solutes in carbon tetrachloride (49, 50), water and chloroform, and methyl ethyl ketone - CCl_4 (48), the functionality was not linear and Equations (3-8) and (3-9) did not apply for them.

To account for the deviations in non-ideal solutions, Roseveare, Powell and Eyring (46) inserted the activity of the solution into Equation (3-7):

$$\left\{\frac{\frac{D_{21}\mu}{T}\Big|_{x}}{\frac{d\ \ln a_2}{d\ \ln x_2}}\right\} = x\left\{\frac{D_{12}\mu}{T}\Big|_{x=1} - \frac{D_{21}\mu}{T}\Big|_{x=0}\right\} + \frac{D_{21}\mu}{T}\Big|_{x=0} \qquad (3\text{-}9)$$

For non ideal solutions in which the components associate, equation (3-9) was found not to be linear (51). In fact, when it was applied to systems containing an associated component and a non-polar component, the activity term 'overcorrected'. To eliminate this 'overcorrection', Rathbun and Babb (49) modified Equation (3-9) to the form:

$$D_{21} = (D_{12}^{o}\, x_2 + D_{21}^{o}\, x_1)(d \ln a/d \ln x)_{T,p}^{s} \qquad (3\text{-}10)$$

A value $s = 0.6$ was applied for systems containing an associated component and a non-polar component. A good agreement was found between the experimental diffusivity-mole fraction curves and those predicted from Equation (3-10).

Using the assumption that the activation energy for diffusion was linear in mole fraction, Vignes (52) derived the Equation:

$$\frac{D_{21}}{\alpha'} = (D_{21}^{o})^{x_1}\,(D_{12}^{o})^{x_2} \qquad (3\text{-}11)$$

where:

$$\alpha' = \frac{d \ln a_2}{d \ln x_2} \qquad (3\text{-}12)$$

Although the Vignes equation correlated existing binary data well for a number of systems, when used as a predictive equation, it also led to substantial error.

Equation (3-11) did not explicitly incorporate the effects of solution viscosity even although relationships between diffusion coefficient and viscosity emerged from statistical mechanical considerations.

Based on a relation between diffusivity and solvent viscosity, Leffler and Culliman (53) modified Vignes equation as follows:

$$\frac{D_{21}\mu}{\alpha'} = (D^{o}_{12}\mu_1)^{x_1}\,(D^{o}_{21}\mu_2)^{x_2} \qquad (3\text{-}13)$$

With binary n-alkane systems excepted, Equation (3-13) improved the correlation in all cases, except for acetone-carbon tetrachloride, in which substantial disagreement still existed. Equations (3-12) and (3-13) have the advantage over Equations (3-10) and (3-11) that activities are not required.

In summary, diffusion coefficients are functions of composition. For ideal binary systems, this functionality is linear, while for non-ideal systems, it may have different forms, incorporating the activities, viscosities and compositions of the components of the system.

Integral and differential diffusion coefficients

The diffusion cell method, as well as most of the other experimental techniques utilized to measure diffusion coefficients (54) are based on a finite difference in concentration of the diffusing substance as the gradient.

Consequently, since the diffusion coefficient is a function of concentration, an interpolated value for this coefficient over the concentration range is obtained. The diffusivities which have theoretical and practical significance are, however, the differential values, related to the integral values through the Equation (55, 56, 57):

$$\bar{D} = \frac{1}{C' - C''} \cdot \int_{C'}^{C''} D \cdot dc \qquad (3\text{-}14)$$

Within a concentration interval C' to C''.

For the capillary diffusion cell method utilized in this work, C' was essentially equal to zero, and the Equation (3-14) can be written in the form:

$$\bar{D} = \frac{1}{C} \cdot \int_{0}^{C} D \cdot dc \qquad (3\text{-}15)$$

The observation that when C is small $\bar{D} \approx D^{o}$ justifies the use of the aforesaid cell to measure diffusion coefficients at infinite dilution for slightly soluble gases, such as ethane (58) and methane (59). It is equally useful for moderately soluble gases, such as propane. For very soluble gases, such as n-butane, however, the integral diffusion coefficients cannot be assumed equal to the differential ones, and unless the functionality between D and C is known for the particular concentration interval, the diffusion coefficients are not meaningful.

For ideal systems for example, D may be expected to vary linearly with C, and for this particular case:

$$\bar{D} = D_{C/2} \tag{3-16}$$

When dealing with non-ideal systems, such as ethanol-benzene, aniline-benzene, aniline-carbon tetrachloride, benzyl alcohol-carbon tetrachloride (50), propanol-toluene (55), ethanol-chloroform, and acetone-benzene (48), the diffusion coefficients tend to change very rapidly for low concentrations of diffusing substance and $\bar{D}$ would be equal to D^o only for very low concentrations.

3-2. Properties of the test fluids

In section 2-3, the properties of the fluids utilized for both solubility and diffusion experiments were presented. In addition, available correlations to predict diffusion coefficients require the knowledge of viscosities for the solvent along with the molar volumes at the normal boiling point. Table 3-1 presents a list of these properties. Properties for n-heptane and n-octane, in which the diffusion coefficients of propane were measured earlier in this laboratory (59) are also presented.

TABLE 3-1. Viscosities (cp) at 25°C and molar volumes at the normal boiling point (ml/gmole)

fluid	viscosity (cp)		V_b (ml/gmole)	
Propane			74.5	(28)
Hexane	0.2969	(58)	140.6	*
Heptane	0.3929	(58)	162.0	(28)
Octane	0.5143	(58)	185.0	*
Hexadecane	3.0909	(58)	362.6	*
n-Butanol	2.582	(20)	103.6	*
Chlorobenzene	0.755	(47)	115.0	(28)

* Calculated from the Le Bas method (28).

3-3. Apparatus and Procedure

Diffusion Cell for propane

The diffusivities for propane were measured using the steady-state capillary cell method described elsewhere (11, 13, 60), which was considered suitable for moderately soluble gases. The diagram for this diffusion cell is presented in Figure 3-1.

Apart from the fact that a top capillary of larger diameter (1 mm) was used, the cells are the same as those utilized before (11, 60). This modification was necessary to guarantee a sufficiently long period of time for the experiments. When a top capillary of 0.508 mm was used by Bromfield (60), the experiments lasted for about 20 minutes, as compared to at least two hours in the present work. The longer period of time permitted a more accurate measurement of the movement of the liquid bead within the capillary.

Procedure

First, the diffusion cell was carefully washed with chromic acid, after with water, and finally with acetone. Then it was dried, its stopcocks properly greased and gas propane purged through it for about 15 minutes. At the same time liquid was degassed in the degassing apparatus described earlier by Cheng (13).

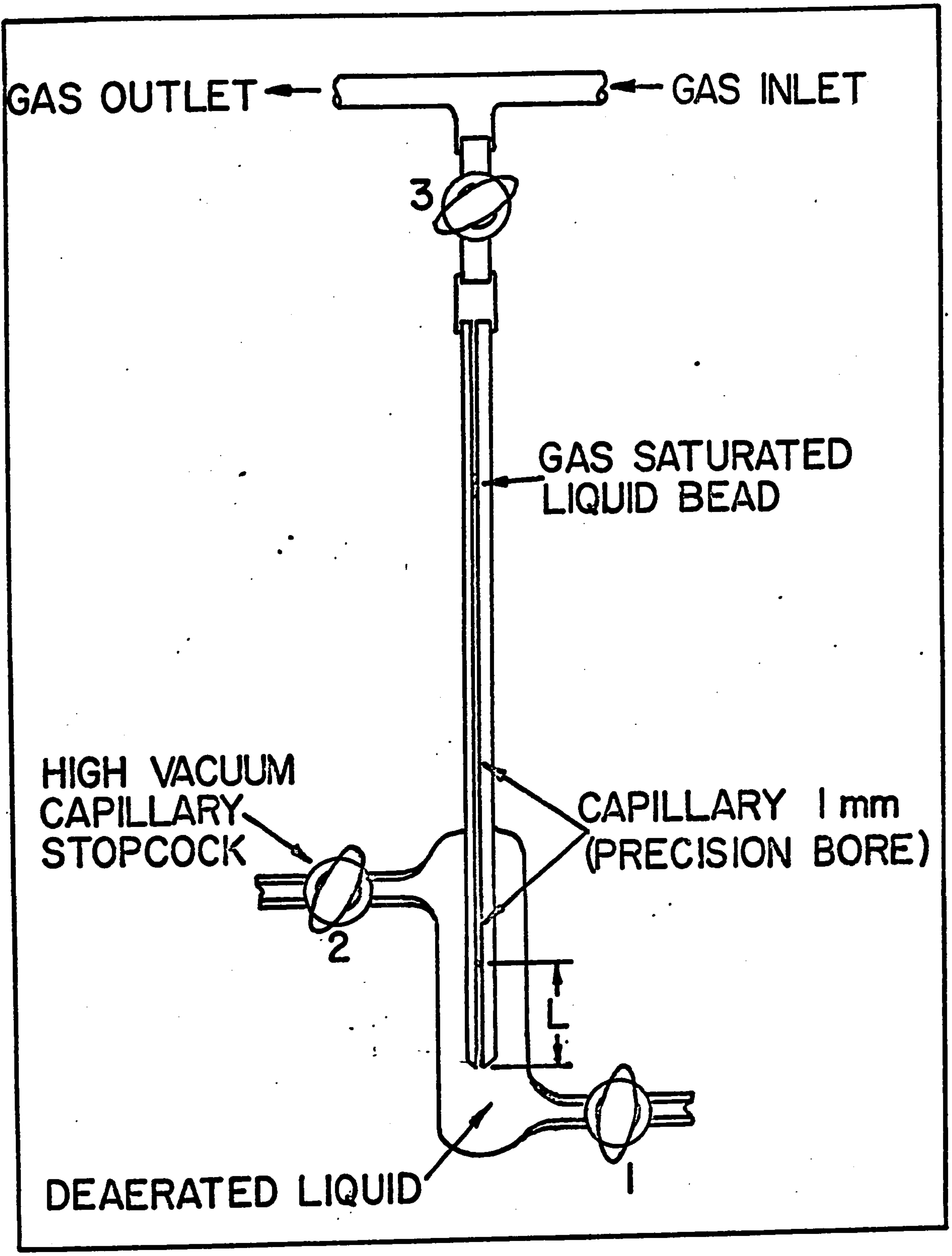

FIGURE 3-1. Diffusion cell.

Next, degassed liquid was allowed into the cell through stopcock 1 (Figure 3-1), at a rate sufficiently low as to eliminate any risk of air contamination. Once the cell was filled with liquid, about 40 mls of it were purged, and the required diffusion path length obtained by adjusting the pressure of the gas within the cell (succesively opening and closing stopcock 3).

Subsequently, the cell was immersed in the temperature bath and allowed to attain steady state during a period of time determined by Crank equation: $D\theta = 0.45 l^2$ (60). For the most viscous solvents, θ was relatively high (about 60 hours for n-butanol) as compared to that value for the less viscous solvents (approximately 20 hours for hexane).

Once steady state was achieved, a bead of saturated liquid was injected just above the mouth of the upper capillary. After one hour, or as soon as the speed of the bead was found constant, the bead position was determined with the help of a cathetometer, for various intervals of time. Because the solubilities of propane are higher than those for gases such as methane and ethane, the rate of bead movement was relatively high, even though propane diffusivities are lower.

3-4. Treatment of data

Reference (12) presents a derivation of the equations involved in the determination of the diffusion coefficients at infinite dilution for slightly soluble gases in liquids, from the capillary cell method.

The two basic equations for the determination of diffusion coefficients used:

$$D_{21} = (\frac{h}{60})(\frac{A_1}{A_2})(\frac{p_2}{\rho_1})(\frac{M_2}{V_2}) \frac{L}{\ln (\frac{L + w_{20}}{1 + x_{2L}})} \qquad (3\text{-}17)$$

and

$$w_{2L} = \frac{(\rho_1 L w_{20}) \mid (D_{21}\theta/L^2) - A_2/6 \mid}{8 \cdot \rho_1} \qquad (3\text{-}18)$$

For the calculation of D_{21} from Equation (3-17), w_{2L} was first assumed to be zero; then a value for w_{2L} was calculated from Equation (3-18) and utilized in Equation (3-17) to obtain a new value for D_{21}. This procedure was repeated until two successive values for D_{21} were essentially identical.

3-5. Experimental results and Discussion

Experimental results, together with those predicted from several empirical equations are presented in Table 3-2. Raw experimental data, from which these experimental results were computed, are given in Appendix IV.

In general, Wilke-Chang equation along with Ratcliff equation seemed to give the best predictions.

TABLE 3-2. Comparisons for diffusion coefficients for Propane in various solvents at 25°C.

Solvent	Diffusivity X 10^5 (cm^2/sec)				
	Mean expt.	Wilke-Chang (3-1)	Scheibel (3-2)	Reddy (3-3)	Ratcliff (3-4)
Hexane	4.48 4.68*	5.19	4.63	3.63	5.96
Heptane	4.30*	4.23	3.32	2.82	4.74
Octane	3.74*	3.45	2.41	2.20	3.80
Hexadecane	1.47	0.81	0.32	0.41	0.84
Chlorobenzene	2.75	2.33	1.97	1.74	2.19
n-Butanol	1.57	0.55	0.60	0.50	0.62

* Obtained earlier in this laboratory (59).

The Reddy equation predicted very low values and the Scheibel correlation predicted diffusivities quite different from the experimentally measured ones.

The result obtained for propane in hexane at 25°C is 4.5% lower than one obtained by Bromfield (59).

The diffusion coefficient for propane in acetone was measured a considerable number of times. The scattering of the different results did not permit a reliable value. In general, the more volatile the solvent, the higher the degree of scattering of the different results; solvents, such as hexane, gave scattered results, but after a sufficient number of runs, various results appeared to converge well towards the reported mean diffusion coefficient. This difficulty, encountered for highly volatile solvents, may have been concerned with keeping the gas phase completely saturated with solvent vapor for the duration of the experiment. The degree of saturation of the gas may have affected the volume of gas confined in the capillary.

The diffusivities of propane in various solvents at 25°C are shown in Figure 3-2 plotted as the logarithm of the diffusity versus the logarithm of the solvent viscosity. The points seem to lie on a straight line covering a wide range of viscosities. This result and that obtained for methane (11) appear to confirm the observation reported in an earlier paper by Hayduk and Cheng (58) that the diffusivity of a substance in a

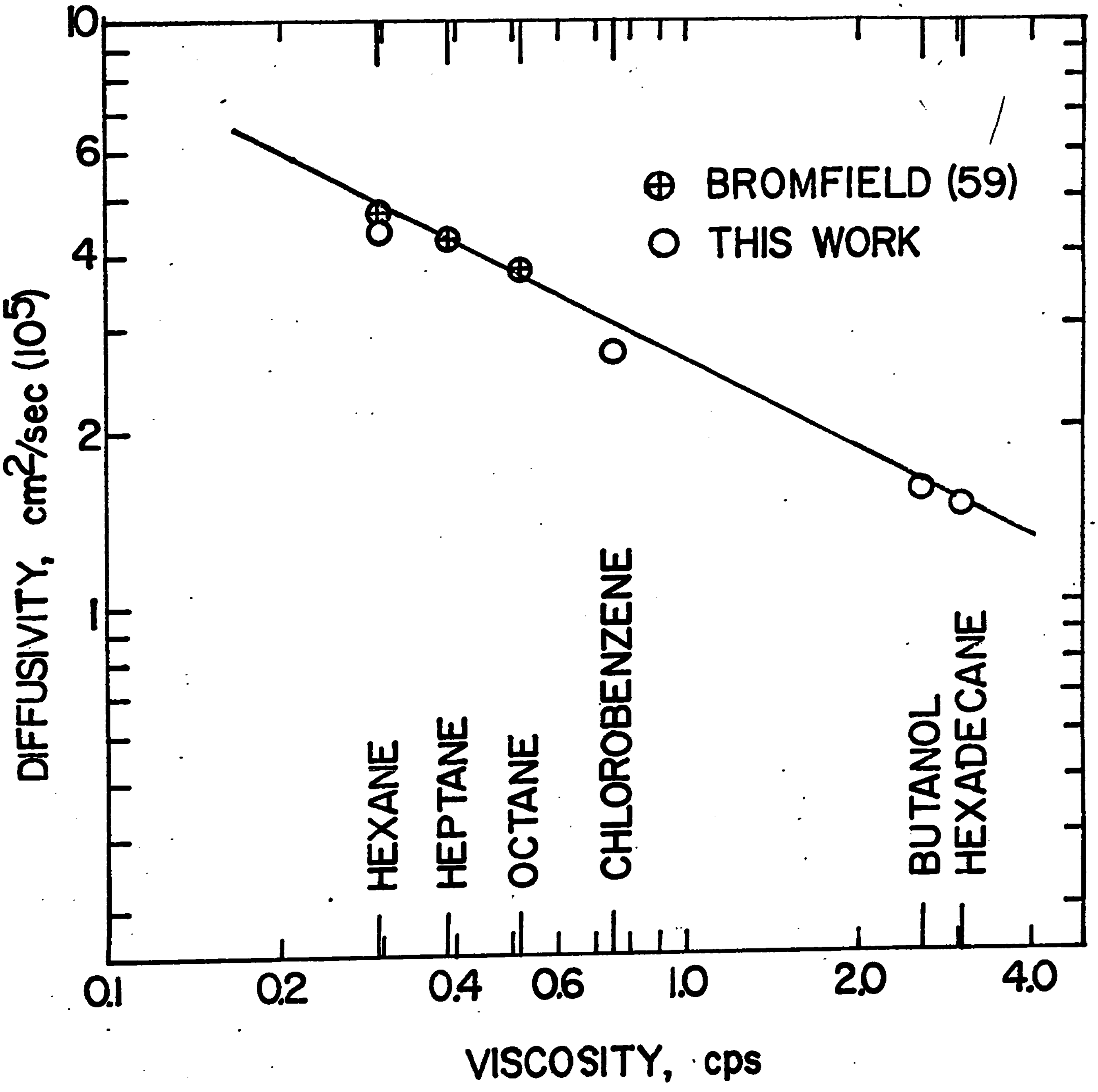

FIGURE 3-2. Diffusivity vs Viscosity of the Solvent.

non-associating solvent depends mainly on the solvent viscosity, in the form:

$$D = A\mu^{B} \qquad (3\text{-}19)$$

For this case, the value of B, the slope of the line, was found to be approximately 0.51 and $A = 2.6 \times 10^{-5}$, so that for diffusion of propane in non-associating solvents, Equation (3-19) becomes:

$$D = 2.6 \times 10^{-5}\mu^{0.51} \qquad (3\text{-}20)$$

Interpolations from this equation promise to give much better results than those obtained from the available empirical correlations. The diffusivity of propane in chlorobenzene gives a result which is slightly lower than that expected from Equation (3-20). This might be a result of the strong tendency of the chloride atoms (-Cl) to interact with surrounding hydrogens from the propane molecules.

According to Ross and Hildebrand (61), the product $D \cdot \sigma^2$ is constant for diffusion in a given solvent. This statement was verified for the diffusion of methane (11), ethane (58) and propane in normal hydrocarbons. The results of this test are presented in Table 3-3. Smoothed values for the molecular diameters (σ) were obtained from Witherspoon and Saraf (62).

TABLE 3-3. Tabulations for the product $D\sigma^2$ [$D(\times 10^5)$, cm^2/sec].

	Methane ($\sigma = 3.81$ Å)		Ethane ($\sigma = 4.52$ Å)		Propane ($\sigma = 5.15$ Å)	
Solvent	D (59)	$D\sigma^2$	D (58)	$D\sigma^2$	D	$D\sigma^2$
Hexane	8.64	125.4	5.79	118.3	4.48	118.8
Heptane	7.52	109.2	5.45	111.3	4.30*	104.0
Octane	6.49	94.2	4.57	93.4	3.74*	99.2
Dodecane	3.94	57.2	2.73	55.8		
Hexadecane	2.66	38.6	1.95	39.8	1.47	39.0

*Data obtained from Reference (60).

Analysis of the results in Table 3-3 seem to confirm the constancy of $D \cdot \sigma^2$ for the systems considered, thus indicating that the diffusion of methane, ethane and propane in normal hydrocarbons is mainly dependent on the size of the diffusing substance.

CHAPTER 4

CONCLUSIONS

Solubility

The solubility apparatus utilized here was found capable of producing data for the highly soluble gases n-butane and n-propane. Comparisons with literature values for the last mentioned gas gave differences less than 1% in hexane and about 3% in hexadecane.

Statistical analyses with a series of literature values for solubilities in polar solvents indicated that a plot of log x_2 versus log T was slightly more linear than versus 1/T, and it was observed that the plots of log x_2 vs log T showed greater tendency to intersect at log T_c than the log x_2 versus 1/T to meet at $1/T_c$.

A correlation relating log x_2 and log T was studied for both polar and non-polar solvents and compared with a similar correlation for log x_2 vs 1/T. For the majority of the cases studied, the first correlation was found to give better results. This correlation was recommended for use in predicting solubilities of non-polar solvents, as well as for slightly polar solvents.

The prediction of the reference solubilities for polar solvents as a function of their solubility parameters was not very successful. It was found that the use of apparent reference solubilities, obtained by interpolation from the line for non-polar solvents, gave reasonable results for solubilities, of gases in slightly polar solvents.

Predictions for the temperature coefficients of solubility in highly polar solvents, appeared to be complicated by molecular interactions.

Diffusion

Diffusivities for propane as calculated from available correlations widely deviated from the experimental results.

For the diffusion of propane, in non-associated solvents, a linear relationship between the logarithm of the solvent viscosity and the logarithm of the diffusion coefficient was found. Interpolations from this type of graphs, when available, promise to give much better results than the use of the more general correlations.

When interactions between the solvent and the diffusing solute appear, the resulting diffusion coefficient is usually lower than expected.

The constancy of the product $D \sigma^2$ was confirmed for the systems involving methane, ethane and propane.

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APPENDIX I

COMPARISONS OF LINEARITIES FOR POLAR SOLVENTS OF THE PLOTS:
LOGARITHM SOLUBILITY VS LOGARITHM TEMPERATURE,
AND
LOGARITHM SOLUBILITY VS INVERSE TEMPERATURE

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV. (LOG X VS. LOG T).	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV. (LOG X VS. 1/T)
SOLVENT : ACETONE.				
CH4	6.424	0.016734	4.277	0.012801
CO2	9.900	0.013975	13.899	0.032330
O2	5.852	0.011921	5.521	0.012090
CO	5.056	0.014375	4.993	0.014694
N2	4.904	0.012754	5.610	0.015443
HELIUM	0.469	0.001702	0.428	0.001544
H2	1.489	0.004017	3.341	0.000089
C2H6	0.276	0.000927	0.228	0.000737
NEON	1.177	0.004281	1.164	0.004184
ARGON	1.332	0.004175	1.257	0.003766
RADON	5.698	0.011191	4.228	0.008020
C2H4	0.577	0.001446	0.310	0.000902
C2H2	0.260	0.000619	1.100	0.002704
SO2	7.669	0.027795	8.426	0.003044
SOLVENT : ANILINE.				
CO2	2.327	0.005994	2.222	0.005703
CO	3.155	0.012941	2.953	0.012941
XENON	9.419	0.031863	8.860	0.030559
N2O	0.528	0.001249	0.500	0.001240
SOLVENT : BROMOBENZENE.				
HELIUM	5.626	0.021492	5.108	0.019509
NEON	1.618	0.005515	1.863	0.005843
ARGON	0.673	0.003366	0.844	0.003541
KRYPTON	0.570	0.001752	0.445	0.001542

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV. (LOG X VS. LOG T).	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV. (LOG X VS. 1/T)
SOLVENT : N-BUTANOL.				
ARGON	1.500	0.005788	1.463	0.005666
N2	3.107	0.005568	2.988	0.005281
O2	1.499	0.004247	1.378	0.003848
CO	2.295	0.008734	2.337	0.008896
N-C4H10	26.612	0.117260	24.894	0.105675
N-C3H8	5.630	0.021800	4.003	0.015382
SOLVENT : CHLOROBENZENE.				
CO2	3.000	0.007749	2.993	0.007733
O2	0.497	0.001554	0.605	0.001851
CO	3.056	0.009283	3.693	0.010734
N2	2.561	0.006855	3.636	0.010570
SO2	11.109	0.030052	6.507	0.017275
H2	0.680	0.001879	2.656	0.007829
CH4	5.568	0.015718	3.566	0.010459
C2H6	3.351	0.008185	1.156	0.003021
C2H4	4.103	0.009879	1.871	0.004497
N-C3H8	6.128	0.023791	4.852	0.018728
N2O	1.150	0.003673	0.646	0.001885
C2H2	3.338	0.008018	1.436	0.003662
HELIUM	1.955	0.007086	1.534	0.005369
NEON	1.023	0.003126	0.748	0.002820
ARGON	1.046	0.004181	1.068	0.004259
KRYPTON	0.640	0.002368	0.731	0.002392
SOLVENT : CHLOROFORM.				
CO2	14.304	0.017177	14.427	0.017528
CO	3.685	0.011113	3.685	0.011113
RADON	8.507	0.017108	6.435	0.012416
H2	1.622	0.005412	1.625	0.005457
N2O	4.694	0.012672	4.928	0.013244

SOLUTE	% ERROR (MAX).	MEAN ST. DEV.	% ERROR (MAX).	MEAN ST. DEV.
	(LOG X VS.	LOG T).	(LOG X VS.	1/T)
SOLVENT : CYCLOHEXANOL.				
HELIUM	0.161	0.000610	0.217	0.000821
NEON	0.353	0.001330	0.312	0.001174
ARGON	0.091	0.000342	0.082	0.000311
SOLVENT : N-ETHANOL.				
CH4	3.095	0.010562	3.092	0.010537
CO2	19.146	0.036417	17.382	0.035518
SO2	4.603	0.018437	5.021	0.020036
HELIUM	0.305	0.000875	0.298	0.000773
NEON	1.348	0.004667	1.284	0.004383
ARGON	0.507	0.001220	0.496	0.001187
RADON	3.885	0.011327	1.901	0.005529
H2	0.889	0.002531	0.973	0.002849
N2	7.754	0.026053	8.161	0.026128
O2	1.345	0.004762	1.148	0.003842
C2H4	1.209	0.002992	1.248	0.003353
N2O	7.799	0.013193	8.038	0.013862
NO	1.053	0.003572	0.973	0.003243
SOLVENT : FLUOROBENZENE.				
HELIUM	1.642	0.007473	1.341	0.006088
NEON	3.529	0.011115	3.745	0.011662
ARGON	0.963	0.002901	0.963	0.002916
KRYPTON	0.666	0.002051	0.763	0.002328
SOLVENT : IODOBENZENE.				
HELIUM	4.727	0.020396	4.126	0.018024
NEON	3.147	0.011299	3.552	0.011803

SOLUTE	% ERROR (MAX). (LOG X VS.	MEAN ST. DEV. LOG T).	% ERROR (MAX). (LOG X VS.	MEAN ST. DEV. 1/T)
ARGON	1.201	0.004649	1.304	0.005134
KRYPTON	0.453	0.001415	0.508	0.001547
SOLVENT : METHANOL.				
CH4	4.913	0.012292	4.865	0.012171
CO2	39.075	0.055312	39.129	0.055481
SO2	4.404	0.017055	4.850	0.018596
HELIUM	0.223	0.000794	0.120	0.000423
NEON	0.329	0.000860	0.293	0.000717
ARGON	0.581	0.001421	0.568	0.001385
N2	5.676	0.014743	5.661	0.014788
O2	1.195	0.004536	1.024	0.003699
N2O	2.069	0.005132	2.113	0.003508
NO	0.939	0.002988	1.014	0.003113
SOLVENT : METHYL ACETATE.				
CO	3.648	0.010978	3.790	0.012030
N2	1.691	0.005017	3.091	0.009502
H2	2.490	0.007446	0.903	0.002506
NO	0.097	0.000367	0.353	0.001325
CH4	5.363	0.015958	3.290	0.010378
C2H2	7.982	0.019049	9.058	0.021836
C2H4	0.541	0.001349	0.577	0.001283
C2H6	0.289	0.000785	0.339	0.001143
SOLVENT : NITROBENZENE.				
CO2	1.581	0.004273	1.592	0.004332
NO	1.571	0.004920	1.767	0.005749
HELIUM	9.004	0.041653	8.327	0.039236
NEON	7.461	0.027415	6.643	0.024573
ARGON	2.245	0.007018	2.138	0.006847

SOLUTE	% ERROR (MAX).	MEAN ST. DEV.	% ERROR (MAX).	MEAN ST. DEV.
	(LOG X VS.	LOG T).	(LOG X VS.	1/T)
KRYPTON	2.475	0.007545	2.496	0.007587
	SOLVENT : I-PROPANOL.			
N-C3H8	1.684	0.006174	0.716	0.002851
N2	0.994	0.003759	1.079	0.004085
O2	1.076	0.004072	0.976	0.003692
CO	0.725	0.002736	0.737	0.002782
	SOLVENT : N-PROPANOL.			
CO	0.355	0.001337	0.350	0.001318
	SOLVENT : TOLUENE.			
HELIUM	1.563	0.004890	1.973	0.005979
NEON	0.973	0.003021	1.293	0.004303
ARGON	0.248	0.000841	0.219	0.000695
KRYPTON	0.084	0.000315	0.199	0.000750
H2	0.180	0.000659	0.250	0.000973

APPENDIX II

SELECTION OF THE BEST SOLUBILITY CORRELATION FOR NON-POLAR SOLVENTS

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
SOLVENT : PERFLUORO-HEPTANE				
CARBON DIOXIDE	1.246	0.000994	2.148	0.001773
SULFUR HEXAFLUORIDE	1.807	0.001262	3.265	0.003462
METHANE	0.344	0.000267	0.361	0.000270
NITROGEN	0.358	0.000374	3.455	0.003341
HYDROGEN	0.289	0.000207	13.004	0.010309
HELIUM	0.597	0.000467	2.569	0.002227
SOLVENT : PERFLUOROTRIBUTYLAMINE				
SULFUR HEXAFLUORIDE	1.870	0.001760	3.167	0.003122
ETHANE	0.400	0.000379	1.207	0.001116
CARBON DIOXIDE	1.960	0.001601	1.610	0.001209
OXYGEN	0.762	0.000630	1.774	0.001588
ARGON	0.821	0.000690	1.965	0.001614
NITROGEN	0.608	0.000570	2.064	0.001801
SOLVENT : PERFLUOROMETHYLCYCLOHEXANE				
XEON	1.670	0.001712	4.301	0.004667
KRYPTON	2.233	0.002113	3.476	0.003071
ARGON	1.062	0.000868	1.060	0.000909
NEON	1.735	0.001735	4.848	0.005051
HELIUM	3.807	0.003623	7.526	0.007777
SOLVENT : ISO-OCTANE				
ETHANE	1.467	0.001374	1.590	0.001312
NITROUS OXIDE	2.980	0.002554	1.032	0.000882

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
XEON	3.024	0.003075	5.166	0.005076
SULFUR HEXAFLUORIDE	1.089	0.001086	2.306	0.001865
CARBON DIOXIDE	1.774	0.001574	0.447	0.000356
METHANE	1.242	0.001012	2.461	0.002137
CARBON TETRAFLUORIDE	1.277	0.001045	4.248	0.004088
OXYGEN	0.894	0.000834	1.502	0.001396
HYDROGEN	3.678	0.003733	12.463	0.011625
SOLVENT : C-CL2-F-C-CL-F2				
SULFUR HEXAFLUORIDE	5.754	0.004663	6.009	0.005694
ETHANE	2.638	0.002128	4.255	0.003562
CARBON DIOXIDE	4.910	0.003730	4.605	0.004080
XEON	1.895	0.001772	2.948	0.002763
C-2 F-6	1.223	0.001170	2.697	0.001997
CARBON TETRAFLUORIDE	1.334	0.001377	2.505	0.002633
METHANE	2.862	0.002095	1.583	0.001382
ARGON	0.757	0.000585	3.349	0.003152
NITROGEN	1.348	0.001075	5.117	0.004940
HYDROGEN	1.775	0.001550	9.340	0.007711
NEON	3.002	0.002259	9.160	0.006810
SOLVENT : N-HEXANE				
METHANE	2.765	0.002569	4.941	0.005369
KRYPTON	5.363	0.004878	8.355	0.007177
ARGON	1.884	0.001717	1.634	0.001474
NEON	4.194	0.004008	8.217	0.007746
HELIUM	2.533	0.002456	7.253	0.007619
SOLVENT : N-HEPTANE				
ETHANE	2.112	0.002168	5.007	0.005455
NITROUS OXIDE	1.888	0.001327	4.843	0.004193

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
SULFUR HEXAFLUORIDE	2.546	0.002128	0.779	0.000759
CARBON TETRAFLUORIDE	1.144	0.000912	5.009	0.003989
KRYPTON	1.192	0.001166	1.691	0.001702
METHANE	1.824	0.001709	2.505	0.002006
ARGON	0.681	0.000686	1.514	0.001394
HYDROGEN	1.886	0.001565	16.157	0.012207
NEON	2.740	0.002648	8.640	0.008856
HELIUM	0.972	0.000952	8.871	0.009040
SOLVENT : N-OCTANE				
KRYPTON	0.128	0.000165	2.031	0.002564
METHANE	2.050	0.002151	6.572	0.005861
ARGON	0.037	0.000048	0.795	0.001009
HYDROGEN	1.197	0.001108	5.008	0.004683
NEON	1.585	0.001681	3.262	0.003160
HELIUM	0.689	0.000645	5.324	0.005333
SOLVENT : N-DODECANE				
XENON	2.476	0.001969	4.439	0.004231
KRYPTON	1.356	0.001310	2.290	0.002259
METHANE	3.440	0.003586	0.856	0.000684
ARGON	0.757	0.000749	0.724	0.000704
NEON	3.570	0.003844	4.864	0.004851
HELIUM	0.816	0.000856	6.687	0.006548
SOLVENT : N-HEXADECANE				
METHANE	1.173	0.001108	0.929	0.000878
SOLVENT : METHYL CYCLOHEXANE				

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
XEON	2.491	0.002446	6.742	0.006921
SULFUR HEXAFLUORIDE	4.239	0.003735	1.469	0.001508
KRYPTON	3.183	0.003055	1.406	0.001369
ARGON	2.647	0.002649	3.268	0.003299
NEON	4.216	0.004350	5.295	0.005485
HELIUM	4.975	0.004679	5.118	0.005295
SOLVENT : OCTADECANE				
PROPANE	8.362	0.006521	13.123	0.007395
PROPYLENE	8.368	0.006038	12.097	0.006895
ETHANE	6.682	0.004744	2.174	0.002080
ETHYLENE	6.269	0.003672	2.168	0.001827
METHANE	9.789	0.007789	25.756	0.020855
SOLVENT : CYCLOHEXANE				
CYCLO PROPANE	0.935	0.000869	4.699	0.004484
PROPANE	2.778	0.002206	9.323	0.006861
CYCLO-C-4F-8	1.409	0.001417	2.204	0.001509
ETHANE	0.374	0.000372	1.635	0.001468
XENON	0.744	0.000821	1.968	0.002160
C-CL-F3	1.305	0.000860	0.417	0.000391
C3F8	1.485	0.001329	1.692	0.001590
CARBON DIOXIDE	0.629	0.000570	0.461	0.000379
SULFUR HEXAFLUORIDE	0.583	0.000601	1.050	0.001023
KRYPTON	2.454	0.002311	0.867	0.000810
C-2F-6	0.544	0.000497	2.861	0.002644
ARGON	1.850	0.001711	6.274	0.006179
CARBON TETRAFLUORIDE	1.828	0.001663	7.607	0.007402
NITROGEN	0.404	0.000338	3.897	0.003401
HYDROGEN	0.159	0.000157	4.570	0.004456
NEON	0.951	0.000871	5.081	0.004922
HELIUM	0.358	0.000341	11.015	0.011424

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV. (LOG X VS. LOG T).	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV. (LOG X VS. 1/T)
SOLVENT : EICOSANE				
PROPANE	3.118	0.002663	5.722	0.004975
PROPYLENE	2.536	0.002751	6.189	0.005196
ETHANE	2.661	0.001960	0.698	0.000685
ETHYLENE	3.280	0.002399	1.022	0.000924
METHANE	6.803	0.005294	17.148	0.016412
SOLVENT : DOCOSANE				
PROPANE	5.568	0.005624	10.123	0.007607
PROPYLENE	5.014	0.005009	9.034	0.008144
ETHANE	3.831	0.003791	2.336	0.002053
ETHYLENE	2.526	0.002588	4.556	0.002966
METHANE	10.674	0.007772	23.463	0.021114
SOLVENT : CARBON TETRACHLORIDE				
NITROUS OXIDE	1.345	0.001370	4.712	0.004104
ETHANE	1.188	0.000812	7.529	0.005981
ACETYLENE	2.679	0.002130	2.193	0.002133
ETHYLENE	0.773	0.000760	5.690	0.005257
SULFUR HEXAFLUORIDE	1.055	0.000980	1.112	0.001195
METHANE	3.385	0.002327	0.486	0.000457
ARGON	0.338	0.000327	3.471	0.002806
OXYGEN	0.429	0.000304	6.685	0.005857
CARBON MONOXIDE	1.225	0.001103	12.195	0.010846
NITROGEN	0.516	0.000379	13.838	0.012832
HYDROGEN	1.799	0.001342	13.445	0.012593
SOLVENT : TOLUENE				
ACETYLENE	9.586	0.007094	6.958	0.004783

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
XEON	1.563	0.001903	11.111	0.012582
ARGON	0.681	0.000592	0.290	0.000265
HYDROGEN	0.711	0.000605	7.296	0.007616
NEON	1.647	0.001474	8.871	0.008995
HELIUM	2.571	0.002089	7.340	0.007838

SOLVENT : BENZENE

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
NITROUS OXIDE	1.022	0.000794	5.942	0.005118
ACETYLENE	6.583	0.006086	0.992	0.000955
ETHANE	1.977	0.001445	10.080	0.008781
ETHYLENE	1.351	0.000928	7.389	0.006732
XENON	5.994	0.005524	10.375	0.008638
SULFUR HEXAFLUORIDE	0.638	0.000610	0.235	0.000224
METHANE	3.188	0.002452	3.335	0.002584
ARGON	0.608	0.000795	1.425	0.001855
OXYGEN	0.368	0.000310	3.815	0.003290
CARBON TETRAFLUORIDE	1.355	0.001442	4.658	0.004729
CARBON MONOXIDE	1.108	0.000852	3.817	0.003943
NITROGEN	1.223	0.001056	6.416	0.006224
HYDROGEN	1.817	0.001413	7.878	0.007962
HELIUM	2.791	0.002925	10.659	0.010248
NEON	7.802	0.007053	5.144	0.005208

SOLVENT : CARBON DISULFIDE

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
NITROUS OXIDE	6.990	0.005800	3.492	0.002843
CARBON DIOXIDE	2.204	0.001803	2.158	0.001775
METHANE	0.767	0.000729	0.263	0.000282
SULFUR HEXAFLUORIDE	0.384	0.000411	0.423	0.000484
ARGON	0.910	0.000712	3.572	0.003220
CARBON TETRAFLUORIDE	3.931	0.003306	7.700	0.006524
NITROGEN	0.684	0.000657	4.148	0.003937
HYDROGEN	0.328	0.000292	9.811	0.010765

APPENDIX III

SELECTION OF THE BEST SOLUBILITY CORRELATION FOR POLAR SOLVENTS

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
	SOLVENT : ACETONE.			
CH4	18.685	0.010163	42.487	0.026551
CO2	130.817	0.055513	48.736	0.036663
O2	29.034	0.014004	88.531	0.039998
CO	26.637	0.017403	71.946	0.045931
N2	30.963	0.016755	101.840	0.047163
C3H8	4.404	0.004581	6.946	0.005813
HELIUM	0.477	0.000454	5.143	0.004359
H2	12.682	0.010450	76.897	0.053824
C2H6	0.880	0.000583	0.673	0.000443
NEON	1.722	0.001519	6.241	0.005217
ARGON	3.404	0.001921	7.578	0.006092
RADON	11.774	0.005211	13.295	0.006638
C2H4	1.515	0.000871	0.522	0.000346
N2O	17.520	0.013268	17.326	0.012633
C2H2	4.678	0.003715	10.526	0.008828
SO2	13.774	0.014672	20.865	0.024058
	SOLVENT : ANILINE.			
CO2	6.311	0.003049	5.948	0.002938
CO	4.347	0.003805	6.447	0.004772
XENON	14.979	0.009887	18.247	0.011512
RADON	4.619	0.005851	7.462	0.009170
N2O	0.845	0.000491	0.981	0.000619
H2	2.123	0.002843	4.110	0.005480
	SOLVENT : BROMOBENZENE.			
HELIUM	1.393	0.000819	1.295	0.000762
NEON	2.248	0.001203	3.689	0.002315

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
ARGON	4.246	0.004147	6.643	0.005331
KRYPTON	0.881	0.000383	0.585	0.000355
XENON	0.105	0.000087	1.320	0.000387

SOLVENT : N-BUTANOL.

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
ARGON	4.459	0.004546	2.646	0.002823
N2	3.054	0.001676	6.592	0.005769
O2	3.772	0.003618	6.301	0.006580
CO	2.864	0.002768	2.419	0.002394
N-C3H8	10.992	0.010549	9.845	0.008192

SOLVENT : CHLOROBENZENE.

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
CO2	2.370	0.002645	2.792	0.002131
O2	0.706	0.000490	9.949	0.007781
CO	5.116	0.003325	23.486	0.017728
N2	3.269	0.002033	29.201	0.019273
SO2	35.409	0.024651	5.759	0.004887
H2	7.091	0.006209	25.353	0.019258
CH4	5.861	0.004466	8.598	0.005532
C2H6	5.128	0.002792	9.305	0.006271
C2H4	5.217	0.003273	9.612	0.005254
N-C3H8	6.276	0.006182	17.259	0.014251
N2O	6.861	0.004872	0.672	0.000553
C2H2	12.378	0.007383	1.784	0.001105
HELIUM	3.849	0.003519	11.672	0.010370
NEON	5.759	0.005218	7.043	0.006953
ARGON	1.237	0.001220	4.759	0.004295
KRYPTON	1.891	0.001633	1.102	0.001055
XENON	6.070	0.007280	11.839	0.013440

SOLVENT : CHLOROFORM.

SOLUTE	% ERROR (MAX).	MEAN ST. DEV.	% ERROR (MAX).	MEAN ST. DEV.
	(LOG X VS. LOG T).		(LOG X VS. 1/T)	
CO2	11.227	0.006676	10.745	0.006229
CO	4.142	0.003097	3.537	0.002953
RADON	31.718	0.014112	46.548	0.022630
H2	13.200	0.011709	23.118	0.020044
N2O	14.004	0.009276	13.126	0.008415
SOLVENT : CYCLOHEXANOL.				
CH4	1.533	0.002016	0.475	0.000612
HELIUM	1.399	0.001344	0.419	0.000402
NEON	0.371	0.000401	1.563	0.001493
ARGON	0.248	0.000231	0.880	0.000928
SOLVENT : N-ETHANOL.				
CH4	3.220	0.002794	5.937	0.005249
CO2	29.795	0.013601	29.179	0.014155
SO2	15.645	0.013681	22.173	0.020824
HELIUM	4.958	0.003809	15.602	0.012910
NEON	6.218	0.004056	16.137	0.012453
ARGON	2.544	0.002067	9.142	0.007056
RADON	9.996	0.005742	9.878	0.006583
H2	17.574	0.013451	40.975	0.029207
N2	25.276	0.012672	63.714	0.027728
O2	11.179	0.011056	31.849	0.030868
C2H4	4.700	0.003583	5.791	0.004386
N2O	8.342	0.006918	9.920	0.007885
NO	9.609	0.007564	16.507	0.013188
SOLVENT : FLUOROBENZENE.				
HELIUM	4.770	0.003794	13.924	0.012681
NEON	3.575	0.003342	11.630	0.010368
ARGON	1.035	0.000788	2.167	0.001632

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
KRYPTON	3.856	0.003470	6.017	0.005417
XENON	0.010	0.000013	1.994	0.002559
SOLVENT : IODOBENZENE.				
HELIUM	9.152	0.008029	5.284	0.005076
NEON	2.860	0.003089	5.828	0.006653
ARGON	2.971	0.002586	1.886	0.001701
KRYPTON	5.395	0.005139	0.690	0.000587
XENON	6.194	0.007994	5.942	0.007007
SOLVENT : METHANOL.				
CH4	7.203	0.005095	16.017	0.011069
CO2	21.728	0.013186	22.112	0.013082
SO2	13.890	0.011644	20.307	0.018511
HELIUM	6.335	0.004803	16.778	0.013865
NEON	7.095	0.005541	16.953	0.014126
ARGON	4.697	0.003918	11.344	0.009397
H2	0.531	0.000703	2.440	0.003247
N2	23.616	0.018902	56.449	0.041018
O2	18.470	0.018043	41.437	0.038820
N2O	1.999	0.001498	2.825	0.001823
NO	7.101	0.007146	14.480	0.014535
SOLVENT : METHYL ACETATE.				
CO	12.581	0.008872	39.932	0.030841
N2	10.547	0.007817	51.758	0.036457
H2	26.502	0.023423	78.675	0.059499
NO	0.255	0.000256	1.948	0.002127
CH4	10.754	0.006842	19.871	0.015966
C2H2	4.259	0.003346	10.596	0.009101
C2H4	4.406	0.003139	5.235	0.004217

SOLUTE	% ERROR (MAX). (LOG X VS. LOG T).	MEAN ST. DEV.	% ERROR (MAX). (LOG X VS. 1/T)	MEAN ST. DEV.
C2H6	4.064	0.003346	5.083	0.004237
SOLVENT : I-PROPANOL.				
N-C3H8	2.000	0.001873	12.796	0.010766
N2	2.013	0.002053	10.847	0.012071
O2	1.106	0.001048	7.156	0.007982
CO	0.773	0.000797	4.805	0.005125
SOLVENT : N-PROPANOL.				
ARGON	0.375	0.000490	1.307	0.001700
C2H6	0.623	0.000810	1.914	0.002451
CO	1.172	0.001185	4.632	0.005075
SOLVENT : TOLUENE.				
HELIUM	4.505	0.003537	2.553	0.002125
NEON	1.482	0.001113	3.067	0.002966
ARGON	2.456	0.002306	6.475	0.005749
KRYPTON	0.274	0.000277	5.950	0.006101
H2	2.529	0.002586	0.280	0.000273

APPENDIX IV

RAW EXPERIMENTAL DATA FOR DIFFUSIVITY

System: propane-hexane

Run #1		Run #2		Run #3	
p: 762.7 mm Hg l: 1.906 cm		p: 751.4 mm Hg l: 2.350 cm		p: 753.5 mm Hg l: 2.632 cm	
(min)	Bead position (cm)	(min)	Bead position (cm)	(min)	Bead position (cm)
20	0.632	25	0.619	20	0.470
80	2.560	40	1.008	40	0.942
110	3.491	60	1.525	60	1.414
140	4.399	80	2.003	80	1.900
180	5.580	100	2.483	100	2.339
200	6.148	125	3.078	120	2.810
220	6.700	140	3.411	180	4.121
h: 0.0303 cm/min w_{20}: 0.05152 w_{21}: 0.01640×10^{-3} D: 4.44×10^{-5} cm^2/sec		h: 0.0243 cm/min w_{20}: 0.05052 w_{21}: 0.00357×10^{-3} D: 4.38×10^{-5} cm^2/sec		h: 0.0229 cm/min w_{20}: 0.05071 w_{21}: 0.00250×10^{-3} D: 4.62×10^{-5} cm^2/sec	

RAW EXPERIMENTAL DATA FOR DIFFUSIVITY

System: propane-hexadecane

Run #1		Run #2		Run #3	
p: 753.3 mm Hg l: 2.217 cm		p: 760.0 mm Hg l: 3.337 cm		p: 760.0 mm Hg l: 2.521 cm	
(min)	Bead position (cm)	(min)	Bead position (cm)	(min)	Bead position (cm)
75	0.370	60	0.232	60	0.316
110	0.537	120	0.431	120	0.604
150	0.725	160	0.576	160	0.774
205	0.986	210	0.743	210	0.998
250	1.204	250	0.872	250	1.152
		300	1.027	300	1.349
h: 0.0048 cm/min w_{20}: 0.02969 w_{21}: 0.00513×10^{-3} D: 1.43×10^{-5} cm^2/sec		h: 0.0033 cm/min w_{20}: 0.02998 w_{21}: 0.01183×10^{-3} D: 1.51×10^{-5} cm^2/sec		h: 0.0043 cm/min w_{20}: 0.02998 w_{21}: 0.00623×10^{-3} D: 1.47×10^{-5} cm^2/sec	

System: propane-chlorobenzene

Run #1		Run #2		Run #3	
p: 762.3 mm Hg l: 3.106 cm		p: 761.4 mm Hg l: 2.528 cm		p: 761.1 mm Hg l: 3.103 cm	
(min)	Bead position (cm)	(min)	Bead position (cm)	(min)	Bead position (cm)
30	0.248	25	0.210	115	0.972
60	0.473	60	0.526	155	1.265
130	1.022	95	0.833	185	1.475
150	1.156	120	1.062	210	1.661
180	1.364	150	1.337	240	1.869
240	1.779	180	1.604	260	2.006
		200	1.785	290	2.225
h: 0.0073 cm/min w_{20}: 0.02285 w_{21}: 0.00587×10^{-3} D: 2.77×10^{-5} cm^2/sec		h: 0.009 cm/min w_{20}: 0.02282 w_{21}: 0.00348×10^{-3} D: 2.77×10^{-5} cm^2/sec		h: 0.0071 cm/min w_{20}: 0.02281 w_{21}: 0.00476×10^{-3} D: 2.70×10^{-5} cm^2/sec	

RAW EXPERIMENTAL DATA FOR DIFFUSIVITY

System: propane-n-butanol

Run #1		Run #2		Run #3	
p: 743.1 mm Hg l: 2.513 cm		p: 743.1 mm Hg l: 2.491 cm		p: 756.2 mm Hg l: 2.041 cm	
(min)	Bead position (cm)	(min)	Bead position (cm)	(min)	Bead position (cm)
160	0.555	160	0.551	30	0.150
210	0.751	210	0.734	60	0.291
250	0.884	250	0.834	90	0.434
290	1.022	290	1.004	120	0.558
310	1.125	310	1.118	150	0.684
370	1.339	370	1.319	180	0.820
				210	0.939
				240	1.081
h: 0.0037 cm/min w_{20}: 0.02176 w_{21}: 0.00283×10^{-3} D: 1.60×10^{-5} cm^2/sec		h: 0.0037 cm/min w_{20}: 0.02177 w_{21}: 0.00279×10^{-3} D: 1.58×10^{-5} cm^2/sec		h: 0.0044 cm/min w_{20}: 0.02216 w_{21}: 0.00265×10^{-3} D: 1.53×10^{-5} cm^2/sec	