ABSTRACT

The diffusivities of ethane in a series of normal paraffinic hydrocarbon liquids, hexane, heptane, octane, dodecane, and hexadecane, were measured using capillary diffusion cells. The diffusivities of ethane in various concentrations of mixed hexane-hexadecane solutions were also investigated.

In view of the lack of solubility data required for diffusivity calculations a solubility apparatus based on the principle of Morrison and Billet (1) was developed. The capability of the apparatus to produce accurate data was demonstrated by solubility determinations of systems for which reliable data were found in the literature. These systems included carbon dioxide-ethanol, ethane-benzene, and ethane-carbon tetrachloride. The solubilities of ethane in the normal paraffinic liquids, hexane, heptane, octane, dodecane, hexadecane, and in solutions of hexane and hexadecane, were also determined.

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NOMENCLATURE

A	a constant, for one gas in all paraffinic liquids
A_1	cross-sectional area of small capillary, $cm.^2$
A_{11}	abnormality factor for the solute
A_2	cross-sectional area of large capillary, $cm.^2$
A_{22}	abnormality factor for the solvent
BP	barometric pressure, atm.
C_N	number of carbon atoms in the paraffinic solvent molecule
C_{NO}	fictitious reference carbon number
D	diffusion coefficient, $cm.^2/sec.$
D_{12}	diffusion coefficient of component 1 in 2, $cm.^2/sec.$
D_{13}	diffusion coefficient of component 1 in 3, $cm.^2/sec.$
D_{1m}	effective binary diffusion coefficient of component 1 in solution m, $cm.^2/sec.$
D_{AB}	diffusion coefficient of component A in component B, $cm.^2/sec.$
F_{AB}	friction coefficient between components A and B
h	slope of graph: bead position vs. time
h_{ms}	slope of graph: volume of gas absorbed vs. three-component solution volume

h_s	slope of graph: volume of gas absorbed vs. solution volume
j_i	mass diffusion flux of component i with respect to a mass average velocity frame of reference
k	Boltzman's constant
L	diffusion path length, cm.
M_A	molecular weight of solute (or gas), g./g.-mole
M_B	molecular weight of solvent, g./g.-mole
M_m	mean molecular weight of multicomponent mixture, g./g.-mole
n_A	mass flux of solute A relative to stationary axis
n_B	mass flux of solvent B relative to stationary axis
n_i	mass flux of component i with respect to a fixed co-ordinate frame of reference
P_A	partial pressure of gas, atm. fraction
$\overset{o}{P}_B$	solvent vapor pressure, atm.
$\overset{o}{P}_{sol}$	solution vapor pressure, atm.

r	radius of diffusing molecule
R	gas constant
t	total time during which unsteady-state diffusion occurred, sec.
T	absolute temperature, $^{\circ}$K.
T_o	fictitious reference temperature, $^{\circ}$K.
v	mass average velocity vector
v_G	molar volume of gas at 25°C. and 1 atm., cm.^{3}/g.-mole
v_i	velocity vector of component i
v_k	volumetric shrinkage of gas and associated vapor, cm.^{3}/sec.-cm.^{2}
V	volume of solution contained in diffusion cell, cm.^{3}
V_2	partial molar volume of gas in solution, cm.^{3}/g.-mole
V_A	molal volume of solute at normal boiling points, cm.^{3}/g.-mole
V_B	molal volume of solvent, cm.^{3}/g.-mole
V_G	volume of gas absorbed, cm.^{3}
V_{GS}	volume occupied by dissolved gas in solution, cm.^{3}
V_L	volume of pure liquid, cm.^{3}
V_m	molal volume of the gas at temperature of the experiment and 1 atm.
V_{mL}	molal volume of solvent solution c.c./g.-mole

V_{PG}	partial molar volume of dissolved gas in solution c.c./g.-mole
V_{sol}	volume of solution, cm.^{3}
w_A	mass fraction of solute A in solution
w_{AL}	solute mass fraction in the bulk liquid
w_{AO}	solubility in mass fraction
x	association parameter
x_2	solubility of gas in mole fraction
x_2^i	ideal gas solubility in mole fraction
x_{25}	mole fraction solubility at 25°C.
x_A	solute mole fraction
x_h, x_{hd}	mole fraction of hexane, hexadecane respectively in the original solvent solution
x_h', x_{hd}'	mole fraction of hexane, hexadecane respectively in the solution after solution of ethane
x_0, x_{TO}	arbitrarily determined reference solubilities
x_T	mole fraction solubility at temperature T, °K.
X_2	mole fraction of component 2
X_3	mole fraction of component 3
z	direction of diffusion
ρ	total mass concentration of solution g./c.c.
ρ_{AL}	effective mass concentration of pure solute A in solution, g./c.c.

ρ_i	concentration expressed as mass of component i per unit volume
ρ_L	density of solvent, g./c.c.
μ, μ_B	viscosity of solvent, c.p.
μ_2	viscosity of component 2, c.p.
μ_3	viscosity of component 3, c.p.
μ_m	viscosity of multicomponent solution, c.p.
δ_1	solubility parameter of solvent
δ_2	solubility parameter of solute
γ	Ostwald coefficient

INTRODUCTION

Diffusion is the net transport of the molecules of a substance from one region to another within a single phase (gas, liquid, or solid). Transport may be as a result of thermal diffusion, pressure diffusion, "ordinary" molecular diffusion, convection or mixing. This research was concerned with isothermal isobaric molecular diffusion.

The diffusion coefficient, sometimes called the diffusivity, is the proportionality constant between the flux density of the diffusing species and the gradient of the appropriate potential, or driving force. Coefficients based on concentration gradients are now almost universally employed for both gas and liquid systems.

Molecular diffusion data for dissolved gases in liquids has always been of interest to chemical engineers for establishing a valid theory or model of the liquid state and in gas-liquid mass transfer calculations and associated correlations. Diffusion plays a very important rôle in chemical engineering particularly in the design of absorption equipment. At present, all the designing of such equipment is based on actual experimental absorption data. However, if the gas diffusivities in similar solvents, such as in a homologous series of hydrocarbons for example, were investigated, one might be able to arrive at a general expression for designing absorption equipment involving similar systems. A knowledge of the gas diffusivities in a homologous series of solvents could also be useful in testing or formulating predictive equations for diffusivity.

The objective of this research was to study the change in diffusivity of the hydrocarbon gas, ethane, in a homologous series of normal paraffins which included hexane, heptane, octane, dodecane and hexadecane. The diffusivities of ethane in a mixed liquid solvent, composed of various concentrations of hexane and hexadecane, were also measured. The particular solvent solution was chosen because of the wide range of solution viscosity and ethane diffusivity anticipated for it.

The calculation of diffusivities required a knowledge of the corresponding solubility data. The necessary data for the substances under study were not available in the literature. Consequently a solubility apparatus was developed, for obtaining fast and accurate solubility data.

Both diffusion and solubility measurements were performed at 25°C. and at atmospheric pressure. The temperature was chosen for two reasons. First, the related physical data, partial molar volume, density, and viscosity for example, were readily available at this temperature. Second, the experimental results obtained in this research could be compared with published literature values which were usually obtained at 25°C. A number of ethane solubility determinations were also made at 20°C. and 40°C.

In the write-up of this thesis, for the sake of convenience and clarity in presentation, each section has been divided into two sub-sections, the first dealing with diffusion, and the second with solubility.

LITERATURE SURVEY

I. Diffusion of Dissolved Gases in Liquids

Most methods used to determine diffusivities of dissolved gases in liquids involve either the measurement of the rate of transfer of gas into or out of a liquid phase or the determination of concentration gradients in a diffusing system. A summary of the various experimental methods for measuring the diffusion of dissolved gases in liquids may be found in the review by Himmelblau (2). In spite of the many ingeneous techniques devised extensive gas diffusivity data cannot be found in the literature. The main difficulties are the accurate measurement of the transfer rate of very small quantities of gas and the prevention of convection currents within the diffusion path caused by thermal or density variations. The steady-state capillary cell technique developed by Malik and Hayduk (3) seems to have overcome such difficulties. By using capillary tubes, mass transfer by convection was minimized if not entirely eliminated. By maintaining a constant temperature to within ±0.01°C. the density of the liquid in the diffusion cell could be kept essentially constant. Furthermore, the method was found to be relatively simple, the cells easy to construct, and the diffusivity data obtained reproducible. Hence, this technique was used in the present research.

II. Gas Solubility

Numerous methods for determining the solubility of gases in liquids are reported in the literature. A volumetric method, rather than an analytical one, was chosen for measuring the solubility because it appeared to be both rapid, and relatively accurate. A very comprehensive review (up to 1965) on the subject of gas solubility was made by Battino and Clever (4). An earlier review was made by Markham and Kobe (5). In general, physical methods of measuring gas solubilities may be divided into two broad classifications: saturation methods which involve the saturation of a degassed solvent by a gas, and extraction methods which involve the extraction of a gas from a saturated solution. Equilibrium between gas and liquid phases has been attained by shaking a mixture of the two, by flowing a film or stream of the liquid through the gas, by bubbling the gas through the liquid, or by flowing the gas over the liquid held stationary on some supported medium (as in gas-liquid partition chromatography). The determination of the quantities of the components in the gas and liquid phases has been carried out chemically, volumetrically by mass spectrometer, and by gas-liquid partition chromatography.

A very precise apparatus for determining gas solubilities was developed by Cook and Hansen (6, 7). The authors claimed reproducibility of ±0.1%. The apparatus was considered to be capable of determining gas solubility for a range of temperatures and pressures with a single charging. However, a drawback was that a good estimate of the solubility was required beforehand because the apparatus was designed for the absorption of 95% of the confined gas. Also the size of the solvent chamber had to be changed for different systems in accordance with different solubilities.

The apparatus designed by Morrison and Billet (1) utilized a thin film of liquid flowing through a spiral tube filled with gas, for achieving saturation. A modification of this design was used by Clever and co-workers (8-11), Saylor and Battino (12) and Koenig (13). An apparatus of this type has the advantage of simplicity in construction, requires only a relatively short time to complete one experimental run, and the solubility data obtained are reproducible to within ±0.5%. A disadvantage is that normally only one solubility determination at one temperature and pressure can be obtained with a single charging of the apparatus.

Other solubility apparatus employing a volumetric method of measurement include those of Ben-Naim and Baer (14) who used a magnetic stirrer to aid in the dissolution of the gas, Scholander (15) who developed the microgasometric technique (using small samples and fine capillaries), Thomsen and Gjaldback (16), Horiuti (17), and many others. Invariably, practically all the volumetric methods of determining gas solubilities described in the literature require an apparatus which is either difficult to construct, cumbersome to operate, requires many precautions, or is time consuming. In this work all these factors have been taken into consideration. Certainly, the probable causes of error which contributes to the discrepancies between published values in literature, often large, must also be considered. These are the result of one or more of the following: (a) failure to attain equilibrium, (b) failure to completely degas the solvent (c) failure to ascertain the true amount of gas dissolved, (d) failure to ascertain the true amount of solvent used, and (e) failure to make certain that the transfer of gas from a primary container to the apparatus does not involve contamination.

THEORY

I. Diffusion of Dissolved Gases in Liquids

The process of mass transfer of a gas through a liquid consists of two consecutive steps, the dissolution of the gas in the liquid, and the travel of the dissolved gas molecules through the liquid. The diffusion of dissolved gases is concerned with the latter step. Dissolved gases form a special class of molecules usually small in size, in the broad category of diffusion. The term 'dissolved gases' refers to those gases which are for practical purposes noncondensable at the temperature and pressure of interest, although not necessarily gases above their critical points.

As a result of our limited understanding of the liquid state no confirmed theory for molecular diffusion in liquids has yet been established. Some workers have imitated models originally developed for diffusion in either the gaseous or solid phases. Predictive models for molecular diffusion in liquids have followed either a kinetic, hydrodynamic, or irreversible thermodynamic approach. These are listed in the review by Himmelblau (2). A wide variety of diffusion coefficients can be defined for liquids by these theoretical approaches and one coefficient cannot be simply related to another.

The rate of diffusion in liquids can be represented by a simple mass balance equation in vector notations:

$$n_i = \rho_i v + j_i = \rho_i v_i \qquad (1)$$

where: n_i = mass flux of component i with respect to a fixed co-ordinate frame of reference.

ρ_i = concentration expressed as mass of component i per unit volume.

v = mass average velocity vector.

v_i = velocity vector of component i.

j_i = mass diffusive flux of component i with respect to a mass average velocity frame of reference.

In this equation the total mass flux is a sum of a fluid bulk flow term, $\rho_i v$, and the diffusive flux can be considered to consist of four terms, the fluxes resulting from molecular diffusion, pressure diffusion, 'forced diffusion' (diffusion resulting from an external force field), and thermal diffusion. However, in the absence of an external force and at constant temperature and pressure the diffusive flux resulting from an external force field, pressure or temperature gradients may be eliminated, we need concern ourselves only with molecular diffusion.

In principle, a molecular theory of the liquid state should lead to the prediction of diffusivity in liquids. However, because of our limited knowledge of the liquid state, current theories provide only a partial basis for the prediction of diffusion coefficients. The most frequently used liquid diffusion theories include those by Einstein and Stokes, the absolute-reaction-rate theory by Eyring, and the statistical-mechanical theory.

Einstein-Stokes Theory

The Einstein equation derived originally for the diffusion of macromolecules through a solvent is:

$$D_{AB} = kT/F_{AB} \tag{2}$$

where: F_{AB} = friction coefficient between components A and B

D_{AB} = diffusion coefficient of component A in component B

Evaluating F_{AB} with the Stokes equation and substituting into the Einstein equation one obtains the expression:

$$D_{AB} = kT/6\pi\mu_B r \tag{3}$$

where: μ_B = liquid viscosity

r = radius of the diffusing molecule

The equation has been shown to apply well to diffusion of very large molecules in a solvent composed of low molecular weight molecules.

Eyring Theory.

Eyring (18) proposed a theory based on a model that the liquid is a quasicrystalline substance with diffusing molecules "jumping" through ordered layers of solvent molecules referred to as the absolute-reaction-rate theory. Olander and co-workers (19,20) have recently modified Eyring's theory by suggesting a method of evaluating the difference between the free energies of activation for viscosity and for diffusion, which Eyring took to be zero. Unfortunately, neither the modified Eyring theory nor the original one provides an adequate quantitative prediction of diffusion coefficients.

Statistical Mechanical Theory.

Bearman (21) developed a unified statistical mechanical theory based on the theory of Kirkwood, relating molecular friction coefficients to the properties of the liquid. However, this theory applies only to regular solutions, i.e., solutions in which the molecules have similar size, shape, and interaction potentials. This approach does not permit the direct calculation of diffusion coefficients from basic considerations; it is still necessary to evaluate certain parameters experimentally.

Effect of Concentration on Diffusivity.

Bearman has shown from the statistical mechanical theory that the product of the mutual diffusion coefficient and the viscosity should be independent of composition for regular solutions. Since the concentration of the 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. Under these circumstances the diffusion coefficient, as predicted by theory, would not be expected to vary significantly with dissolved gas concentration.

Effect of Temperature on Diffusivity

The temperature dependence of diffusivity cannot be clarified by the existing theoretical and semi-empirical equations because all these equations contain temperature-dependent parameters or variables (e.g. viscosity). Furthermore, experimental data are so scattered even for CO_2 and the temperature range is usually only from 15° to 25°C. that no conclusion can be drawn on the effect of temperature on diffusion coefficients from empirical evidence.

However, since the solvent viscosities are often known gas diffusivities at various temperatures can be extrapolated by the relation: $\frac{D\mu}{T}$ = constant, which is essentially equation (3), the Einstein-Stokes equation. This method has been found to give good approximations for the diffusivities of dissolved gases in liquids.

Semi-Empirical Correlations of Diffusivity

Many attempts have been made to correlate diffusivities with theoretical equations modified by the introduction of empirically determined parameters. Some of the more important semi-empirical correlations applicable to gas diffusion in liquids are listed briefly below.

A. Arnold Correlation

Applying the classical kinetic theory for gaseous diffusivity to liquid systems Arnold (22) developed the following semi-empirical equation:

$$D_{AB} = \frac{0.010\ (V_B)\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{\left(V_A^{\frac{1}{3}} + V_B^{\frac{1}{3}}\right)^2 A_{11}A_{22}V_B/\mu_B^{\frac{1}{2}}} \qquad (4)$$

M_A, M_B = molecular weight of solute, solvent respectively

V_A, V_B = molal volumes of solute, solvent

A_{11}, A_{22} = abnormality factors for the solute, solvent

μ_B = viscosity of solvent

The assumptions involved in applying the above theory are:

- a. all collisions binary
- b. collision rate unaffected by the volume occupied by the molecules
- c. no intermolecular forces

Arnold's equation is not found to be useful in predicting diffusivities since the abnormality factors

A_1, A_2 are usually not known in advance.

B. Wilke-Chang's Equation

Basing on Eyring's absolute reaction rate theory and the Einstein-Stokes equation Wilke and Chang (23) developed the equation:

$$D_{AB} = 7.4 \text{ x } 10^{-8} \left(\frac{T \ (xM_B)^{\frac{1}{2}}}{(V_A)^{0.6} (\mu_B)} \right) \qquad (5)$$

M_B = molecular weight of solvent

T = temperature, °K

μ_B = viscosity of solution, (solvent) c.p.

V_A = molal volume of solute at normal boiling point

x = association parameters: for unassociated liquids, $x = 1.0$

The Wilke-Chang equation was found to give reasonable predictions for many systems.

C. Scheibel Correlation

Scheibel's method (24) is essentially a correction to Wilke-Chang's equation. He introduced the parameter, V_B, which is the molal volume of the solvent and discarded the association parameter, x.

$$D_{AB} = 8.2 \times 10^{-8} \times \frac{\left(1 - (3V_A/V_B)^{\frac{2}{3}}\right) T}{\mu_B V_A} \qquad (6)$$

When V_A V_B, better agreement is obtained by observing the following rules in these solvents:

Water	if $V_A < V_B$,	use $V_A = V_B$
Benzene	if $V_A < V_B$,	use $V_A = 2V_B$
Methanol	if $V_A < 1.5\ V_B$,	use $V_A = 1.5\ V_B$
Miscellaneous	if $V_A < 2.5\ V_B$,	use $V_A = 2.5\ V_B$

This equation is considered to be the best known at the present time for the prediction of diffusivities in non-aqueous solutions. The average absolute error was estimated to be less than 20% within the temperature range of 10 to 30°C.

D. Other Correlations

A modification to the Wilke-Chang correlation has also been proposed by Othmer and Thakar (25), involving the activation energies for diffusion and for viscosity, and by Sitaraman, Ibrahim, and Kaloor (26) who introduced the latent heats of vaporisation of the solute and solvent into their semi-empirical equations. While these formulations have been shown to predict diffusivities quite well for some systems, in others they were found to be inadequate.

Diffusion of Gases in Multicomponent Solvents

The diffusion of gases dissolved in multicomponent solvent solutions has been studied very little. The term "effective binary diffusion" is often used to describe the diffusion of a substance in mixed solvents by considering the mixed solvent as a pseudo pure liquid and an "effective binary diffusion coefficient" can be defined in a way analogous to that for a binary system.

Several empirical or semi-empirical methods have been given in the literature to predict the effective binary diffusion coefficients in multicomponent systems from the respective binary diffusion coefficients. Unfortunately, the equations proposed have generally been found unsatisfactory, although an insufficient amount of experimental data is available for conclusive tests of their applicability. In the expressions developed by Tang (25) the binary coefficients were assumed to be known. He derived two alternate expressions:

$$D_{1m}\mu_m^{\frac{1}{2}} = X_2 D_{12}\mu_2^{\frac{1}{2}} + X_3 D_{13}\mu_3^{\frac{1}{2}} \quad (7)$$

$$\log (D_{1m}\mu_m^{\frac{1}{2}}) = X_2 \log (D_{12}\mu_2^{\frac{1}{2}}) + X_3 \log (D_{13}\mu_3^{\frac{1}{2}}) \quad (8)$$

where: D_{1m} = effective binary diffusion coefficient of component 1 in solution m.

μ_m = viscosity of the multicomponent solution.

X_2, X_3 = mole fractions of component 2, 3 respectively.

From the appearance of these equations it is evident that the relationships between the binary and multicomponent diffusivities of a dissolved gas is not well understood. Furthermore, a knowledge of the solution viscosity is required, which is in itself difficult to predict with accuracy. In a test of six systems for which diffusivity data were available the equations gave reasonable predictions for diffusivities in non-ideal solvent mixtures including ethanol-water solutions. The range of diffusivities measured, however, was relatively small so that the test of the equations cannot be considered conclusive.

Theory of the Capillary Cell Method

A good account of the theory of the capillary cell method has been given by Malik (27). Considering the mass density of solute in the liquid phase is approximately equal to that of the solvent, Fick's equation (1) reduces to equation (9) when diffusion occurs in one direction and as a result of a concentration gradient only:

$$n_A = -\rho D \frac{dW_A}{dZ} + W_A (n_A + n_B) \tag{9}$$

where: n_A = mass flux of solute A relative to stationary axis.

n_B = mass flux of solvent B relative to stationary axis.

ρ = total mass concentration of solution.

D = diffusion coefficient.

W_A = mass fraction of solute A in solution.

Z = direction of diffusion.

The slight displacement of the liquid (bulk flow) as a result of a volume increase of the solution during absorption is given by:

$$\frac{n_A + n_B}{\rho} = - \frac{n_A}{\rho_{AL}} \qquad (10)$$

where: ρ_{AL} = effective mass concentration of pure solute A in solution.

For liquids of constant mass density ($\rho = \rho_{AL}$) the following expression may be obtained from equations (9) and (10):

$$D = \frac{n_A \; L}{\rho \log\left(\frac{1 + W_{AO}}{1 + W_{AL}}\right)} \qquad (11)$$

where: W_{AO} = solubility in mass fraction.

W_{AL} = solute mass fraction in the bulk liquid.

If $\rho \neq \rho_{AL}$ one can obtain the expression:

$$D = \frac{n_A \; L}{\rho_{AL} \log\left(\frac{1 + KW_{AO}}{1 + KW_{AL}}\right)} \qquad (12)$$

where: $K = \frac{\rho}{\rho_{AL}}$ L = diffusion path length, cm.

Equation (11) was used for evaluating diffusion coefficients from the experimentally measured steady-state absorption rates.

II. Gas Solubility

In gas-liquid systems, solubility is a measure of the amount of gas that dissolves in a certain quantity of liquid at equilibrium when the temperature and pressure remain constant.

Gas solubility data are frequently reported either as Ostwald coefficients, Bunsen coefficients or in mole fractions. The Ostwald coefficient is the volume of gas dissolved per unit volume of liquid at the temperature of the experiment. The Bunsen coefficient is the volume of gas reduced to 0°C. and 1 atmosphere, which dissolves in a unit volume of the solvent at the temperature of the experiment and at a gas partial pressure of 1 atmosphere.

According to Hildebrand (28), when a gas below its critical temperature dissolves in a liquid to form an approximately ideal solution Raoult's law holds. In such cases when the solubility of the gas is expressed in terms of its mole fraction the following conditions may be expected:

1. The solubility of a gas is proportional to its partial pressure (Henry's law).
2. The gas with the higher critical temperature (and boiling point) is

more soluble than one with a lower critical temperature since the vapor pressure is smaller for the former.

3. The solubility of a gas diminishes with increasing temperature.
4. The mole fraction of dissolved gas is the same in all solvents which form ideal solutions.

The premises outlined above form only a framework for describing gas solubility. The solubility of a number of real gases increases with an increase in temperature and the mole fraction solubility of a single gas is usually quite different in a number of solvents.

A number of aspects of non-ideality such as the change in liquid volumes on mixing, the internal heat of solution, and vapor pressure have been investigated by Horiuti (17).

A theoretical approach toward gas solubility considered to be most consistent is the regular solution theory of Hildebrand and Scott (28). They defined a regular solution 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 remains unchanged".

Two equations based on the regular solution theory are frequently used to calculate gas solubilities. The first is for systems in which solvent and solute molecules do not differ greatly in size:

$$- \log x_2 = - \log x_2^i + \frac{0.4343 V_2}{RT} (\delta_1 - \delta_2)^2 \quad (13)$$

where:
x_2 = solubility of gas in mole fraction
x_2^i = ideal gas solubility, mole fraction
V_2 = partial molar volume of the gas in the solution, cm^3/gm. mole
V_B = molal volume of the solvent, cm^3/gm. mole
δ_1, δ_2 = solubility parameters of solvent, solute, respectively
R = gas constant
T = absolute temperature, °K

For solutions where the molecules differ considerably in size a second equation corrects for the molecular size difference:

$$- \log x_2 = - \log x_2^i + \log \frac{V_2}{V_B} + 0.4343 \left(1 - \frac{V_2}{V_B}\right) + \frac{0.4343 V_2}{RT} (\delta_1 - \delta_2)^2 \quad (14)$$

For gases above their critical points the terms: x_2^i, δ_2, and V_2 are evaluated by various extrapolations and approximations.

Equations (13) and (14) have been applied to non-polar gas-liquid systems for which solubility data were experimentally determined by Gjaldbaek and co-workers (29, 16, 30, 31, 32). They have provided the most extensive testing of these two equations. To fit the experimental data to these equations, the solubility parameters were adjusted in some cases.

Prausnitz (33) also applied the regular solution theory to non-polar gas-liquid systems. He considered a three step process:

1. Isothermal compression of the pure gas from its partial pressure and the liquid from its vapor pressure to an isometric mixing pressure.
2. Isothermal, isometric, and isopiestic mixing at the isometric mixing pressure (at the isometric mixing pressure the pure gas has a volume equal to its partial molar volume in solution).
3. Isothermal expansion of the solution from the isometric mixing pressure to the equilibrium pressure.

Prausnitz found that the resulting equations obtained from the considerations of such a three-step process seemed to give reasonable estimates of the solubilities of gases and also of the temperature coefficient of solubility.

APPARATUS

I. The Diffusion Cell

The Capillary diffusion cell used was similar to that used by Malik (3). A diagram of the diffusion cell is shown in Figure 1. A cell consisted of a capillary sealed into a closed resevoir which could be filled by means of two high vacumn stopcocks. The capillary stem was made of two capillary tubes of different diameters permanently joined together. The upper portion, A, had a diameter of 0.0160 inch and was about 15 cm. long. The lower part, B, had a diameter of 0.0400 inch I.D. and was about 5 cm. long. The purpose of joining two capillaries of different diameters was to magnify the change in volume of the gas confined in the capillaries resulting from diffusion. A comparison of the cross-sectional areas of the two capillaries showed that the magnification was approximately six times. Hence the time requirement for the experiment was greatly reduced and the precision of the measurements increased. The diameter of the capillary, B, was chosen at not more than 0.0400 inch (approximately 1 mm.) to avoid possible convection inside the capillary and the diameter of the capillary, A, not less than 0.016 inch (approximately 0.4 mm.) to assure the free travel of the saturated liquid bead at a desired velocity down the capillary. The capacity of the bulk reservoir, C, was about 6 c.c. To facilitate purging of the reservoir with degassed liquid, stopcock, E, was permanently joined to the reservoir at a higher level than stopcock, D.

As a result of the simplicity in construction and the relatively long period required to achieve steady-state, two cells were used simultaneously at a time for the diffusion measurements. The capillaries were purchased from Wilmad Glass Company of Buena, New Jersey, with a manufacturer's tolerance for the bore of ±0.0002 inch. The diameters of these capillaries were verified by mercury displacement assuming the bore to be uniform along the length of the capillaries. The end of the larger capillary, F, enclosed by the reservoir was conically ground to aid in dissipating the solute.

The diffusion cells were immersed in a constant temperature water bath, controlled to ±0.01°C. and made of glass to allow external observation of the bead position and diffusion path length by means of a cathetometer. The pure gas used was passed through a drying tube containing calcium sulphate to absorb any water vapor present. The auxiliary equipment is shown in Figure 2.

The capillary cells used differ somewhat from that originally designed by Malik (3). The differences are:

1. The inlet and outlet stopcocks are sealed to the reservoir of the capillary cell at different levels to facilitate purging.
2. A slightly larger bore for the upper capillary, 0.0160 inch I.D. (compared to the bore of 0.0130 inch I.D. used by Malik) was used to increase the time of descent of the bead.
3. Pure dry gas was used for purging the cells. Hence, the difficulty in filling the diffusion cells with vapor-saturated gas was eliminated.

II. Solubility Apparatus

A diagram of the solubility apparatus is shown in Figure 3. The main advantage of this type of apparatus over that developed by Morrison and Billet (1) is that it permits the use of pure dry gas in the solubility determinations instead of vapor-saturated gas. Considerable difficulty was experienced in obtaining completely saturated gas without entrainment. Horiuti (17) also mentioned the existence of frequent errors in solubility determinations when attempts were made to saturate a gas with the vapor of a liquid at constant temperature.

The apparatus consisted of a long gas supply line, A, permanently connected to a calibrated gas burette, G, and a mercury levelling bottle, P. The level of mercury in the tubing, Q, could be controlled by adjusting the height of the mercury bottle. A motorized device was used to raise the bottle at an adjustable rate utilizing a variable speed motor connected by pulleys to a threaded rod. Burette, G, opened into the spiral-shaped absorption chamber, H, through a small nozzle, D. The purpose of the nozzle, approximately 0.5 inch in length was to guard against the creeping flow of liquid from the absorption chamber back into the gas burette. Without the nozzle a creeping back flow had been observed with several liquids including ethanol, benzene, and especially octane. Degassed liquid was introduced through a fine nozzle, E, by opening the stopcock, B. The absorption chamber, H, consisted of nine circular spirals whose diameter was about 3 inches. The spiral coils provided the long contact time required to saturate the liquid with gas while occupying a relatively small space. A calibrated burette (originally 25 ml.), L, was connected to the spiral coils through a U-tube, F, of about 2 mm. I.D., thus providing a liquid seal separating the absorption chamber from the calibrated liquid chamber, L. This separation of the absorption chamber from both the liquid and gas chambers enabled one to record directly the actual volume of gas dissolved and the volume of solution containing the gas, since no volume correction resulting from the displacement of gas by saturated liquid was required. The capillary tube, N, connected the liquid burette to the atmosphere. Because of the length of the capillary N, air was prevented from diffusing from the atmosphere into the liquid burette. The saturated solution could be drained by the stopcock, C. A water circulating pump capable of maintaining the temperature to within ±0.1°C was used to keep a constant temperature for the solubility measurements.

Degassing equipment consisted of a vacumn bottle with the lower outlet connected to a short capillary by a tygon tubing. The capillary, 0.040 inch I.D. and about 2 inches long, was sealed to a long narrow glass tubing which served as a storage for degassed liquid. The top end of the tubing was connected to vacumn during degassing and the flow of degassed liquid obtained could be regulated through a pinchcock at the bottom outlet.

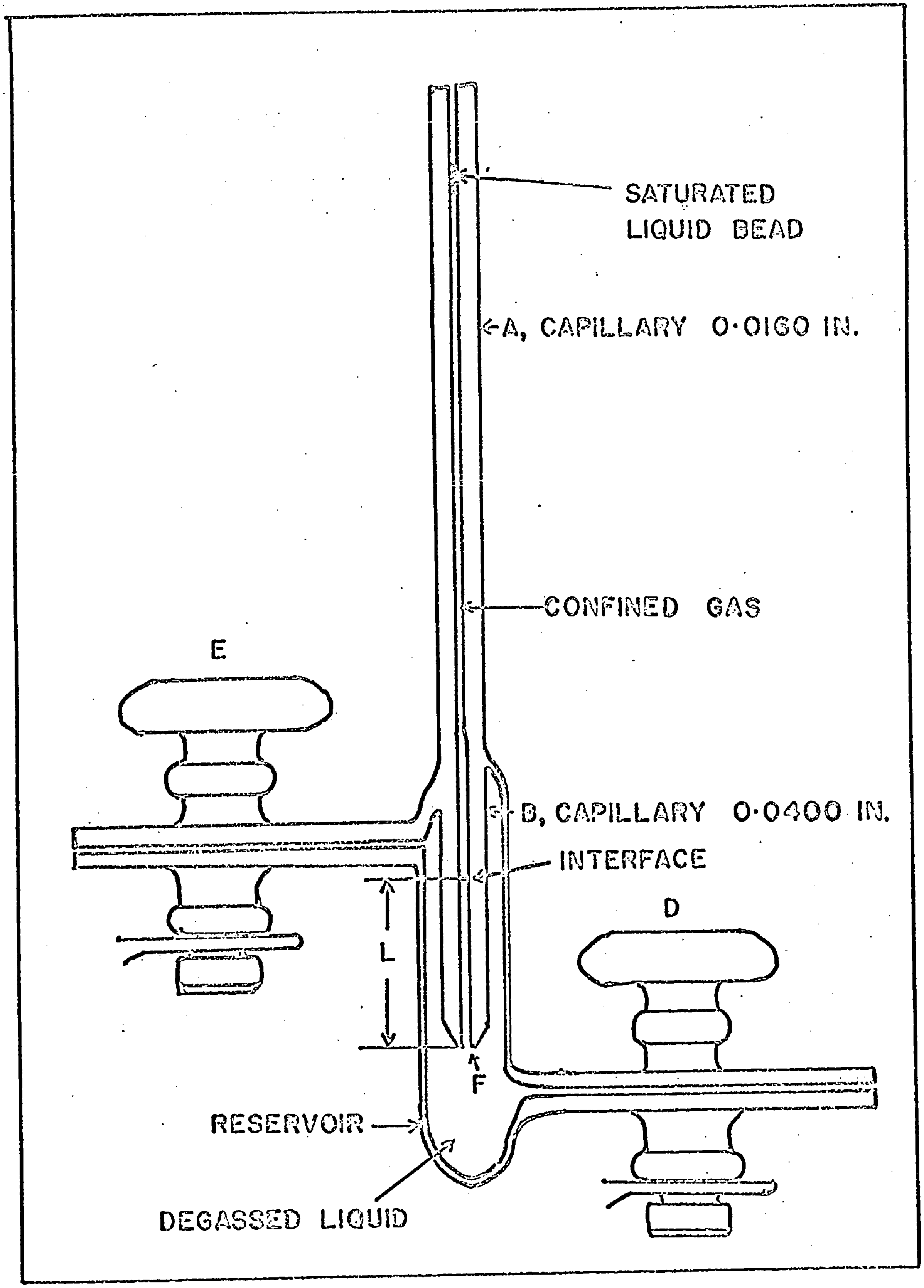

Figure 1. Diffusion Cell

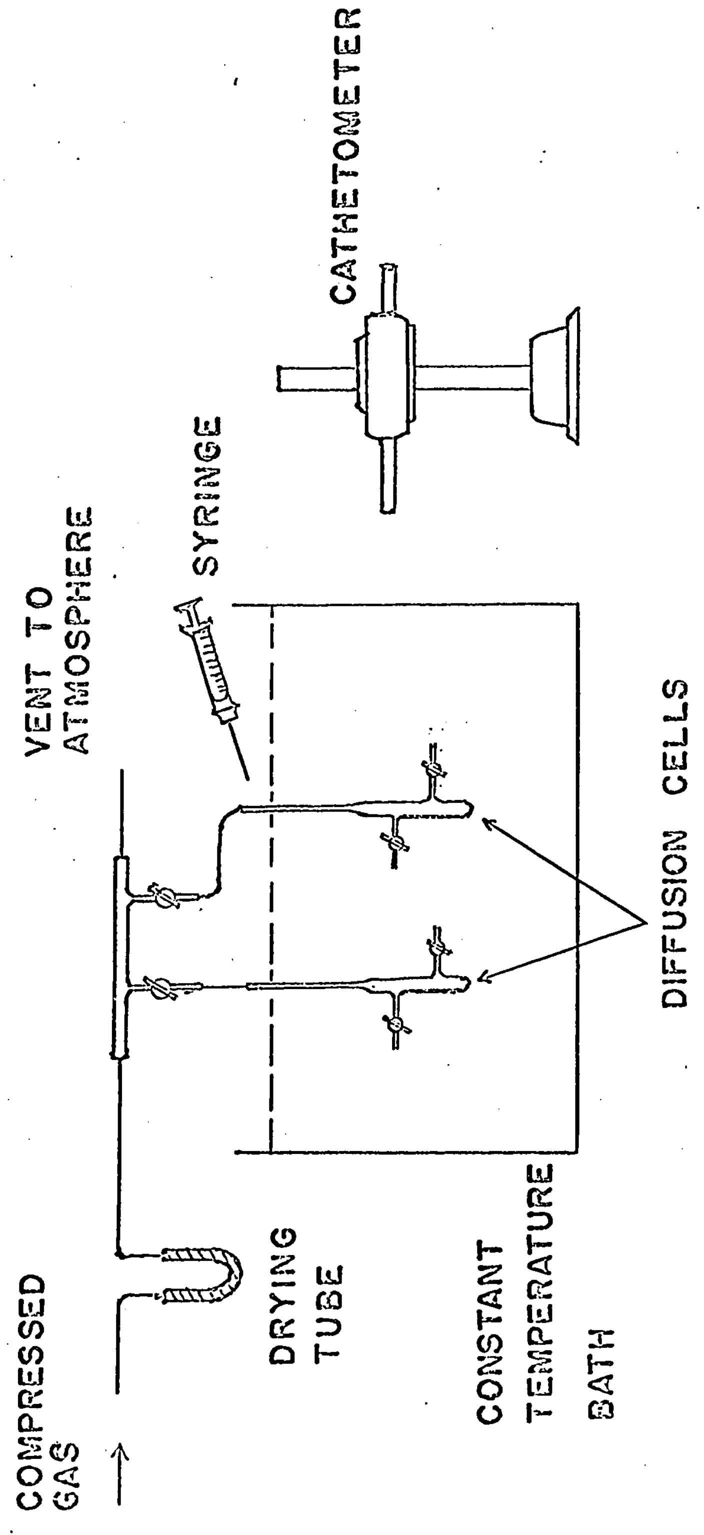

Figure 2. Auxillary Equipment For Diffusivity Measurements

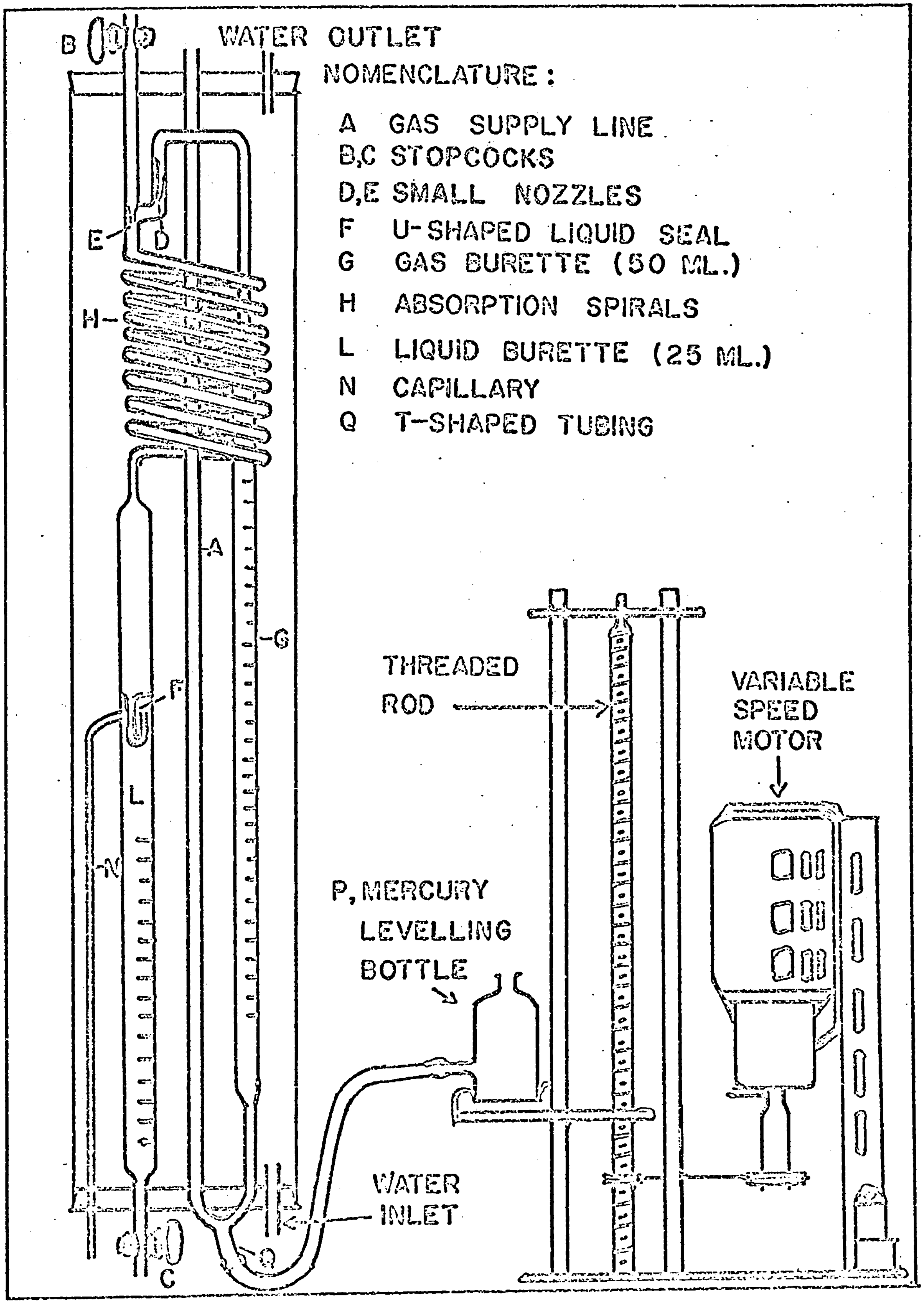

Figure 3. Solubility Apparatus

PROCEDURE

I. Diffusivity Measurements

It was found essential that the diffusion cells should be completely free of foreign material. It was difficult to fill the cells without trapping tiny bubbles of gas along the inside walls of the cells, or to obtain a smooth descent of the liquid bead in the capillaries unless the cells were suitably cleaned.

The diffusion cells were cleaned with acetone and dried with compressed air. They were then purged thoroughly with ethane, the diffusion coefficient of which was to be measured. Degassed liquid was introduced slowly through the lower stopcock of the cell until the liquid completely filled the reservoir and the lower portion of the large capillary to a height of 2 to 3 cm. About 100 ml. of additional liquid was used to flush out the cell so that any liquid which had been even briefly in contact with gas was adequately purged. The diffusion path length was adjusted by either adding or draining a small amount of liquid through one of the stopcocks.

A small amount of gas was permitted to flow through the gas supply manifold and was vented outside the building. The top of the capillary was connected to the manifold at all times after the initial purging of the cell so that an atmosphere of ethane (uncontaminated with air) was continually maintained.

The cell was then placed in the constant temperature water bath until steady-state was achieved. The length of time required which depended on the diffusion path length and the diffusivity, was estimated using the equation given by Crank (34):

$$\frac{Dt}{L^2} = 0.45 \qquad (15)$$

where: D = diffusion coefficient, cm.^{2}/sec.

t = time required to achieve steady-state, sec.

L = diffusion path length, cm.

The time, t, was usually less than 24 hours.

To measure the steady-state diffusion rate a droplet of saturated liquid was injected through the connecting tygon tubing by means of a syringe and placed at the entrance of the small capillary open to the gas. Both the position of the liquid bead, observed by means of a cathetometer, and the corresponding time, were read and recorded at regular intervals.

The same procedure was followed in measuring the diffusivities of ethane in hexane-hexadecane solutions. The actual degassed solution compositions were determined by first measuring the refractive indices of the solutions and then finding the compositions corresponding to these refractive indices on the calibration graph shown in Appendix I. The calibration data, also tabulated in Appendix I, were prepared by weighing known amounts of hexane and hexadecane, mixing them and measuring their refractive indices. This method of determining solution composition was also used in solubility measurements of ethane in hexane-hexadecane solutions.

The solution densities which were also required were measured with hydrometers supplied by Fisher Scientific Company. The solution viscosities were determined experimentally by means of calibrated Cannon-Fenske viscometer.

II. Solubility Determinations

The burettes and connecting tubing of the solubility apparatus were cleaned with acetone prior to each experiment and chromic acid when necessary. The apparatus was dried with compressed air and then purged thoroughly with the gas, the solubility of which was to be measured. While the gas continued to flow through the apparatus a small stream of degassed liquid was introduced through the entrance nozzle by opening the appropriate stopcock. The liquid flow rate was adjusted by means of the stopcock before the fine nozzle while observing the rate at which liquid was dropped from the liquid U-tube into the liquid accumulating chamber. A flow rate of about 0.1 ml. per minute was used in most of the measurements. This rate was used for the ease of equilibrating the pressures in the liquid chamber, the absorption chamber, and the gas chamber during the solubility measurements. In a series of several experiments it was established that liquid flow rates within limits did not affect the solubility results; for the system, ethane-hexane, four different flow rates ranging from 0.017 to 0.2 ml. per minute were tested and the same value of solubility was obtained. Liquid rates lower than 0.017 ml. per minute were difficult to control and with flow rates higher than 0.2 ml. per minute the pressure could not be kept constant within the apparatus.

When a constant rate of liquid was achieved the mercury level was raised slowly by means of the motorized device, closing off the supply of gas and confining some gas within the apparatus. The mercury levelling bottle was raised at a rate corresponding to the rate of solution of the gas so that a constant gas pressure was maintained. Care was taken not to break the liquid seal in the U-tube because it was found that too slow or too fast a rate of rise in mercury level could create a considerable pressure difference. In fact the liquid levels in the U-tube provided a very sensitive pressure sensing device. Successive readings of the gas volume in the burette together with the corresponding readings of solution volume in liquid burette were recorded at regular time intervals. The solubility was calculated from the corresponding dry gas and liquid solution volumes, as well as the barometric pressure.

SPECIFICATIONS AND PROPERTIES OF TEST FLUIDS

The gases which were used in these experiments, carbon dioxide and ethane, were supplied by Matheson of Canada and had specified minimum purities of 99.5 and 99.0 mole % respectively. One of the solvents, absolute ethanol, which was supplied by Canadian Industrial Alcohols and Chemicals Limited had a specified minimum purity of 99.4 volume %. Two other solvents, carbon tetrachloride and benzene, were spectroquality reagents supplied by Matheson Coleman and Bell. The normal paraffinic solvents, hexane, heptane, octane, dodecane and hexadecane, were chromatoquality reagents with a minimum purity of 99 mole %, and were also supplied by Matheson Coleman and Bell.

The properties of gases and liquids together with their literature sources are listed in the following tables. These properties were required in the calculations of solubilities and diffusivities. The purities of the hydrocarbon liquids were verified by refractive index determinations and are also listed for comparison with literature values.

Table Ia shows the gas molal volumes, partial molar volumes of dissolved gases, the ideal solubilities and solubility parameters. The partial molar volume of ethane was assumed to be approximately constant and independent of the solvent. Such an assumption appeared to be justified in view of the fact that the partial molar volume of ethane at its normal boiling point (-88°C.) was 55 c.c./g.-mole (28) compared with its partial molar volume of 66 c.c./g.-mole in benzene (16) at 25°C.

Table Ib and Ic show the pure solvent densities and molar volumes, refractive indices both experimental and from a reference source, vapor pressures, viscosities, and solubility parameters.

These are some of the physical properties at 25°C. and atmospheric pressure.

The reference for the data are indicated in brackets in all three tables.

TABLE Ia

Gas	Molal Volume at 25°C., 1 atm. (ml./g. - mole)	Partial Molar Vol. at 25°C., 1 atm. (ml. /g.-mole)	Ideal Solubility (mole fraction)	Solubility Parameter $(\text{Cal./ml.})^{\frac{1}{2}}$
Ethane	24,064 (35)*	66 (17)	0.0327 (16)	6.6 (16)
Carbon Dioxide	24,560 (31)	47 (31)	0.0230 (29)	5.1 (29)

TABLE Ib

Liquid	Density (g./c.c.)	Molal Volume (ml./g.-mole)	Vapor Pressure (mm.Hg)	Viscosity (c.p., absolute)
Hexane	0.65481 (36)*	131.6 (38)	151.2 (36)	0.2985 (36)
Heptane	0.67951 (36)	147.5 (38)	45.7 (36)	0.3967 (36)
Octane	0.69849 (36)	163.5 (38)	13.9 (36)	0.5151 (36)
Dodecane	0.74516 (36)	228.6 (38)	0.27 (36)	1.378 (36)
Hexadecane	0.76996 (36)	294.1 (38)	0.013(36)	3.095 (36)
Ethanol	0.78508 (37)	------	57 (37)	0.1068 (37)
Benzene	0.87370 (36)	89.4 (38)	96 (36)	0.6028 (36)
Carbon tetrachloride	1.5843 (37)	97 (37)	114 (36)	0.8876 (36)

---

*Brackets indicate reference number

TABLE Ic

Liquid	Solubility Parameter (cal./ml.)$^{\frac{1}{2}}$	Refractive Index	Exp't Refractive Index**
Hexane	7.3 (39)*	1.37226 (36)	1.37258
Heptane	7.4 (39)	1.38511 (36)	1.38546
Octane	7.5 (39)	1.39505 (36)	1.39519
Dodecane	7.8 (39)	1.41949 (36)	1.41983
Hecadecane	8.0 (39)	1.43250 (36)	1.43258

* Brackets indicate reference number.

** Refractive index measurements were made with an Abbe-3 type precision refractometer by Bausch and Lomb Optical Company of Rochester, New York.

TREATMENT OF DATA

I. Diffusion of Dissolved Gases in Liquids

The rate of travel of the liquid bead down the capillary, denoted by h(cm./min.), was the slope of the straight line obtained by plotting the bead position measured by the cathetometer vs. time, as shown Figure 4.

To calculate the diffusion coefficient the movement of the liquid bead in the small capillary must be related to the diffusive flux of the solute gas through the liquid in the large capillary. The appropriate flux of dissolved gas in the liquid is the mass flux since the mass concentrations in the liquid solution is more constant than the molar concentrations. An expression for the mass flux will be first derived in connection with the movement of the bead, then it will be related to one rate of diffusion through the column of liquid using as a basis a unit cross-sectional area of the large capillary.

$$v_K = \frac{h}{60}\left(\frac{A_1}{A_2}\right) \qquad (1)$$

where: v_K = volumetric rate of shrinkage of gas and associated vapor, cm.^{3}/sec.-cm.^{2}

h = slope of graph: bead position vs. time

A_1 = cross-sectional area of small capillary, cm.^{2}

A_2 = cross-sectional area of large capillary, cm.^{2}

$$n_A = \frac{v_k}{v_G} P_A M_A \qquad (2)$$

where: n_A = mass flux of solute gas, g./cm.^{2}-sec.

v_G = molar volume of gas at 25°C. and 1 atm.

P_A = partial pressure of gas, atm. fraction

M_A = molecular weight of gas, g./g.-mole

The mass flux through the liquid must be written with respect to fixed axes because the movement of the bead was recorded with respect to stationary axes. With the assumption that the density remains constant Fick's law can be applied to describe the rate of diffusion. The bulk flow or the slight upward displacement of the whole column of liquid in the large capillary can be considered to equal the mass flux through the column of liquid because the reservoir of the cell has a constant volume.

Then: $$n_A = -(n_A + n_B) \qquad (3)$$

By Fick's law: $$n_A = (n_A + n_B)W_A - \rho D\frac{dW_A}{dZ} \qquad (4)$$

Substituting equation (3) in equation (4) and integrating W_A from W_{AL} to W_{AO} and Z from zero to L:

$$n_A = \left(\frac{\rho D}{L}\right) \ln\left(\frac{1 + W_{AO}}{1 + W_{AL}}\right) \qquad (5)$$

where: $n_A + n_B$ = bulk flow of solution, g./cm.^{2}-sec.

ρ = solution mass density, g./cm.^{3}

D = diffusivity, cm.^{2}/sec.

Z = direction of diffusion

W_A = mass fraction of solute A in solution

W_{AO} = solubility in mass fraction of solute A in solution

W_{AL} = mass fraction of solute A in bulk liquid

L = diffusion path length, cm.

Evidently equations (2) and (5) are equivalent. Hence, they are equated to obtain the expression for the diffusivity:

$$D = \left(\frac{h}{60}\right)\left(\frac{A_1}{A_2}\right)\left(\frac{P_A}{\rho}\right)\left(\frac{M_A}{v_G}\right) \frac{L}{\ln\left(\frac{1 + W_{AO}}{1 + W_{AL}}\right)} \qquad (6)$$

Since the quantity of solute gas is small the solution density can be considered to be simply the solvent liquid density in the above expression. The mass fraction of dissolved gas at the interface can be evaluated from the saturated solubility expressed as an Ostwald coefficient and using 1 cm.^{3} of solvent as a basis.

$$W_{AO} = \frac{\gamma P_A (M_A/v_G)}{\rho_L + (\gamma P_A M_A/v_G)} \qquad (7)$$

where: γ = Ostwald coefficient

ρ_L = density of solvent, g./c.c.

The second term in the denominator is negligible compared to the first one so that equation (7) simplifies to:

$$W_{AO} = \frac{\gamma P_A M_A}{\rho_L v_G} \qquad (8)$$

The mass fraction at the end of the capillary open to the reservoir of the cell can be assumed to remain zero for the duration of the experiment; however, an estimate of the actual concentration in the bulk of the cell can be made by considering the cell volume and the total time during which unsteady-state diffusion through the liquid in the capillary occurred. Such an equation is given by Crank (34):

$$W_{AL} = \frac{A_2 \; L \; W_{AO}}{V}\left(\frac{Dt(3600)}{L^2} - \frac{1}{6}\right) \qquad (9)$$

where: V = volume of solution contained in cell, cm. ^{3}

t = total time during which unsteady-state diffusion occurred, sec.

Equation (9) is given in terms of the diffusivity; therefore, an initial estimate of the diffusivity is required before the actual diffusivity can be calculated.

Raoult's law was assumed to apply to the solvent for the purpose of calculating the solvent vapor pressure. The solute concentration in the solution could not be neglected because ethane was very soluble.

$$P_A = BP - \overset{o}{P}_B \; (1 - x_A) \qquad (10)$$

where: BP = barometric pressure, atm.

$\overset{o}{P}_B$ = solvent vapor pressure, atm.

x_A = solute mole fraction

Hexane-Hexadecane Solvent Solutions

Raoult's law was also applied in the determination of the solvent vapor pressures of the hexane-hexadecane solutions. For the purpose of calculating the solution vapor pressure, the vapor pressure of the hexadecane was ignored because the vapor pressure of hexane was 151.2 mm. of mercury compared with 0.013 mm. of mercury for hexadecane at 25°C. Realizing that the mole fractions of hexane and hexadecane would be different before and after the dissolution of x_2 mole fraction of ethane although the ratio of hexane and hexadecane remained the same throughout, the following three equations applied:

Before ethane dissolution, $x_h + x_{hd} = 1$ (11)

After addition of ethane, $x_2 + x_h' + x_{hd}' = 1$ (12)

$$\frac{x_h}{x_{hd}} = \frac{x_h'}{x_{hd}'} \qquad (13)$$

where:

x_h, x_{hd} = mole fraction of hexane, hexadecane in the original solvent solution

x_h', x_{hd}' = mole fraction of hexane, hexadecane in the solution after solution of ethane

x_2 = mole fraction of ethane in solution (estimated by equation (17) in the gas solubility section which follows)

Substituting equation (13) into equation (12) the following expression was obtained:

$$x_h' = (1 - x_2)\, x_h \qquad (14)$$

The mixed solvent vapor pressure was estimated by the product of the mole fraction of hexane in the mixture and the pure hexane vapor pressure. The mole fractions of hexane in the two component solutions x_h, were determined by refractive index measurements.

II. Gas Solubility

To determine the solubility the volume of vapor-free gas absorbed was plotted against the corresponding volume of solution accumulated as shown in Figure 5. The slope of the graph gave the volume of (vapor free) gas absorbed per volume of solution, h_s, where the gas volume was measured at a total pressure equal to atmospheric pressure.

It was assumed that the pure liquid interface was readily saturated with the contacting gas, and that the gas interface was likewise saturated with solution vapor on contact. The equivalent volume of gas absorbed per volume of solution could be calculated at a gas partial pressure equal to that which existed in the solubility apparatus. From a knowledge of the partial molal volume of dissolved gas in the solution and the volume dissolved it was possible to calculate an Ostwald coefficient. The Ostwald coefficient represents the volume of gas dissolved in a unit volume of solvent. The unique feature of the Ostwald coefficient is that the volume of gas dissolved is independent of the actual gas partial pressure as long as Henry's law applies.

It was necessary to calculate the volume occupied by the dissolved gas in solution, V_{GS}, because in these experiments the solution volume rather than the solvent volume was measured. Using as a basis 1 cm.^{3} of solution, the equivalent solvent volume can be calculated:

$$V_{GS} = \frac{h_s \, V_{PG} \, (BP)}{V_m} \qquad (15)$$

where: V_{PG} = partial molar volume of dissolved gas in solution c.c./g.-mole (assumed constant for the systems studied)

V_m = molal volume of the gas at temperature of the experiment and 1 atm.

BP = barametric pressure, atm.

Hence the Ostwald coefficient, was obtained by converting the volume of solution, V_{sol} to equivalent volume of pure liquid, V_L:

$$\gamma = \frac{V_G}{V_L} = \frac{V_G}{1 - V_{GS}} \qquad (16)$$

where: $V_G = h_s \frac{BP}{P_A}$

The mole fraction of gas dissolved, x_2, could be computed from the Ostwald coefficient using a unit volume of solvent as a basis.

$$x_2 = \frac{\frac{\gamma}{V_m}}{\frac{\gamma}{V_m} + \frac{1}{V_L}} = \frac{\gamma}{\gamma + \frac{V_m}{V_L}} \qquad (17)$$

The vapor pressure of the solvent was calculated from Raoult's law.

$$\overset{o}{P}_{sol} = \overset{o}{P}_{B} (1 - x_2) \tag{18}$$

The solubilities were expressed as both Ostwald coefficients and mole fractions.

Solubility of Ethane in Hexane-Hexadecane Solutions

The solubility of a gas in a mixed liquid had to be treated in a slightly different manner. A plot of the volume of gas assorbed versus corresponding three-component solution volume gave the slope, h_{ms}, similar to that for pure solvents.

The main differences existed in the method with which the vapor pressure and the molal volume of the mixed liquid solution were calculated. The vapor pressure was computed using Raoult's law as described in section I. The molar volume was calculated based on the assumption that no volume change occurred on mixing the two solvent components, hexane and hexadecane. One can observe the validity of such an assumption from Figure 6 which shows the essentially linear relationship between the densities of the solutions and the volume fractions. Another assumption here was that the partial molar volume of ethane remained the same (66 cm.^{3}/g. mole) in all the solutions.

The Ostwald coefficient and mole fractions were then calculated as before:

$$\gamma = \frac{V_G}{V_L} = \frac{h_{ms}\left(\frac{BP}{P_A}\right)}{1 - h_{ms}(BP)\left(\frac{V_{PG}}{V_m}\right)} \qquad (19)$$

$$x_2 = \frac{\gamma}{\gamma + \frac{V_m}{V_{mL}}} \qquad (20)$$

where: V_{mL} = molal volume of solvent solution, c.c./g.-mole

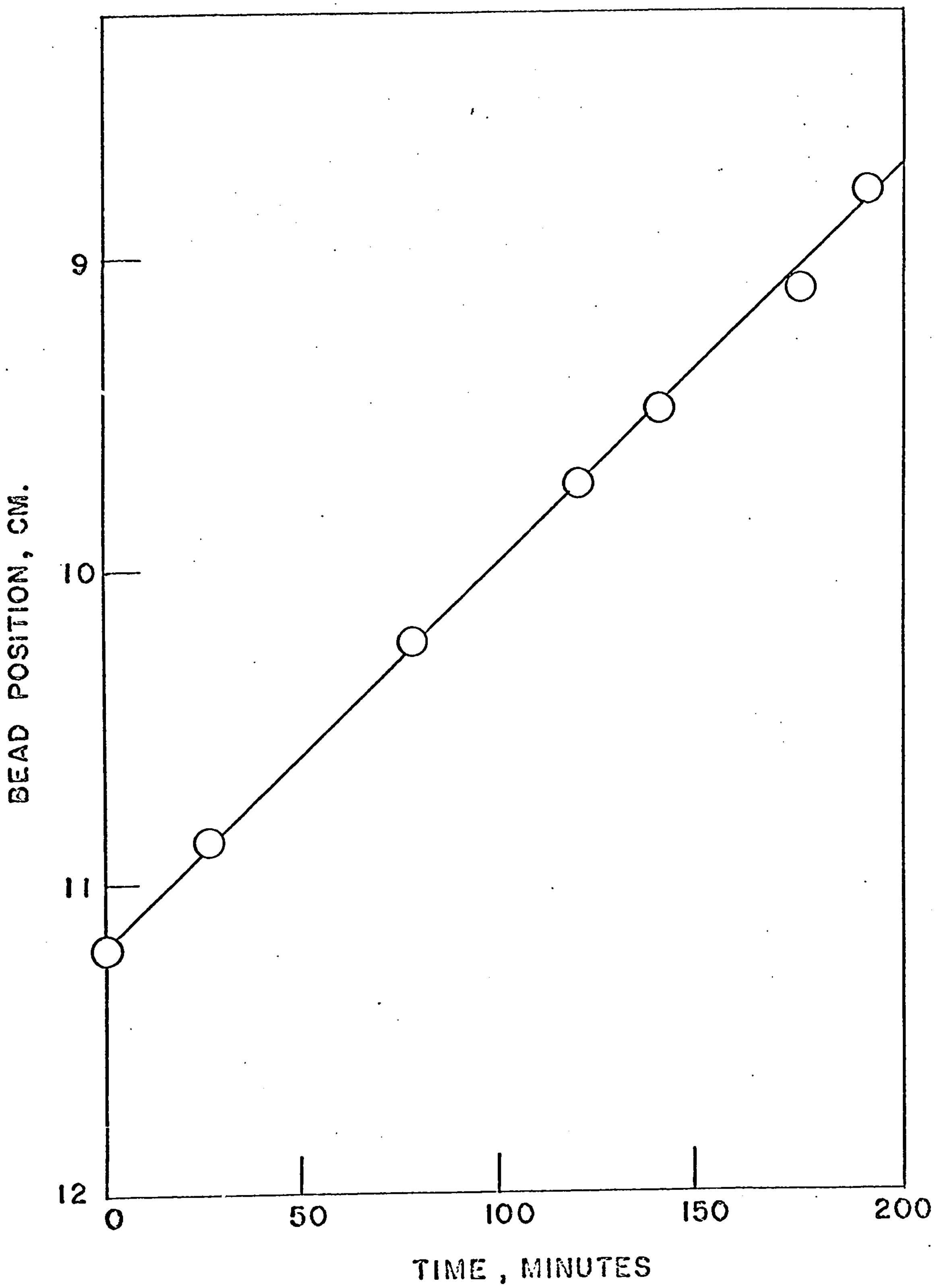

Figure 4. Rate of Travel of Liquid Bead

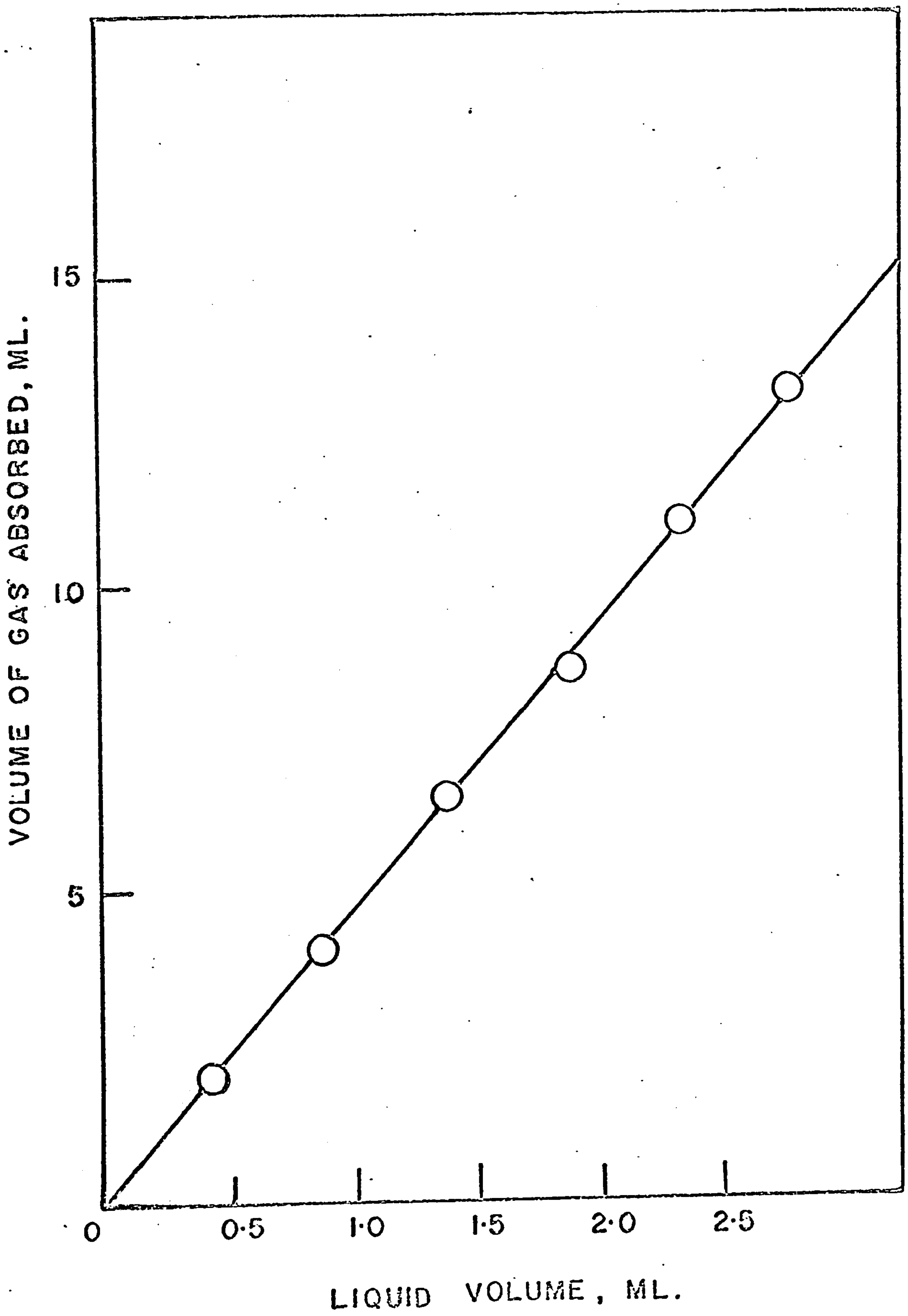

Figure 5. Gas Volume vs. Solution Volume

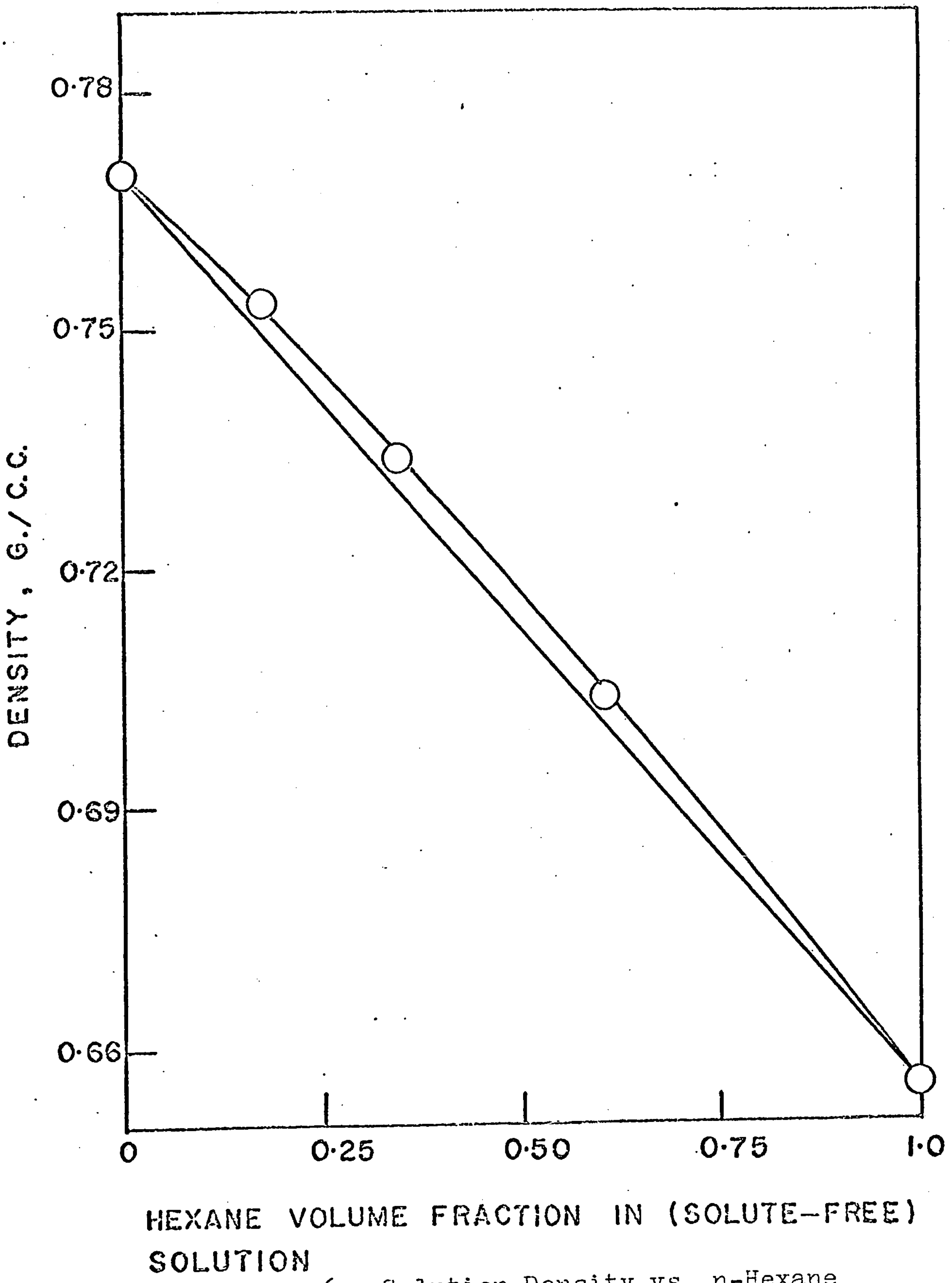

Figure 6. Solution Density vs. n-Hexane Volume Fraction

EXPERIMENTAL RESULTS

All experimental work was carried out at atmospheric pressure. Experimental results together with those predicted from existing theoretical and empirical equations are tabulated and compared. Raw experimental data from which these experimental results were computed are given in Appendices II and III.

I. Diffusion of Dissolved Gases in Liquids

The Wilke-Chang empirical equation (5) was used to predict the diffusion coefficients of ethane in normal paraffinic liquids and the predicted diffusion coefficients are tabulated in Table Id. The modified Wilke-Chang correlations of Scheibel, Reddy, etc. were found to give even greater deviations and therefore the corresponding predicted diffusivities are not listed.

The densities, and viscosities at different compositions were obtained experimentally for solutions of hexane and hexadecane.

The variation of experimental diffusivities and viscosities with carbon number for the paraffinic liquids is shown in Figure 7. These values are tabulated in Table II and were used in the empirical correlations.

Several correlations suggested by Tang and Himmelblau (4) for the prediction of diffusion coefficients in mixed solvents were tested. The equations were as follows:

$$D_{1m} = \frac{1 - X_A}{\frac{X_2}{D_{12}} + \frac{X_3}{D_{13}}} \tag{1}$$

$$D_{1m} = X_2 D_{12} + X_3 D_{13} \tag{2}$$

$$D_{1m}\mu_m = X_2 D_{12}\mu_2 + X_3 D_{13}\mu_3 \tag{3}$$

$$D_{1m}\mu_m^{\frac{1}{2}} = X_2 D_{12}\mu_2^{\frac{1}{2}} + X_3 D_{13}\mu_3^{\frac{1}{2}} \tag{4}$$

$$D_{1m} = 7.4 \times 10^{-8} \times \frac{T \quad (xM_m)^{\frac{1}{2}}}{\mu_m V_A{}^{0.6}} \tag{5}$$

$$\text{Log } (D_{1m}\mu_m^{\frac{1}{2}}) = X_2 \log (D_{12}\mu_2^{\frac{1}{2}}) + X_3 (\log D_{13}\mu_3^{\frac{1}{2}}) \tag{6}$$

where:

D_{1m} = pseudo-binary diffusivity of ethane in the liquid solvent solution, cm.^{2}/sec.

X_2 = mole fraction of hexane in solution

X_3 = mole fraction of hexadecane in solution

D_{12} = diffusion coefficient of ethane in hexane, cm.^{2}/sec.

D_{13} = diffusion coefficient of ethane in hexadecane, cm.^{2}/sec.

μ_m = viscosity of the solution, cps.

μ_2, μ_3 = viscosities of hexane and hexadecane respectively, cps.

The diffusion coefficients calculated from these equations using experimental values of D_{12} and D_{13}, and those calculated from the Wilke-Chang equation are compared with experimental values in Table III.

Figure 8 represents the variation in solute gas diffusivity with composition in hexane-hexadecane solutions. The predicted values calculated from equation (1) are also plotted on the same graph.-

II. Gas Solubility

The solubility data of ethane in the normal paraffinic liquids are listed in Table IV, both as Ostwald coefficients and mole fractions.

A comparison of theoretical (based on regular solution theory) and experimental solubilities is shown in Table V. Ethane solubility data found in the literature are also included. The theoretical equations used were those of Hildebrand and Scott (39), equation (14) of the theory section, derived from the regular solution theory.

Solubilities of ethane in hexane and heptane at different temperatures (20^{o}, 30^{o} and $40^{o}C$.) are listed in Table VI. In the same table the solubilities of carbon dioxide in ethanol and ethane in both benzene and carbon tetrachloride are also reported. The latter determinations were made to test the realiability of the apparatus.

Solubilities of ethane in mixed liquid solutions are tabulated in Table VII. Graphs of Ostwald coefficient and solvent composition, as well as mole fraction solubility and solvent composition, are plotted in Figure 9 and 10 respectively.

TABLE Id

Experimental and Predicted Diffusion Coefficients

System	No. of Exp't Runs	D_{AB} (10^5) cm.^{2}/sec. Mean D_{AB}	Predicted from Wilke-Chang Eq.	% Deviation
Ethane, Hexane	5	5.79	6.22	-- 7.4
Ethane, Heptane	3	5.51	5.07	+ 8.0
Ethane, Octane	3	4.66	4.16	+10.7
Ethane, Dodecane	3	2.73	1.90	+30.4
Ethane, Hexadecane	3	1.95	0.98	+49.8

TABLE II

Variations of Density and Viscosity with Composition

System	Mole Fraction Hexane*	Density (g./c.c.)	Viscosity (c.p. absolute)
Mixture of hexane and hexadecane	0	0.7699	3.095
	0.115	0.7647	2.490
	0.453	0.7410	1.326
	0.798	0.6980	0.5675
	1.0	0.6548	0.2985

*Solute-free mole fraction hexane

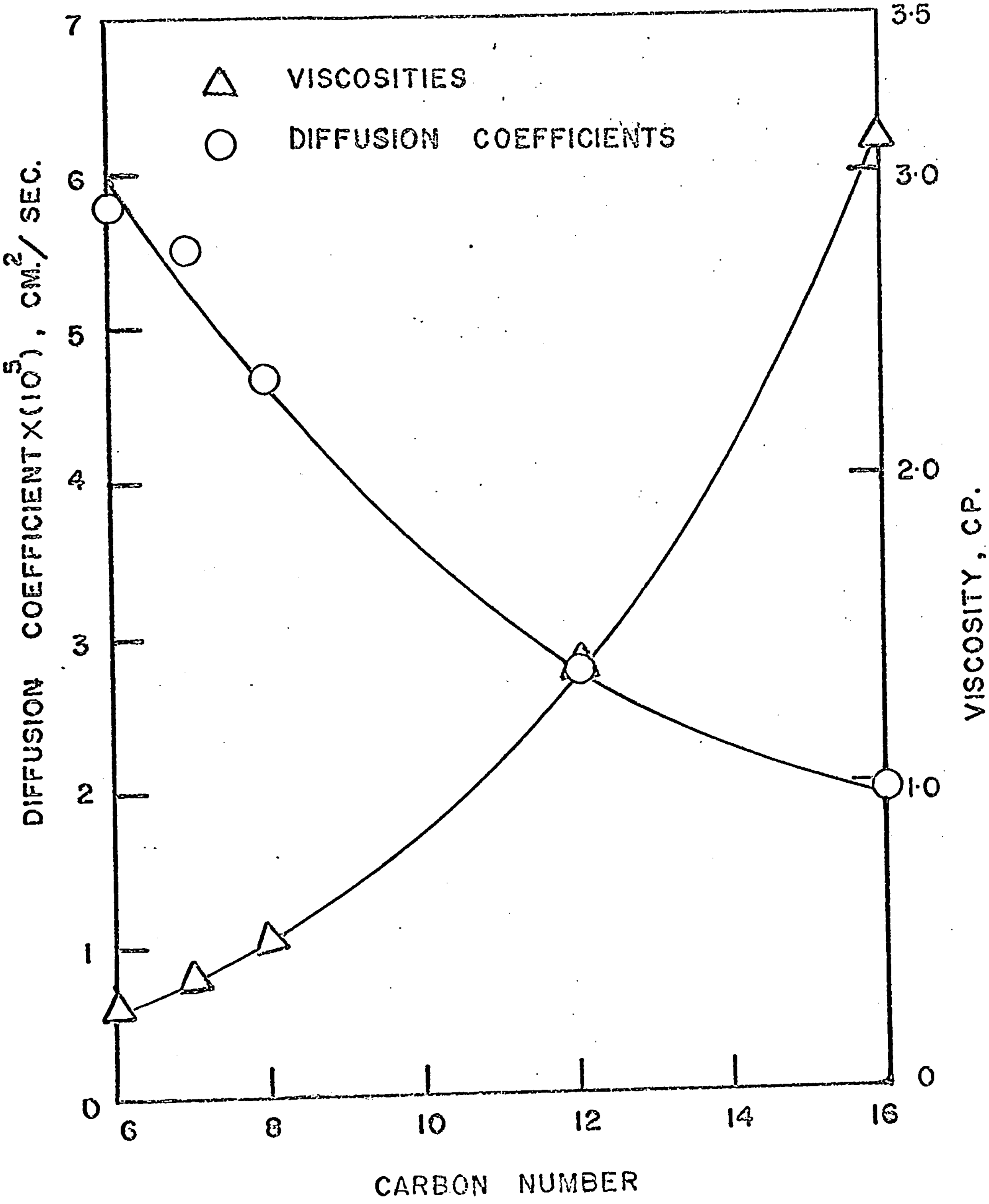

Figure 7. Variation of Diffusivity and Viscosity with Carbon Number

TABLE III

Comparison of Predicted and Experimental Diffusion Coefficients of Ethane in Hexane-Hexadecane Solutions

		D_{1m} (10^5) cm.^{2}/sec.						
Mole Fraction Hexane	No. of Runs	Exp't	(1)*	(2)	(3)	(4)	(5)	(6)
0.115	2	2.04	2.07	2.40	2.22	2.14	1.165	2.15
0.453	2	2.28	2.71	3.73	3.09	2.88	1.93	2.89
0.798	2	3.85	4.08	5.08	4.61	4.32	3.78	4.30

* Brackets indicate equation numbers listed in the Experimental Results section

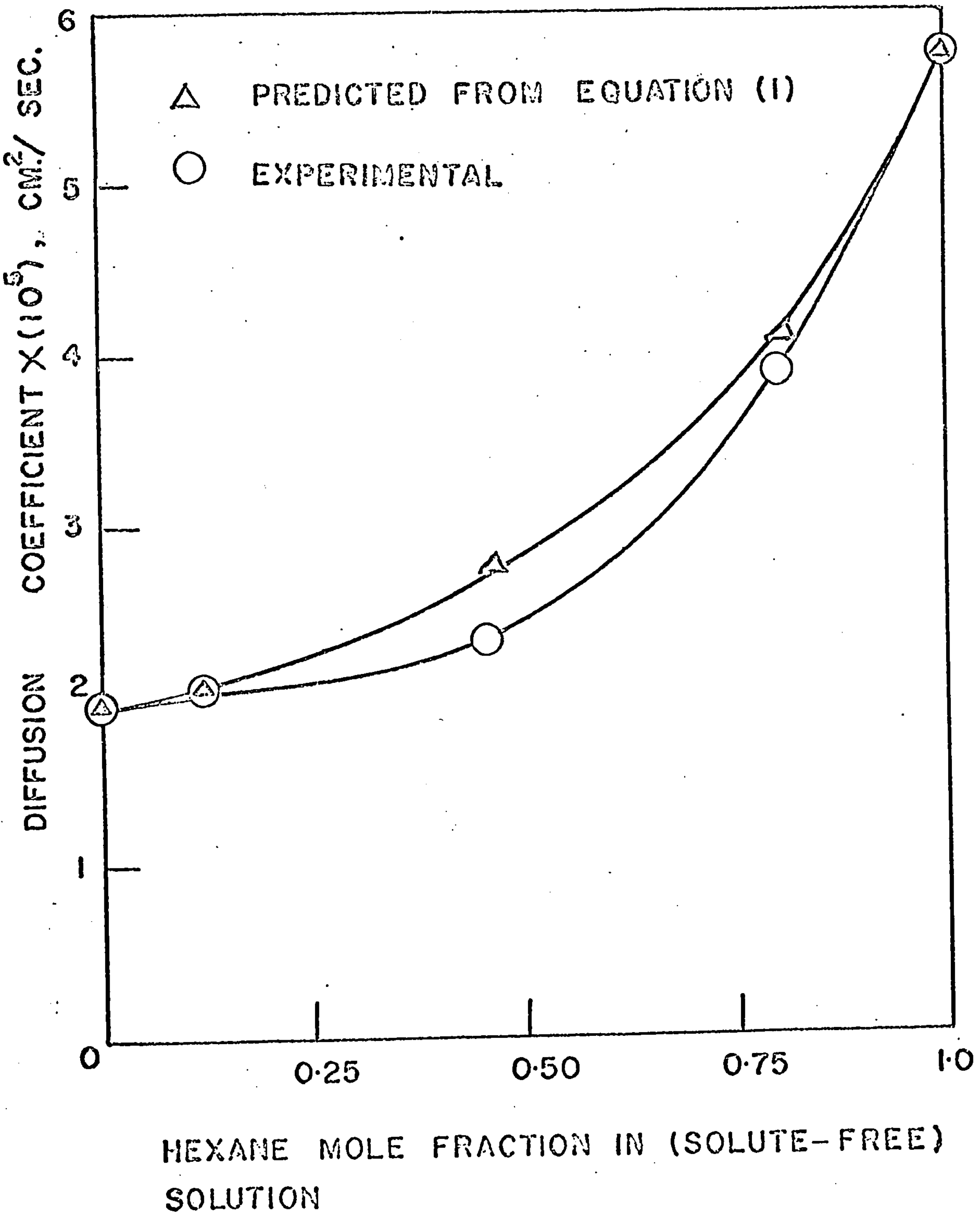

Figure 8. Variation of Diffusivity with Solvent Composition

TABLE IV

Solubility of Ethane in Normal Paraffins at 25°C.

Liquid	Ostwald Coefficient		Solubility in Mole Fraction
Hexane	6.12		
	6.06	mean = 6.09	0.0320
	6.09		
Heptane	5.41		
	5.38	mean = 5.39	0.0321
	5.39		
Octane	4.95		
	4.90	mean = 4.92	0.0324
	4.90		
Dodecane	3.82		
	3.82	mean = 3.83	0.0351
	3.84		
Hexadecane	3.23		
	3.21	mean = 3.22	0.0379
	3.23		

TABLE V

A Comparison of Theoretical and Experimental Solubilities for Ethane at 25°C.

Liquid	V_1	δ_1	Mole Fraction Solubility (10^2)		
			Theoretical	This Work	Gjaldbaek (16)
Hexane	131.6	7.3	3.09(a) 3.75(b)	3.20	
Heptane	147.5	7.4	3.04(a) 3.92(b)	3.21	3.29
Octane	163.5	7.5	2.98(a) 4.08(b)	3.24	3.37
Dodecane	228.6	7.8	2.78(a) 4.74(b)	3.51	
Hexadecane	294.1	8.0	2.62(a) 5.39(b)	3.79	

V_1 = molal volume of liquid

δ_1 = solubility parameter of liquid

(a) - calculated from equation (13) of Theory section

(b) - calculated from equation (14) of Theory section

TABLE VI

Solubilities of Ethane and Carbon Dioxide at Various Temperatures

Gas	Solvent	Temp. °C.	Ostwald Coefficient	Solubility in Mole Fraction	Ostwald Coefficient (literature)
Carbon dioxide	Ethanol	25	2.71		
			2.73		
			2.74		
			2.71		
			mean = 2.725	0.00660	2.745 (41)
Ethane	Carbon Tetra-chloride	25	5.35		
			5.37		
			5.31		
			mean = 5.34	0.0211	5.366 (17)
Ethane	Benzene	25	3.98		
			3.94		
			3.98		
			mean = 3.97	0.0145	4.120 (17)
Ethane	Heptane	20	5.74		
			5.73		
			5.76		
			mean = 5.74	0.0342	
Ethane	Heptane	30	5.09	0.0300	
Ethane	Heptane	40	4.45		
			4.39		
			mean = 4.42	0.0256	
Ethane	Hexane	30	5.74	0.0299	

TABLE VII

Solubilities of Ethane in Hexane-Hexadecane Solutions at 25°C.

Fraction (solute-free) Hexane		Ostwald Coefficient	Mole Fraction Ethane Solubility
Mole	Volume		
0	0	3.22	0.0379
0.223	0.110	3.47	0.0359
0.345	0.198	3.68	0.0350
0.580	0.384	4.18	0.0336
0.627	0.431	4.32	0.0334
0.725	0.530	4.58	0.0326
0.820	0.675	5.10	0.0330
0.904	0.810	5.42	0.0322
1.0	1.0	6.09	0.0320

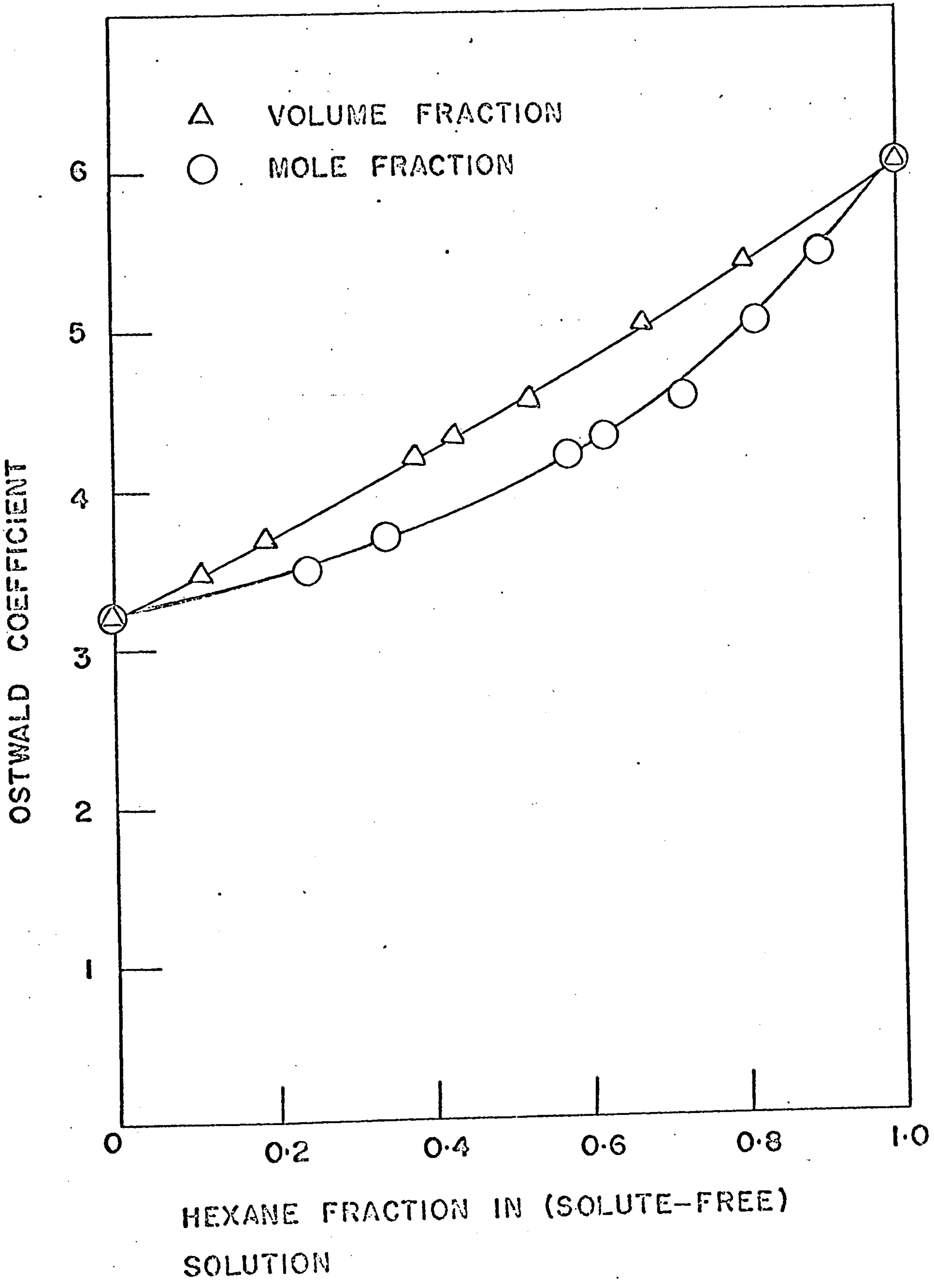

Figure 9. Ostwald Coefficient vs. Solvent Composition

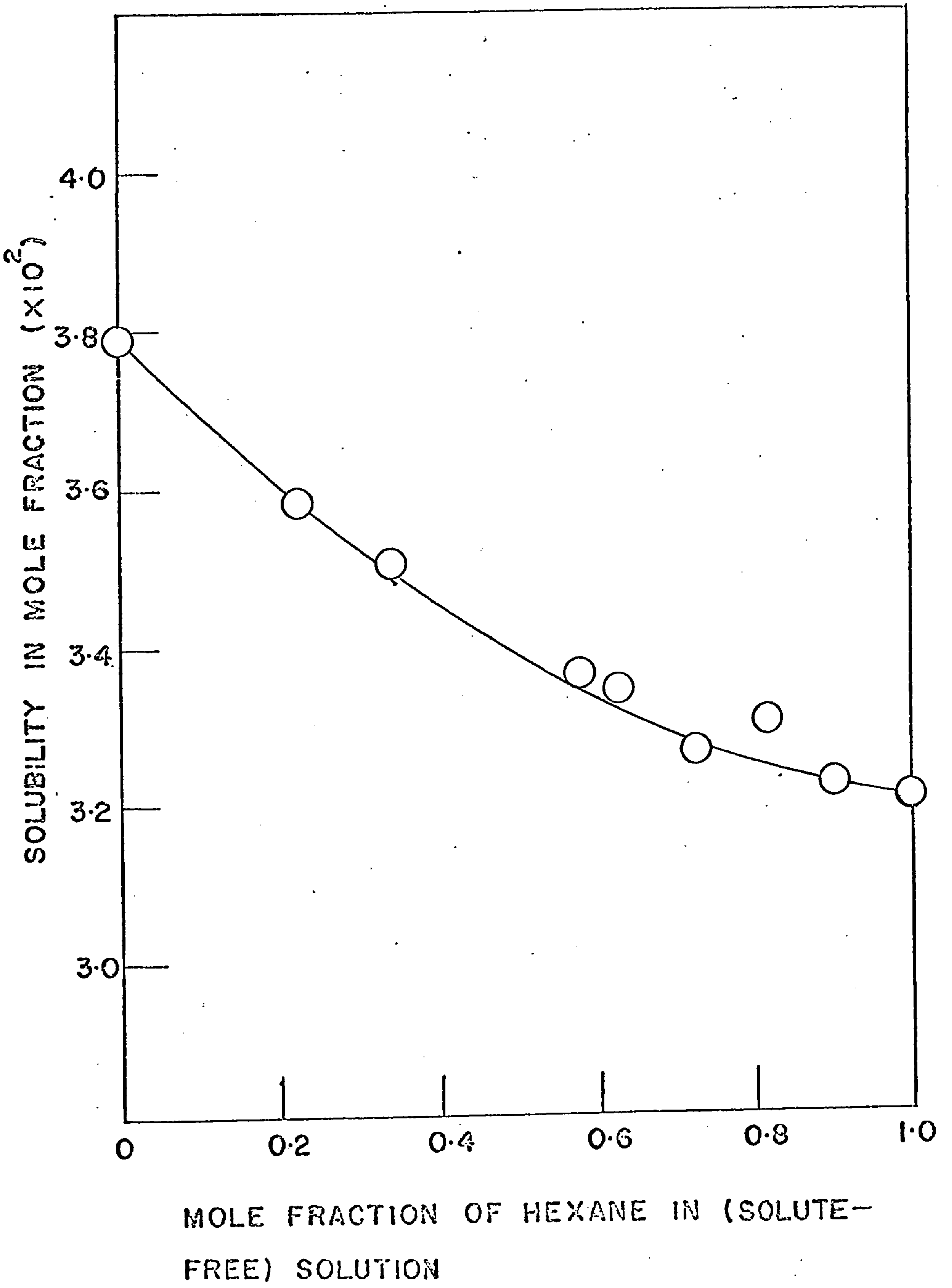

Figure 10. Mole Fraction Solubility vs. Solvent Composition

DISCUSSION

I. Diffusion of Dissolved Gases in Liquids

The application of the Wilke-Chang equation to the prediction of diffusivity of ethane in normal paraffinic liquid was found to be unsatisfactory. For the system ethane-hexane, the deviation from experimental results was 7.4%. The deviation increased for the solvents of increasing carbon content until the ethane-hexadecane system where a 49.8% deviation occurred. However, since a plot of $\log(D_{AB}\mu)$ versus $\log M_B$ gave an approximate straight line as shown in Figure 11, similar to the Wilke-Chang equation could be used to describe the experimental results.

$$D_{AB}(10^7)\mu = bM_B^a \tag{1}$$

where: D_{AB} = diffusion coefficient, cm.^{2}/sec.

= viscosity of solvent, cp.

M_B = molecular weight of solvent, g/g.-mole

a,b = constants

The constants, a and b were determined and found to be:

a = 1.225

b = 0.738

The diffusion coefficients calculated by means of equation (1) gave a maximum deviation of 6.2% from the experimental results as shown in Table VIII.

TABLE VIII

Comparison of Experimental and (Proposed) Theoretical Diffusivities

	$D_{AB}(10^5)$ cm.^{2}/sec.		
System	Experimental	Calculated	% Deviation
Ethane-Hexane	5.79	5.79	0
Ethane-Heptane	5.51	5.19	-5.6
Ethane-Octane	4.66	4.73	1.5
Ethane-Dodecane	2.73	2.90	6.2
Ethane-Hexadecane	1.95	1.84	-6.0

Although equation (1) was of essentially the same form as the Wilke-Chang equation yet there existed a considerable difference between the two. In the Wilke-Chang equation a power of 1/2 was specified for the molecular weight of solvent, M_B, whereas the power of M_B was calculated to be 1.225 from the experimental results. It was found that a better agreement between the predicted diffusion coefficients calculated with these two equations could not be obtained by assuming a different association parameter in the Wilke-Chang equation. The association parameter could be expected to equal one, otherwise ethane should be considered unassociated in the paraffinic solvents. It can be concluded, therefore, that the power of M_B as stated in the Wilke-Chang equation is incorrect at least for the normal paraffin systems studied here. The experiments performed were well suited to test the effect of the solvent molecular weight on gas diffusivity because the range of the solvent molecular weights was relatively large and by using the same gas the solute molar volume at its normal boiling point remained constant. In his review Himmelblau (2) suggested that the power of M in the Wilke-Chang equation appeared to be "an eye-ball choice". Further evidence showing that the power of M_B may not even be constant is available in the work of Groothuis and Kramers (42) who measured the diffusivities of sulphur dioxide in a series of normal paraffins from heptane to hexadecane. Their results, also plotted in Figure 11, indicate an even greater

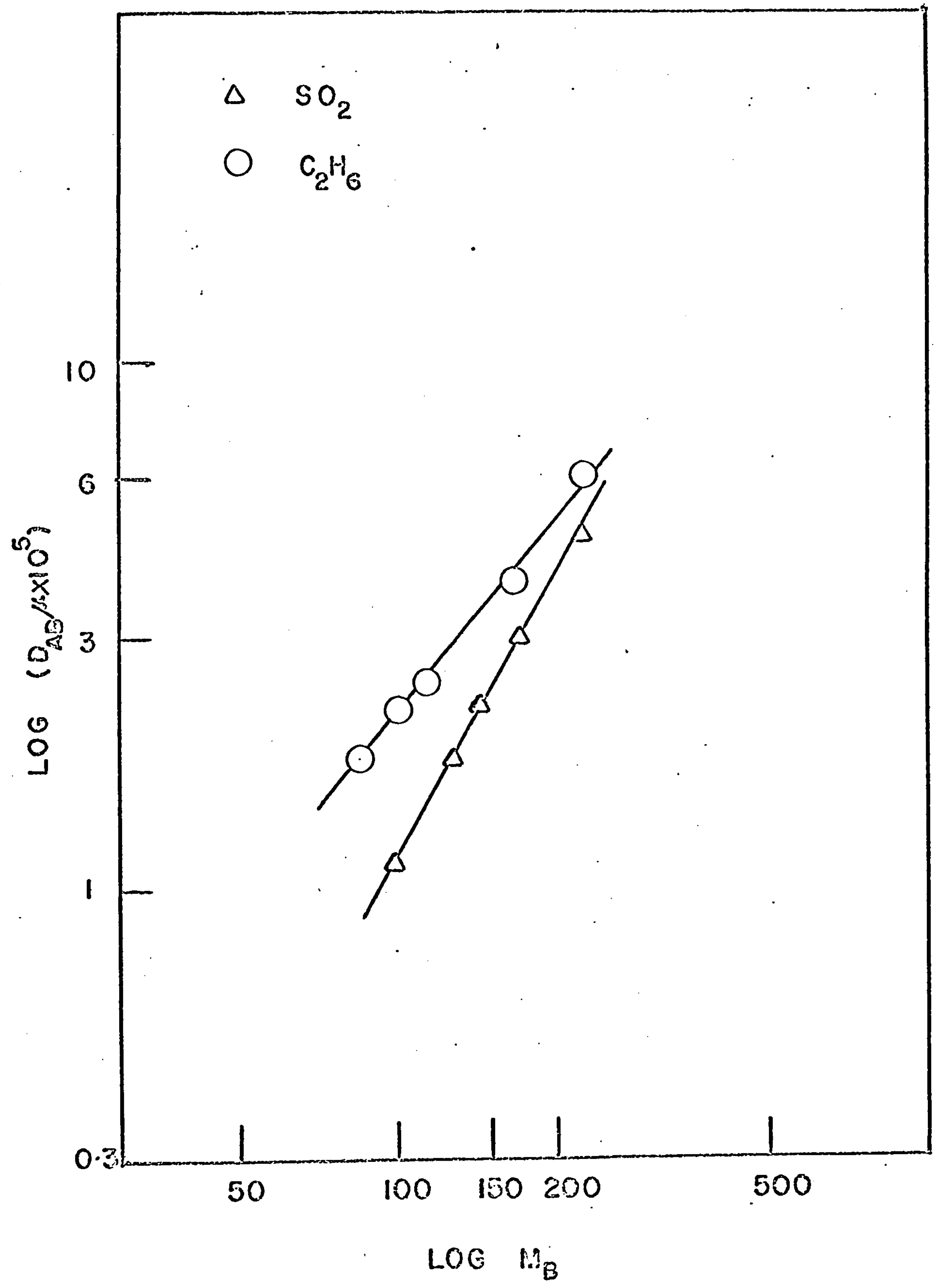

Figure 11. Log ($D_{AB}\mu$) vs. log M_B

power of the solvent molecular weight. Although the Wilke-Chang equation has been relatively successful in predicting liquid phase diffusivities it would appear that the equation should not be used indiscriminately especially for paraffinic solvents of high molecular weights.

Diffusivity of Ethane in Mixed Solvents

Pseudo-binary diffusivities of ethane in solutions of hexane and hexadecane have been calculated using equations (1), (2), (3), (4), (5) and (6) of the Experimental Results Section and listed in Table III. It could be seen that none of these equations is satisfactory in the prediction of diffusion coefficients of ethane in hexane-hexadecane solutions. Errors up to as much as 40% were obtained. Furthermore, a plot of log $(D_{1m}\mu_m)$ versus log (M_m) resulted in a curve, indicating that equations similar to that applicable to binary diffusion systems, equation (1), could not be used.

Cullinan and Cusick (43) proposed a predictive theory for diffusion coefficients in mixed solvents. The present system appeared to be ideal to test its validity. Unfortunately, since the diffusion coefficient of the solvent pair, i.e., diffusivity of hexane in hexadecane was not known, the predictive accuracy of the proposed empirical equations could not be determined.

Although Tang and Himmelblau (40) had studied gas diffusivity in several mixed liquid systems yet no empirical equations could be critically tested with the data they obtained. This was the result of the small differences in diffusivities of the gas in the respective liquids of which the solvent mixture was composed. In the systems studied here, on the contrary, the differences between the diffusivities, molecular weights, and viscosities of hexane and that of hexadecane were considerable. Hence, one might be in a better position to assess the validity of the empirical equations proposed. Among the five equations tested it appeared that equation (1) of the Experimental Results Section gave the best prediction of gas diffusivities as could be seen from Table III and Figure 8. The maximum deviation from the experimental value was about 19%. A further advantage of using equation (1) was that it did not require solution viscosities.

II. Gas Solubility

The system, oxygen-water, could not be used as a standard test of reliability as suggested by Battino and Clever (4) because the solubility was too low to be measured by the present apparatus which was designed for moderately soluble gases. Instead, the gas-liquid systems, carbon dioxide-ethanol, ethane-carbon tetrachloride and ethane-benzene were used as a test of the apparatus reliability. The solubility data are listed in Tables V and VI.

The solubility of carbon dioxide in ethanol, expressed in Ostwald coefficient, was determined experimentally to be 2.725, which agreed with the value published by Kunerth (41), to within 1%. A comparison of the experimental solubility for ethane in carbon tetrachloride with the literature value also showed a deviation of less than 1%. The solubility of ethane in benzene remained about 3% lower than that of Horiuti (17) in spite of many repetitions. The solubilities of ethane in heptane and in octane did not agree well with those of Gjaldback (16). The deivations were about 2.5 and 4%, respectively. Although such discrepancies are not uncommon for solubilities measured by different workers, they cannot be considered satisfactory for data of high accuracy. The sizable deviation in the solubility of ethane in octane might be attributed to the difficulty in ascertaining the true amount of liquid used since the tendency of an upward creeping flow was observed in liquid octane. In this research necessary steps had been taken to insure against such a possible error. Also, a closer examination of the method used by Gjaldback in determining ethane solubilities in normal paraffinic liquids revealed that the actual amount of solvent he used was only about 0.5 ml. In the present work, however, the solvent used was several times this quantity. Hence, under these circumstances the experimental results obtained here could be considered likely to be more accurate and the disagreement was ignored.

Of the systems studied for which solubility data were found in the literature only the system, carbon dioxide-ethanol, had been investigated by more than one worker. On the grounds that the experimental value for this system agreed with literature value to less than 1% and that an overall reasonably good agreement was obtained for all the systems compared, it was concluded that the solubility apparatus developed was capable of producing accurate data.

Both equations (13) and (14) from the regular solution theory (Theory Section) were found to be unsatisfactory in predicting the solubilities of ethane in paraffinic liquids. The mole fraction ethane solubility was found experimentally to increase from 0.0320 mole fraction for hexane to 0.0379 for hexadecane whereas equation (13) predicted a decrease in solubility with solvents of increasing carbon number. Although equation (14) predicted an increase, it gave values of 10 to 30% higher than those experimentally measured. The experimental and calculated solubilities are shown in Table V. The value of $\delta_2 = 6.6$ and $x_2^i = 0.327$ were used in equations (13) and (14) because they gave better agreement with experimental results as found by Gjaldback (16).

Further investigation indicated that the solubility of all gases in paraffinic liquids at 25°C. followed a definite pattern. When the logarithm of the mole fraction solubilities, available in literature, was plotted against carbon number (the number of carbon atoms per molecule of liquid solvent) straight lines were obtained as shown in Figure 12. If these lines were extrapolated they would all converge to a point which could be defined by a reference solubility, x_0, and a fictitious negative carbon number, C_{NO}. Consequently, provided that one solubility value in one paraffinic liquid was known the solubilities of that gas in any other paraffinic liquid could be calculated from the following equation:

$$\log \frac{x_{25}}{x_0} = A(C_N + C_{NO}) \qquad (2)$$

where:

x_{25} = mole fraction solubility at 25°C.

x_0 = reference mole fraction solubility at 25°C.

A = a constant, for one gas in all paraffinic liquids

C_N = number of carbon atoms in the paraffinic solvent

C_{NO} = fictitious reference carbon number

By computational methods the numerical values of C_{NO} was determined to be -115 and $x_0 = 0.0018$. The constants, A's, computed for each gas, solubility data together with the literature sources, solubilities calculated with equation (2), and the deviations between experimental and theoretical values are listed in Table IX.

It is evident from Table IX that equation (2) satisfactorily fitted the existing data since the maximum

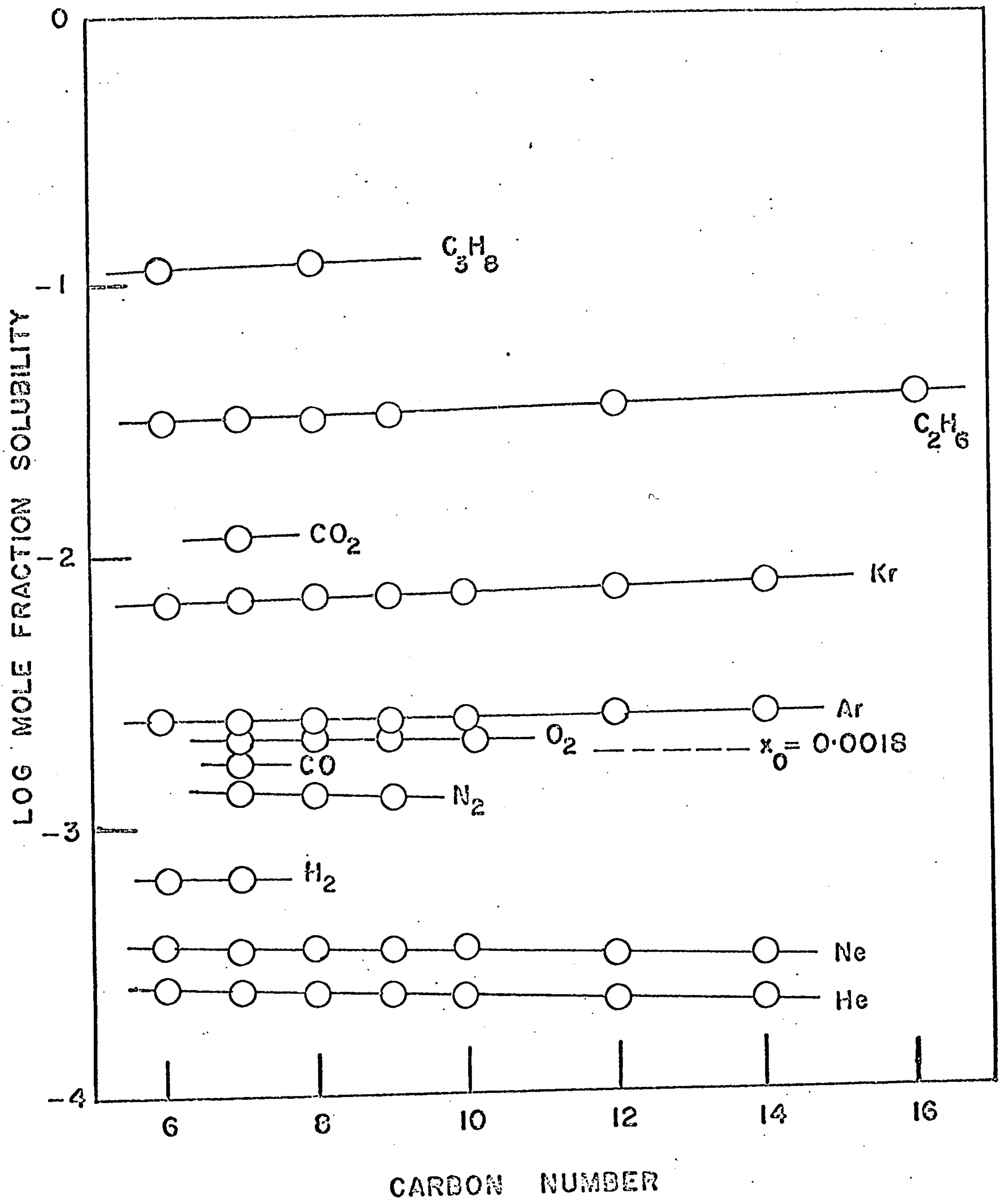

Figure 12. Log Mole Fraction Solubility vs. Carbon Number

TABLE IX

Solubility Variations with Carbon Number of Solvent

Gas	Carbon No. of Solvent	Solubility in Mole Fraction Calc.	Exp't	Ref.	% Deviation	Constant A
Propane	6	0.114	0.116	4	-1.77	0.0148902
	8	0.122	0.120	4	1.69	
Ethane	6	0.0312	0.0320	*	-2.72	0.01023536
	7	0.0319	0.0321	*	-0.64	
	7	0.0319	0.0329	3	-3.15	
	8	0.0326	0.0324	*	0.78	
	8	0.0326	0.0337	3	-3.38	
	9	0.0334	0.0336	3	-0.49	
	12	0.0359	0.0351	*	2.18	
	16	0.0394	0.0379	*	3.88	
Carbon Dioxide	7	0.0121	0.0121		0	0.0067829
Krypton	6	0.00696	0.00676	8	2.87	0.0048573
	7	0.00703	0.00716	8	-1.72	
	8	0.00712	0.00706	8	0.81	
	9	0.00720	0.00708	8	1.63	
	10	0.00728	0.00722	8	0.80	
	12	0.00744	0.00764	8	2.77	
	14	0.00761	0.00781	8	-2.77	

TABLE IX (cont'd)

Gas	Carbon No. of Solvent	Solubility in Mole Fraction Calc.	Exp't	Ref.	% Deviation	Constant A
Methane	6	0.00508	0.00508	50	0	0.00372389
Argon	6	0.00249	0.00253	8	-1.41	0.00117549
	7	0.00250	0.00250	8	0	
	8	0.00250	0.00245	8	2.32	
	9	0.00251	0.00248	8	1.39	
	10	0.00252	0.00255	8	-1.11	
	12	0.00253	0.00255	8	-0.56	
	14	0.00255	0.00259	8	-1.59	
Oxygen	7	0.00211	0.00216	7	-1.97	0.00058318
	8	0.00212	0.00209	7	1.45	
	9	0.00212	0.00212	7	0	
Carbon Monoxide	7	0.00173	0.00173	7	0	-0.00014120
Nitrogen	7	0.00131	0.00135	3	-2.66	-0.00111336
	8	0.00131	0.00131	3	0	
	9	0.000130	0.00128	3	2.16	
Hydrogen	6	0.000658	0.000651	7	1.18	-0.00360287

TABLE IX (cont'd)

Gas	Carbon No. of Solvent	Solubility in Mole Fraction Calc.	Solubility in Mole Fraction Exp't	Ref.	% Deviation	Constant A
Neon	6	0.000363	0.000380	8	-4.41	-0.00573261
	7	0.000359	0.000348	8	3.10	
	8	0.000354	0.000358	8	-1.00	
	9	0.000349	0.000350	8	-0.06	
	10	0.000345	0.000357	8	-3.41	
	12	0.000336	0.000324	8	3.63	
	14	0.000327	0.000324	8	1.05	
Helium	6	0.000252	0.000257	8	-1.66	-0.00704031
	7	0.000248	0.000249	8	-0.11	
	8	0.000244	0.000242	8	1.11	
	9	0.000240	0.000241	8	-0.09	
	10	0.000237	0.000239	8	-0.88	
	12	0.000229	0.000224	8	2.33	
	14	0.000222	0.000226	8	-1.78	

* indicate data obtained from present research

deviation was about 4%, realizing that a possible error of 1 to 2% might occur in each of the individual experimental measurements depending on the method used.

Temperature Dependence of Solubility

A similar pattern was observed when the variation in solubility of the same gases with temperature was investigated. Graphs of the logarithm of the mole fraction solubility versus the logarithm of the absolute temperature were found to be straight lines as shown in Figure 13, which could be extrapolated to converge at a point defined by a reference solubility, x_{TO}, and a fictitious temperature, T_o °K. A general equation for these straight lines could be derived readily by simple symmetry:

$$\log \frac{x_T}{x_{TO}} = \log\left(\frac{x_{25}}{x_{TO}}\right)\left(\frac{\log T_o - \log T}{\log T_o - \log 298}\right) \tag{3}$$

where: x_T = mole fraction solubility at temperature T(°K.)

x_{25} = mole fraction solubility at 25°C.

To avoid the introduction of too many constants the same reference solubility as in the case of solubility dependence on carbon number was tried, i.e., $x_{TO} = x_0 =$ 0.0018 mole fraction. Graphically, by approximation this reference was found to give the best fit of existing solubility data. Hence, substituting $x_{TO} = x_0$ into equation (3) the following expression was obtained:

$$\log \frac{x_T}{x_0} = A(C_N + C_{NO})\left(\frac{\log T_o - \log T}{\log T_o - \log 298}\right) \tag{4}$$

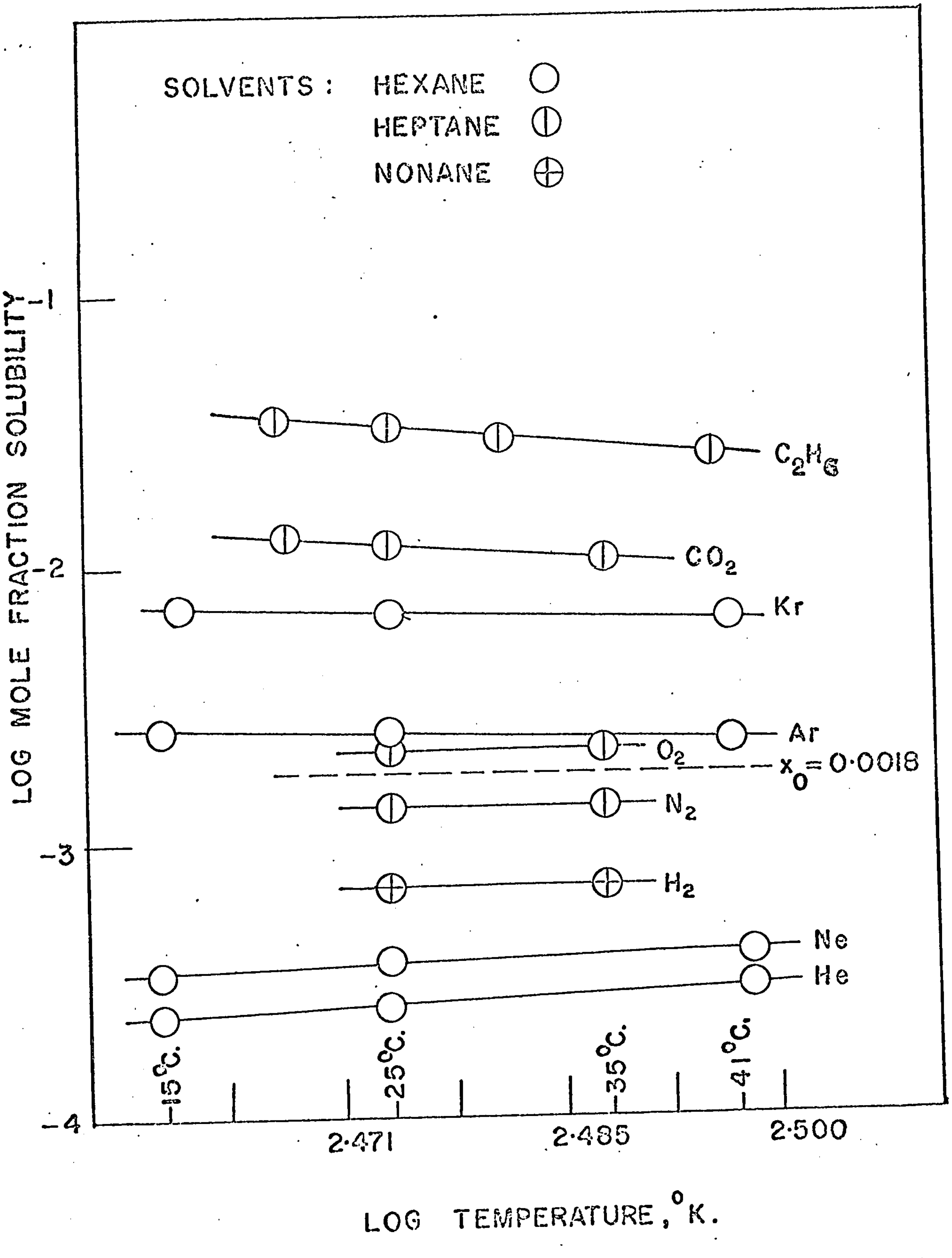

Figure 13. Log Mole Fraction Solubility vs. Temperature

By trial-and-error with the aid of a computer the fictitious reference temperature was found to be 573 °K. or 300 °C. A comparison of the calculated and experimental values together with the percentage deviations and the literature sources from which experimental data have been obtained, are tabulated in Table X.

It may be concluded that equation (4) is satisfactory for the predicting the temperature dependence of solubility, keeping in mind that any deviations in the calculations of A and C_{NO} by equation (2) will be accumulated in the deviations listed in Table X because these terms have been substituted to derive equation (4). The use of the constant, A, eliminates the necessity of basing the calculations on a single solubility measurement at 25°C. Several literature data points were not included in Table X because a plot of log x_2 versus log T did not give a straight line - a data accuracy test suggested by Hildebrand (44).

Although equations (2) and (3) have been developed on an empirical basis it is of interest to note that the reference temperature, T_o, is a temperature at which the molar solubilities of all the gases is the same and which is roughly the critical temperature of octane (595 °K.). For the reason that the solubility of all the gases is the same at a temperature roughly equivalent to the critical temperature the principle of corresponding states may be expected to apply. In other words, the

TABLE X
Solubility Variations With Temperature

Gas	Carbon No. of Solvent	Temp. °C.	Solubility in Mole Fraction Calc.	Exp't	Ref.	% Deviation
Ethane	6	30	0.02897	0.02990	*	-3.10
	7	20	0.03436	0.03420	*	0.46
		30	0.02964	0.03000	*	-1.18
		40	0.02570	0.02560	*	0.38
Carbon Dioxide	7	20.5	0.01263	0.01284	5	-1.60
		34.5	0.01103	0.01073	5	2.80
Krypton	6	15	0.00747	0.00748	8	-0.13
		41.8	0.00621	0.00640	8	-2.92
	7	15	0.00756	0.00759	8	-0.41
		41.8	0.00628	0.00638	8	-1.61
	8	15	0.00765	0.00752	8	1.69
		41.6	0.00635	0.00640	8	-0.77
	9	15	0.00774	0.00755	8	2.49
		41.8	0.00641	0.00652	8	-1.73
	10	15	0.00783	0.00759	8	3.16
		41.4	0.00649	0.00653	8	-0.60
	12	15	0.00801	0.00792	8	1.21
		41.4	0.00663	0.00691	8	-4.10
	14	15.2	0.00819	0.00834	8	-1.74
		40.95	0.00678	0.00703	8	-3.49

TABLE X (cont'd)

Gas	Carbon No. of Solvent	Temp. °C.	Solubility in Mole Fraction Calc.	Solubility in Mole Fraction Exp't	Ref.	% Deviation
Argon	6	15	0.00254	0.00260	8	-2.39
		41.8	0.00242	0.00237	8	2.41
	7	15	0.00254	0.00253	8	0.59
		41.8	0.00243	0.00243	8	0
	8	15	0.00255	0.00244	8	4.60
		41.6	0.00244	0.00241	8	1.24
	9	15	0.00256	0.00256	8	0
		41.8	0.00244	0.00242	8	1.04
	10	15.2	0.00256	0.00257	8	-0.15
		41.4	0.00245	0.00244	8	0.53
	12	15	0.00258	0.00260	8	-0.70
		41.4	0.00246	0.00255	8	-3.32
	14	15	0.00259	0.00265	8	-2.05
		41.4	0.00244	0.00250	8	-0.82
Oxygen	7	34.8	0.00210	0.00217	3	-3.49
	8	35.0	0.00210	0.00207	3	-1.50
Nitrogen	7	35	0.00133	0.00137	3	-2.84
	8	34.9	0.00133	0.00133	3	0

TABLE X (cont'd)

Gas	Carbon No. of Solvent	Temp. °C.	Solubility in Mole Fraction Calc.	Exp't	Ref.	% Deviation
Neon	6	15	0.000335	0.000336	8	-0.35
		41.8	0.000416	0.000404	8	2.99
	7	15	0.000330	0.000330	8	0
		41.8	0.000411	0.000396	8	3.81
	8	15	0.000325	0.000329	8	-1.02
		41.6	0.000405	0.000414	8	-2.04
	10	15.2	0.000317	0.000318	8	-0.23
		41.4	0.000395	0.000390	8	1.32
	14	15.2	0.000300	0.000300	8	0
		40.95	0.000375	0.000363	8	3.32
Helium	6	15	0.000228	0.000235	8	-2.90
		41.8	0.000298	0.000311	8	-4.18
	7	15	0.000224	0.000224	8	0
		41.8	0.000294	0.000295	8	-0.47
	8	15	0.000220	0.000217	8	1.62
		41.6	0.000288	0.000287	8	0.59
	9	41.8	0.000285	0.000287	8	-0.69
	10	15.2	0.000213	0.000204	8	4.69
		41.4	0.000279	0.000269	8	3.97
	12	15	0.000205	0.000200	8	2.98
		41.4	0.000271	0.000258	8	5.23

TABLE X (cont'd)

Gas	Carbon No. of Solvent	Temp. °C.	Solubility in Mole Fraction Calc.	Solubility in Mole Fraction Exp't	Ref.	% Deviation
Helium	14	15.2	0.000199	0.000210	8	-4.99
		40.95	0.000262	0.000260	8	0.89

* indicate data obtained from present research

solubility of all gases is the same at the solvent (or solution) critical temperature. In fact, a slightly better fit of the data could be obtained if the critical temperature of dodecane and hexadecane had been used for reference instead of the reference temperature, T_o. Unfortunately, as a result of insufficient solubility data over a wide temperature range, especially at temperatures closer to the solvent critical temperature, the applicability of the principle of corresponding states to this situation cannot be confirmed.

Solubility of Ethane in Hexane-Hexadecane Solutions

O'Connell and Prausnitz (45) studying thermodynamics of gas solubilities in non-ideal mixed solvents found that the deviation could be as much as 20% if ideal solution were assumed for a non-ideal solvent solution. Correction of non-ideality required the evaluation of Margules constants using the unsymmetric convention for activity coefficients. They also stated that in non-polar systems, the logarithm of the gas solubility at low pressures was, to a good approximation, a linear function of solvent composition. This statement was found applicable to the system, ethane in hexane-hexadecane, because the maximum error would be less that 3% if a straight line relationship were used, as shown in Figure 14.

Further investigation showed that the solubility of ethane in mixed solvents of hexane and hexadecane was

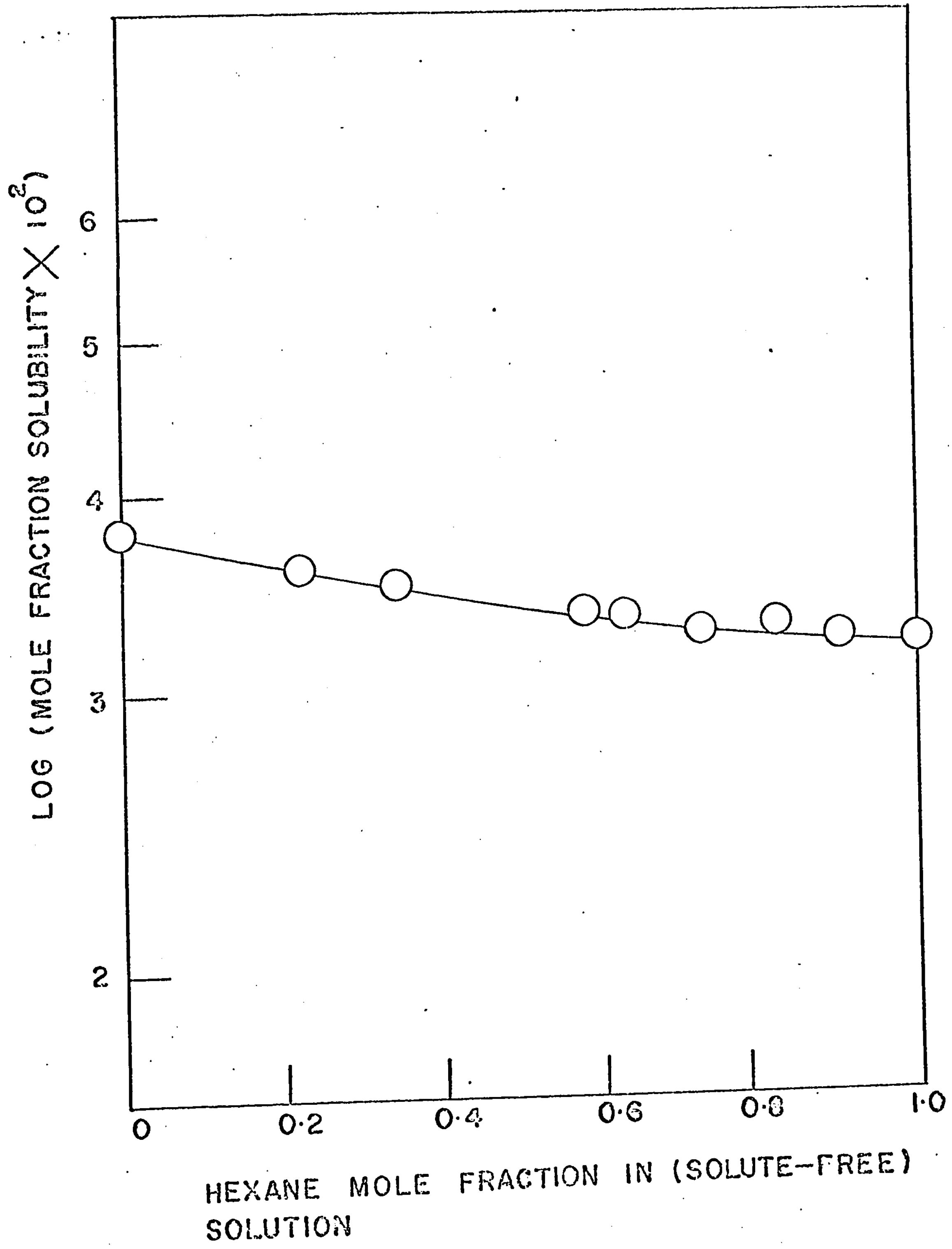

Figure 14. Log Mole Fraction Solubility vs. Solvent Composition

approximately linear functions of the hexane fraction in the solute-free solvent. A maximum deviation of 3% occurred when mole fraction ethane solubilities were plotted against hexane mole fractions (Figure 10). An even better fit of experimental data was obtained if the solubilities, expressed in Ostwald coefficients, were plotted against volume fractions (Figure 9). The maximum deviation amounts to only about 2% in this case.

Solution density measurements have shown than hexane and hexadecane form non-ideal solutions (Figure 6). Further evidence can be found in the work of Brønsted and Koefoed (46). However, the deviation from ideality was found to be quite small, in the order of 1 to 2%. Hence, Raoult's law was applied as an approximation in the vapor pressure calculations.

CONCLUSION

I. Diffusion of Dissolved Gases in Liquids

The diffusivity of ethane in a normal paraffinic liquid is a function of viscosity and molecular weight of the solvent. An empirical equation similar in form to the Wilke-Chang equation seems to give reasonable predictions of diffusivities of ethane in normal paraffinic liquids. The power of solvent molecular weight in the equation appears to be a variable depending on the solute gas rather than a fixed value of ½, when normal paraffinic liquids are used as solvents.

The semi-empirical equation (equation (1) of the Experimental Results Section), originally derived by Wilke (47) from the Stefan-Maxwell equations for the diffusion of a single gas into a stagnant multicomponent gas mixture, gives the best prediction of ethane diffusivities in hexane-hexadecane solutions among the equations tested. The maximum deviation is about 19% at a (solute-free) mole fraction of 0.453 in the solvent solution. An error of such magnitude can be expected since Himmelblau (2) in his review has stated that none of the existing empirical or semi-empirical equations is satisfactory in predicting the diffusion coefficients of dissolved gases in non-ideal mixed solvents.

II. Gas Solubility

The solubility apparatus developed was found capable of producing accurate data. The deviations of experimental results from literature values for the test system, carbon dioxide-ethanol, was less than 1%.

An extrapolation method of predicting gas solubilities in paraffinic solvents and at various temperatures is proposed. Theoretically, only one solubility determination, at 25°C. for example, is required to calculate the solubility of that gas at any temperature and in any paraffinic solvent by this method. The discovery of a better fit of experimental data by using the critical temperatures as reference for ethane in dodecane and in hexadecane, leads to the anticipation that the principle of corresponding states may apply. Accordingly, gas solubilities may possibly be calculated from the critical properties of the solvents. Unfortunately, as a result of insufficient experimental data, especially at higher temperatures, further research is required for the confirmation of the applicability of the principle.

The solubilities of ethane in hexane-hexadecane solutions can be correlated with the method of O'Connell and Prausnitz (45) to within 3%. Close approximations to experimental values (2 to 3%) can also be obtained by assuming that hexane and hexadecane form ideal solutions. The deviations from linearity can be considered approximate measures of non-ideality of the solvent solutions.

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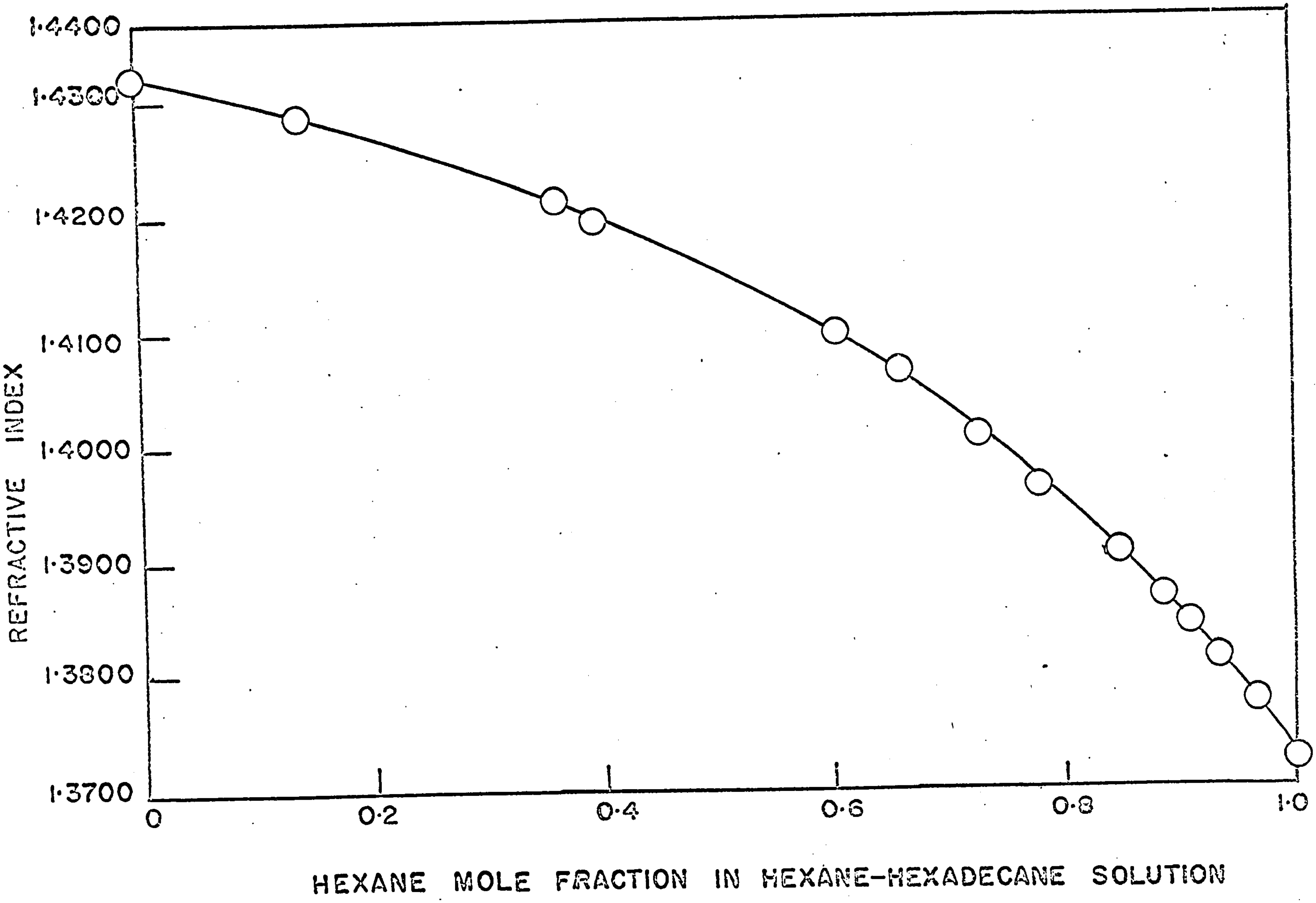
APPENDIX I

CALIBRATION DATA FOR COMPOSITION ANALYSIS OF HEXANE-HEXADECANE SOLUTIONS AT 25°C.

Mole Fraction Hexane	Refractive Index
0	1.43258
0.1423	1.42913
0.3675	1.42163
0.4008	1.42023
0.6072	1.41028
0.6620	1.40691
0.7303	1.40149
0.7794	1.39687
0.8507	1.39132
0.8892	1.38724
0.9108	1.38479
0.9332	1.38191
0.9657	1.37785
1.0	1.37258

I-2


1·4400
1·4300
1·4200
1·4100
1·4000
1·3900
1·3800
1·3700
REFRACTIVE INDEX
0
0·2
0·4
0·6
0·8
1·0
HEXANE MOLE FRACTION IN HEXANE-HEXADECANE SOLUTION

APPENDIX II

Raw Experimental Data for Diffusivity Measurements at 25°C.

Run No.: A-1

System: Ethane,n-Hexane

Bar. Pressure: 763.4 mm.Hg

Diffusion Path Length: 2.470 cm.

Time min.	Bead Position cm.
0	12.683
8	12.216
12	12.050
20	11.858
21	11.620
24	11.516
50	10.120
75	8.815

D = 5.62 x 10^{-5} cm.^{2}/sec.

Run No.: A-2

System: Ethane,n-Hexane

Bar. Pressure: 758.6 mm.Hg

Diffusion Path Length: 2.480 cm.

Time min.	Bead Position cm.
0	12.630
30	11.070
40	10.473
55	9.770
72	8.515
99	7.694
119	6.240

D = 5.88 x 10^{-5} cm.^{2}/sec.

Run No.: A-3

System: Ethane,n-Hexane

Bar. Pressure: 759.2 mm.Hg

Diffusion Path Length: 2.184 cm.

Time min.	Bead Position cm.
0	12.522
23	11.162
42	9.954
54	9.192
71	8.136
81	7.535

D = 5.94 x 10^{-5} cm.^{2}/sec.

Run No.: A-4

System: Ethane,n-Hexane

Bar. Pressure: 759.2 mm.Hg

Diffusion Path Length: 2.20 Km.

Time min.	Bead Position cm.
0	11.519
16	10.642
31	9.672
44	8.890
58	8.067
72	7.245

D = 5.81 x 10^{-5} cm.^{2}/sec.

Run No.: A-5

System: Ethane,n-Hexane

Bar. Pressure: 756.8 mm.Hg

Diffusion Path Length: 2.480 cm.

Time min.	Bead Position cm.
0	12.630
22	11.500
36	10.772
44	10.346
59	9.525
69	8.985
80	8.488

$D = 5.68 \times 10^{-5}$ cm.^{2}/sec.

Run No.: B-1

System: Ethane,n-Heptane

Bar. Pressure: 762.6 mm.Hg

Diffusion Path Length: 2.512 cm.

Time min.	Bead Position cm.2
0	9.535
10	9.065
28	8.255
44	7.610
72	6.336
80	5.955

$D = 5.56 \times 10^{-5}$ cm.^{2}/sec.

Run No.: B-2

System: Ethane,n-Heptane

Bar. Pressure: 757.7 mm.Hg

Diffusion Path Length: 2.632 cm.

Time min.	Bead Position cm.
0	12.545
10	12.063
24	11.524
34	11.140
49	10.474
58	10.120
71	9.553

$D = 5.50 \times 10^{-5}$ cm.^{2}/sec.

Run No.: B-3

System: Ethane,n-Heptane

Bar. Pressure: 748.2 mm.Hg

Diffusion Path Length: 2.437 cm.

Time min.	Bead Position cm.
0	12.074
35	10.540
53	9.673
100	7.530
112	7.022
125	6.419

$D = 5.46 \times 10^{-5}$ cm.^{2}/sec.

Run No.: C-1

System: Ethane, n-Octane

Bar. Pressure: 756.0 mm.Hg

Diffusion Path Length: 2.754 cm.

Time min.	Bead Position cm.
0	12.685
19	12.064
60	10.880
96	9.738
118	9.080
122	8.864

$D = 4.56 \times 10^{-5}$ cm.^{2}/sec.

Run No.: C-2

System: Ethane, n-Octane

Bar. Pressure: 764.4 mm.Hg

Diffusion Path Length: 2.152 cm.

Time min.	Bead Position cm.
0	11.432
25	10.480
45	9.699
54	9.335
66	8.871
75	8.517
87	8.065

$D = 4.69 \times 10^{-5}$ cm.^{2}/sec.

Run No.: C-3

System: Ethane, n-Octane

Bar. Pressure: 755.5 mm.Hg

Diffusion Path Length: 1.961 cm.

Time min.	Bead Position cm.
0	11.615
38	10.050
57	9.108
75	8.326
105	6.964
120	6.350

$D = 4.73 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-1

System: Ethane, n-Dodecane

Bar. Pressure: 758.5 mm.Hg

Diffusion Path Length: 2.590 cm.

Time min.	Bead Position cm.
0	12.710
22	12.394
63	11.800
72	11.637
85	11.482
110	11.100

$D = 2.67 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-2

System: Ethane,n-Dodecane

Bar. Pressure: 756.6 mm.Hg

Diffusion Path Length: 3.116 cm.

Time min.	Bead Position cm.
0	12.665
23	12.360
36	12.189
42	12.114
54	11.990
59	11.935
72	11.750
95	11.480

D = 2.73 x 10^{-5} cm.^{2}/sec.

Run No.:D-3

System: Ethane,n-Dodecane

Bar. Pressure: 756.6 mm.Hg

Diffusion Path Length: 2.923 cm.

Time min.	Bead Position cm.
0	11.935
27	11.579
36	11.477
46	11.328
56	11.184
80	10.875
96	10.700

D = 2.79 x 10^{-5} cm.^{2}/sec.

Run No.: E-1

System: Ethane,n-Hexadecane

Bar. Pressure: 762.8 mm.Hg

Diffusion Path Length: 2.368 cm.

Time min.	Bead Position cm.
0	12.821
56	12.235
76	11.994
174	11.025
292	9.871
348	9.368

D = 1.97 x 10^{-5} cm.^{2}/sec.

Run No.: E-2

System: Ethane,n-Hexadecane

Bar. Pressure: 762.8 mm.Hg

Diffusion Path Length: 2.680 cm.

Time min.	Bead Position cm.
0	12.414
26	12.177
118	11.376
180	10.850
238	10.316
289	9.990

D = 1.97 x 10^{-5} cm.^{2}/sec.

Run No.: E-3

System: Ethane,n-Hexadecane

Bar. Pressure: 742.2 mm.Hg

Diffusion Path Length: 3.076 cm.

Time min.	Bead Position cm.
0	10.908
79	10.278
138	9.890
219	9.291
300	8.672

$D = 1.92 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-1

System: Ethane,n-Hexane and n-Hexadecane

Solvent Comp.: 0.453 mole fraction n-Hexane
0.547 mole fraction n-Hexadecane

Bar. Pressure: 750.1 mm.Hg

Diffusion Path Length: 1.728

Time min.	Bead Position cm.
0	11.947
42	11.035
78	10.368
113	9.715
141	9.118

$D = 2.35 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-2

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.453 mole fraction n-Hexane
0.547 mole fraction n-Hexadecane

Bar. Pressure: 750.1 mm.Hg

Diffusion Path Length: 1.865 cm.

Time min.	Bead Position cm.
0	12.726
37	12.104
76	11.470
108	10.914
144	10.275

$D = 2.22 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-3

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.115 mole fraction n-Hexane
0.885 mole fraction n-Hexadecane

Bar. Pressure: 750.1 mm.Hg

Diffusion Path Length: 2.158 cm.

Time min.	Bead Position cm.
0	9.222
26	8.874
77	8.214
121	7.768
142	7.475
178	7.104

$D = 2.05 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-4

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.115 mole fraction n-Hexane
0.885 mole fraction n-Hexadecane

Bar. Pressure: 763.1 mm.Hg

Diffusion Path Length: 1.680 cm.

Time min.	Bead Position cm.
0	8.608
30	8.168
79	7.417
125	6.690
143	6.493
183	5.872

$D = 2.03 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-5

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.798 mole fraction n-Hexane
0.202 mole fraction n-Hexadecane

Bar. Pressure: 760.7 mm.Hg

Diffusion Path Length: 2.555 cm.

Time min.	Bead Position cm.
0	11.507
30	10.680
88	9.106
114	8.370
143	7.514
177	6.577

$D = 3.87 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-6

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.798 mole fraction n-Hexane
0.202 mole fraction n-Hexadecane

Bar. Pressure: 760.7 mm.Hg

Diffusion Path Length: 2.630 cm.

Time min.	Bead Position cm.
0	11.866
24	11.258
89	9.555
109	9.022
143	8.081
173	7.286

$D = 3.82 \times 10^{-5}$ cm.^{2}/sec.

APPENDIX III

Raw Experimental Data for Solubility Determinations

Run No.: G-1

System: Ethane,n-Hexane

Temperature: 25°C.

Bar. Pressure: 749 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.41	2
0.85	4
1.26	6
1.87	9
2.49	12
2.89	14

Ostwald coeff. = 6.12

Run No.: G-2

System: Ethane,n-Hexane

Temperature: 25°C.

Bar. Pressure: 754 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.41	2
0.82	4
1.24	6
1.86	9
2.90	14
3.29	16

Ostwald coeff. = 6.06

Run No.: G-3

System: Ethane,n-Hexane

Temp.: 25°C.

Bar. Pressure: 758 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.4	2
0.83	4
1.66	8
2.07	10
2.67	13

Ostwald coeff. = 6.09

Run No.: H-1

System: Ethane,n-Heptane

Temp.: 25°C.

Bar. Pressure: 767 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.38	2
0.77	4
1.17	6
1.77	9
2.36	12
2.77	14

Ostwald coeff. = 5.41

Run No.: H-2

System: Ethane,n-Heptane

Temp.: 25°C.

Bar. Pressure: 766 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.40	2
0.99	5
1.79	9
2.38	12
3.19	16

Ostwald coeff. = 5.38

Run No.: H-3

System: Ethane,n-Heptane

Temp.: 25°C.

Bar. Pressure: 756 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.60	3
0.80	4
1.40	7
1.79	9
2.19	11
2.58	13

Ostwald coeff. = 5.39

Run No.: I-1

System: Ethane,n-Octane

Temp.: 25°C.

Bar. Pressure: 758 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.42	2
0.84	4
1.26	6
1.47	7
1.89	9
2.31	11

Ostwald coeff. = 4.95

Run No.: I-2

System: Ethane,n-Octane

Temp.: 25°C.

Bar. Pressure: 751.4 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.42	2
0.83	4
1.27	6
1.69	8
2.11	10
2.53	12

Ostwald coeff. = 4.90

Run No.: I-3

System: Ethane,n-Octane

Temp.: 25°C.

Bar. Pressure: 749.2 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.22	1
0.43	2
0.86	4
1.27	6
1.69	8
2.11	10
2.53	12

Ostwald coeff. = 4.90

Run No.: J-1

System: Ethane,n-Dodecane

Temp.: 25°C.

Bar. Pressure: 754 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.53	2
1.32	5
1.85	7
2.64	10
2.93	11
3.48	13

Ostwald coeff. = 3.82

Run No.: J-2

System: Ethane,n-Dodecane

Temp.: 25°C.

Bar. Pressure: 756.3 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.53	2
1.34	5
1.86	7
2.38	9
2.92	11
3.73	14

Ostwald coeff. = 3.82

Run No.: J-3

System: Ethane,n-Dodecane

Temp.: 25°C.

Bar. Pressure: 756.3 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.79	3
1.31	5
2.10	8
3.15	12
3.69	14

Ostwald coeff. = 3.84

Run No.: K-1

System: Ethane, n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 753.5 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.94	3
1.88	6
2.51	8
3.44	11
4.07	13

Ostwald coeff. = 3.23

Run No.: K-2

System: Ethane, n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 755.5 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.91	3
1.53	5
2.49	8
4.05	13
4.37	14

Ostwald coeff. = 3.21

Run No.: K-3

System: Ethane, n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 755.5 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.62	2
1.26	4
1.89	6
2.51	8
3.12	10
4.09	13

Ostwald coeff. = 3.23

Run No.: L-1

System: Carbon Dioxide, Ethanol

Temp.: 25°C.

Bar. Pressure: 763.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.40	1
1.19	3
1.57	4
3.18	8
3.95	10
4.34	11
4.73	12

Ostwald coeff. = 2.71

Run No.: L-2

System: Carbon Dioxide, Ethanol

Temp.: 25°C.

Bar. Pressure: 762.2 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.39	1
0.77	2
1.16	3
1.54	4
3.52	9
3.80	10

Ostwald coeff. = 2.73

Run No.: L-3

System: Carbon Dioxide, Ethanol

Temp. 25°C.

Bar. Pressure: 747.6 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.79	2
1.64	4.2
2.34	6
2.71	7
3.89	10
4.66	12
5.44	14

Ostwald coeff. = 2.74

Run No.: L-4

System: Carbon Dioxide, Ethanol

Temp.: 25°C.

Bar. Pressure: 760.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
1.39	3.5
2.38	6
2.77	7
3.56	9
4.73	12
5.11	13

Ostwald coeff. = 2.71

Run No.: M-1

System: Ethane, Carbon Tetrachloride

Temp.: 25°C.

Bar. Pressure: 762.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.64	3
1.60	7.50
2.46	11.20
2.91	13.30
3.06	14.00
3.45	15.80

Ostwald coeff. = 5.35

Run No.: M-2

System: Ethane, Carbon Tetrachloride

Temp.: 25°C.

Bar. Pressure: 753.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.44	2.00
0.90	4.10
1.74	7.80
2.74	12.40
2.84	13.00
3.03	14.00

Ostwald coeff. = 5.37

Run No.: M-3

System: Ethane, Carbon Tetrachloride

Temp. 25°C.

Bar. Pressure: 763.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.21	1
0.86	4
1.30	6
1.51	7
1.75	8
1.96	9
2.18	10
2.42	11
2.65	12
2.86	13

Ostwald coeff. = 5.31

Run No.: N-1

System: Ethane, Benzene

Temp.: 25°C.

Bar. Pressure: 763.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.58	2
1.46	5
2.04	7
2.30	8
2.89	10
3.77	13
4.06	14
4.63	16
5.22	18
5.81	20

Ostwald coeff. = 3.98

Run No.: N-2

System: Ethane, Benzene

Temp.: 25°C.

Bar. Pressure: 766.5 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.28	1
1.18	4
1.45	5
2.03	7
2.62	9
3.22	11
3.80	13

Ostwald coeff. = 3.94

Run No.: N-3

System: Ethane, Benzene

Temp.: 25°C.

Bar. Pressure: 768 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.38	2
1.15	4
1.73	6
2.30	8
2.88	10
3.47	12
4.08	14
4.63	16
5.21	18
5.78	20

Ostwald coeff. = 3.98

Run No.: O-1

System: Ethane, n-Heptane

Temp.: 20°C.

Bar. Pressure: 749.1 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.36	2
0.69	4
1.07	6
1.42	8
1.80	10
2.16	12
2.52	14
2.89	16

Ostwald coeff. = 5.74

Run No.: O-2

System: Ethane,n-Heptane

Temp.: 20°C.

Bar. Pressure: 752.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.35	2
0.73	4
1.26	7
1.44	8
1.81	10
2.18	12
2.54	14

Ostwald coeff. = 5.73

Run No.: O-3

System: Ethane,n-Heptane

Temp. 20°C.

Bar. Pressure: 752.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.75	4
1.30	7
1.84	10
2.75	15
3.30	18
3.49	19

Ostwald coeff. = 5.76

Run No.: P-1

System: Ethane,n-Heptane

Temp.: 30°C.

Bar. Pressure: 753.5 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.40	2
1.05	5
1.50	7
1.70	8
2.11	10
2.55	12
3.19	15

Ostwald coeff. = 5.09

Run No.: Q-1

System: Ethane,n-Heptane

Temp.: 40°C.

Bar. Pressure: 756.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.54	2
1.34	5
1.86	7
2.66	10
3.17	12
4.24	16

Ostwald coeff. = 4.95

Run No.: Q-2

System: Ethane,n-Heptane

Temp.: 40°C.

Bar. Pressure: 756.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.76	3
1.80	7
2.59	10
3.35	13
4.41	17

Ostwald coeff. = 4.39

Run No.: R-1

System: Ethane,n-Hexane

Temp.: 30°C.

Bar. Pressure: 758.3 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.48	2
0.95	4
1.41	6
1.89	8
2.59	11
3.53	15

Ostwald coeff. = 5.74

Run No.: S-1

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.223 mole fraction n-Hexane
0.777 mole fraction n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 759.4 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.62	2
1.23	4
1.83	6
2.45	8
3.05	10
3.65	12

Ostwald coeff. = 3.47

Run No.: S-2

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.345 mole fraction n-Hexane
0.655 mole fraction n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 755.6 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.90	3
1.80	6
2.38	8
2.97	10
3.55	12
3.83	13
4.13	14

Ostwald coeff. = 3.68

Run No.: S-3

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.580 mole fraction n-Hexane
0.420 mole fraction n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 758.3 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.29	1
0.58	2
0.85	3
1.38	5
1.67	6
2.20	8
3.02	11

Ostwald coeff. = 4.18

Run No.: S-4

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.627 mole fraction n-Hexane
0.373 mole fraction n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 756.8 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.53	2
1.04	4
1.57	6
2.11	8
2.87	11

Ostwald coeff. = 4.32

Run No.: S-5

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.725 mole fraction n-Hexane
0.275 mole fraction n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 758.2 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.53	2
1.06	4
1.81	7
2.85	11
3.09	12
3.60	14
3.86	15

Ostwald coeff. = 4.58

Run No.: S-6

System: Ethane, n-Hexane and n-Hexadecane

Solvent Comp.: 0.820 mole fraction n-Hexane
0.180 mole fraction n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 757.6 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.70	3
1.18	5
1.90	8
2.83	12
3.57	15

Ostwald coeff. = 5.10

Run No.: S-7

System: Ethane,n-Hexane and
n-Hexadecane

Solvent Comp.: 0.904 mole fraction n-Hexane
0.096 mole fraction n-Hexadecane

Temp.: 25°C.

Bar. Pressure: 759.0 mm.Hg

Solution Volume c.c.	Vol. of Gas Absorbed c.c.
0	0
0.65	3
0.89	4
1.10	5
1.54	7
2.22	10
2.91	13
3.35	15

Ostwald coeff. = 5.42