MEASUREMENT OF GAS-LIQUID DIFFUSION COEFFICIENTS BY STEADY-STATE CAPILLARY CELL METHOD

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

in the

DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF OTTAWA

1968

Research Director

M.Sc. Candidate

ABSTRACT

A capillary cell apparatus was developed for the measurement of gas-liquid diffusivities. The diffusion coefficients of the systems carbon dioxide-water, methane-carbon tetrachloride, carbondioxide-ethanol, ethane-normal hexane, ethane-normal heptane and ethane-hexane, heptane mixtures were determined using this apparatus. Solubilities of ethane in n-hexane, ethane in n-heptane and ethane in mixtures of n-hexane and n-heptane were also determined.

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ACKNOWLEDGEMENT

The author wishes to express his gratitude to Dr. W. Hayduk, under whose supervision this work was undertaken, for his assistance and guidance.

Appreciation is also extended to Mr. G. Gasperetti for his willing assistance in the construction of equipment.

CHAPTER I

INTRODUCTION AND SCOPE OF RESEARCH

Molecular diffusion is a process by which matter is transported from one part of a system to another as a result of purely random molecular motions, with a net transfer from a region of higher concentration to one of lower concentration. This process takes place without the aid of mechanical stirring. When random molecular motion is the sole means of molecular transport, the rate of diffusion can be expressed by means of a diffusion coefficient, which is the proportionality constant between the rate of diffusion and the gradient of potential causing diffusion. Accurate diffusion coefficients are essential for the determination of mass transfer rates in the design of chemical process equipment. Such data is particularly useful for hydrocarbon systems because of their importance in the growing petroleum and petrochemical industries.

Diffusion coefficients can be broadly classified into: (1) differential coefficients, which represent conditions when diffusion occurs between two solutions of only differential concentration difference, and (2) integral coefficients, where diffusion occurs between two solutions of significant concentration difference and in which ordinarily a significant change in concentration difference occurs during the diffusion process. Since most experimental diffusion measurements have been made where both a concentration difference and a change in concentration difference were observed during the experiment, most reported coefficients are integral, in a strict sense. It is not possible, in general, to measure differential diffusion coefficients. Consequently their measurement is approached by making the concentration gradients small and assuming that the

measured coefficient is a differential coefficient for the mean of two starting concentrations. This is usually a valid assumption and yields a value within the experimental error of the measurements. In this work, integral diffusion coefficients have been measured.

There is yet no comprehensive liquid solution theory which can be used to predict diffusion coefficients accurately. The lack of sufficient and accurate data hinders such a development because it is not possible to verify suggested improvements. The main reason for the lack of extensive diffusivity data is the considerable experimental difficulty involved. The most common difficulties are:

(1) Elimination of convection within the path of diffusion - whether generated by thermal or mechanical means. Thus good temperature control as well as the absence of mechanical vibrations is important.

(2) Measurement of the transport of very small quantities of the diffusing substance.

This research involves the development of a simple but accurate method for the determination of gas-liquid diffusivities at atmospheric pressure. The diffusion coefficients of carbon dioxide in water, methane in carbon tetrachloride, carbon dioxide in ethanol, ethane in n-hexane, ethane in n-heptane and ethane in mixtures of n-hexane n-heptane have been determined. Solubilities of ethane in n-hexane, in n-heptane and in mixtures of n-hexane and n-heptane have also been determined. These solubility measurements were required for calculating diffusion coefficients.

CHAPTER II

METHODS FOR MEASURING GAS-LIQUID DIFFUSION COEFFICIENTS

The great variety of experimental methods used to measure diffusion coefficients is evidence that considerable ingenuity and effort have been spent in devising them. Almost all methods of measuring gas-liquid diffusivities either (a) measure the transfer of gas into or out of a liquid, or (b) measure concentration gradients along the path of diffusion.

The following are some of the more important methods:

A. Gas Absorption in a Steady State Laminar Flow Jet

Determination of diffusion coefficients by means of laminar jets consists of measuring the absorption rates of gases in liquids at very short periods of exposure. Laminar jets have been used by a number of investigators (1, 2, 3, 4, 5) and are usually formed by allowing the liquid to flow through a specially designed orifice plate fixed in a circular tube. For an isothermal, steady-state system in the laminar regime, the diffusion equation in the absence of chemical reaction is:

$$v \cdot \nabla c = \nabla \cdot (D \nabla c)$$

where v = liquid velocity

c = concentration of dissolved gas

D = diffusion coefficient

Solutions of this equation have been obtained by several authors (1, 2, 6) and are of the form:

$$G = 4\, c^{*}\, (D\, Q\, Z)^{1/2} \qquad \text{..... (1)}$$

where G = rate of absorption

c^{*} = saturation concentration

Q = liquid flow rate

Z = height of the jet

It is interesting to note that the rate of absorption is independent of diameter so long as velocity across any section is uniform and the length of free surface is not much different from jet height.

Measurement of diffusivities by means of laminar jets is widely used because there is no rippling at reasonable flow rates, end effects are small and contact time is so little that surface-active agents do not have time to adsorb on the surface. Jets are suitable for obtaining values for industrial work ($\pm$ 5 per cent) and with more care, data of $\pm$ 1 per cent precision can be obtained. In equation (1), the biggest single error-introducing factor is solubility (55). Even an error of one per cent in the value of solubility introduces an error of two per cent in the value of diffusivity.

B. Laminar Flow Around a Sphere

The technique of determining diffusivities by measuring the rate of gas absorption by a liquid flowing in the laminar region over a sphere is equivalent to using a short wetted wall column. It is a rapid method requiring only about one hour for each experiment. It has a general application to all sparingly soluble gases but is unsuitable for highly soluble gases because of heat and concentration effects (7).

In relation to errors due to solubility, the remarks that applied to laminar jets are equally applicable here. Moreover, the wetted

sphere methods have involved metering of very small flow rates of the solute gases and as Baird and Davidson have pointed out (8), extraneous factors such as aberrations of temperature within the gas space, can affect the apparent flow rates. Leakages can also be important. These problems are most serious for the least soluble gases and an examination of the results of Davidson and Cullen (7), and Baird and Davidson (8) reveals that the deviation from the results of Vivian and King (9) and Houghton (10) increases when the solubility decreases. Vivian and King used the diaphragm cell technique for their measurements. Houghton's method consisted in observing the rate of dissolution of small stationary bubbles.

C. Diaphragm Cells

In the diaphragm cell method, the gas in solution is allowed to diffuse through the pores of a sintered glass or metal disc into a solution of lower concentration. The concentrations on each side of the disc are maintained uniform by convective mixing for low-viscosity liquids and by mechanical stirring for more viscous ones. When the volume of solution on each side of the disc is sufficiently large, steady-state transfer conditions exist across the disc and the rate of transfer can be found by measuring the small changes in concentration on each side of the disc. Since neither the area, nor the length of the diffusion path can be determined by direct measurement, each cell has to be calibrated by a substance of known diffusivity. Moreover, the cell constant is a function of viscosity and therefore the calibration must be performed with a liquid of approximately the same viscosity as the one under investigation. The effective diameter of the pores in the diaphragm must be such that gross streaming through the diaphragm is avoided, but, at the same time, the pores must be

large in comparison with molecular dimensions. The extent of surface effects within the pores of the disc and their influence on the rate of transport of material, as well as their change with concentration and solvent is not fully understood. A good discussion of the diaphragm cell method is given by Gordon (11).

D. Rate of Solution of Small Stationary Bubbles

Diffusion coefficients can be determined by measuring the rate of collapse of bubbles smaller than 0.4 mm. in diameter, held stationary to an impermeable wall by surface tension forces. By observing the bubble diameter as a function of time, the diffusivity is obtained from the initial linear slope of a plot of bubble diameter squared vs. time. The initial rate of bubble collapse has been described by a quasi-steady state theory incorporating a theoretical geometrical factor to account for the retarding effect of the impermeable wall (12).

This method is simple and uses only the first power of solubility. Thus errors in solubility are not magnified. A factor that cannot be controlled is the small change in the shape of the bubbles as they collapse, but it is claimed that since the bubbles are very small, any deformation of the bubble shape from spherical will introduce negligible error.

E. Interferometric Techniques

The interferometric method for measuring diffusivities depends on the degree of dispersion of a beam of monochromatic light directed through a liquid solution. Changes of gas concentration in the liquid are observed as shifts of interference fringes. In most other methods, the experimental arrangements are such that liquid and gas are moved relative to each other. By using a stationary fluid, the possible

influence of motion is eliminated.

Interferometry is a delicate technique and requires expensive equipment, but can also give results of high precision.

F. Laminar Dispersion in a Capillary

A very recent method for measuring diffusion coefficients (13) involves imposing a known concentration change of solute gas on a fluid in laminar flow, which is passing through a long slender duct (capillary). The diffusivity can be obtained from measurements of the concentration distribution downstream from the injection point obtained by a mass spectrometer.

This method has been used to measure diffusivities of very slightly soluble gases e.g. helium, hydrogen and nitrogen in water, for which consistent results have been difficult to obtain. The method has certain advantages in that no gas-liquid interfaces are present, no calibration is necessary and knowledge of gas solubility is not required.

G. Capillary Cells

The general principle, in methods using capillaries, involves diffusion from the capillary into a much larger volume of solvent. Capillaries of uniform diameter, sealed at the bottom, are filled with a solution of known concentration. Since the volume in the capillary is so small compared to that in the vessel, the concentration in the latter may safely be assumed to remain constant during the experiment. At the end of an experiment, the diffusion coefficient can be determined if one can measure either the concentration gradient in the capillary or the total amount of material which remains in the capillary. The method fell into disfavour because of the length of experiments (several days) and the analytical difficulty of determining the amount

of solute in an extremely small volume of solution. The recent work of Johnson and Babb (14) and of Wang (15) has revived the method. Analytical difficulties have been largely overcome by the use of such devices as Geiger-Mueller counters and gas chromatographs equipped with hydrogen-flame ionization detectors (16).

Ringbom (17) modified Stefan's (18) original method by using an apparatus in which a gas-saturated and a gas-free solvent column, introduced from either end into a capillary, were separated by a pure gas phase. With the gas-saturated solvent connected to a large reservoir and the pure solvent fixed as a dead-end column of sufficient length, the volume of gas diffusing into the pure solvent was measured by observing the movement of the gas-saturated water column into the displaced gas space. The rate of shrinkage of gas volume in this unsteady-state absorption process gave a measure of the diffusion coefficient.

In both Ringbom's and Stefan's methods, the transient rates of diffusion were observed and from these, the diffusion coefficients could be calculated using the appropriate unsteady-state mathematical solutions.

H. Steady-State Diffusion Through Multiple Capillaries

Recently Ross and Hildebrand (19) used multiple capillaries for measuring diffusion coefficients. Several holes of 1 mm. were drilled through a steel circular plate of known thickness. The pure degassed solvent was forced into a vessel below the plate until it formed a shallow layer above it. The solute gas was introduced into the space above the plate which was connected to an open manometer. The partial pressures of the gas and solvent vapor were balanced by the barometric pressure. As diffusion proceeded, this pressure

balance was kept constant by raising the level of mercury in the manometer, the rise giving a measure of the amount of gas that had diffused into the liquid.

I. Proposed Steady-State Capillary Cell Method

An attempt has been made in this work to develop a simple method for measuring diffusion coefficients. This method does not require complicated analyses and the diffusion process can be described accurately and mathematically. The steady-state rate of diffusion is measured volumetrically using a moving bead. Thus the method does not require different analytical devices for different gases. The steady-state rate of diffusion is measured because it is easier to measure a constant absorption rate than a variable one. To make the volumetric method more precise, the cross sectional area of the capillary used for measuring the volume change of the gas is only a fraction (one-tenth) of the area of the column of liquid confined in the bigger capillary. The movement of the column of liquid resulting from bulk flow is negligible i. e. volume change on absorption is very small. A knowledge of gas solubility is required to calculate the diffusion coefficient from the absorption rate.

CHAPTER III

THEORY

No satisfactory method has yet been proposed for estimating diffusion coefficients in liquids from either basic molecular data or other physical properties. This is, no doubt, because of the lack of understanding of the liquid state which makes the basic premises of any proposed theory somewhat uncertain. The theories proposed so far have either lacked accuracy or are extremely complex. Rigorous theories have limited application unless extensive simplifications and approximations are made with the result that the complex bases of the theories are invalidated. From a practical point of view, more success has resulted by the use of a simple "model" structure which is known to be inexact but whose mathematical treatment is relatively simple.

Attempts to develop suitable expressions for diffusion coefficients have generally followed either a kinetic, hydrodynamic or thermodynamic approach.

Kinetic Theory of Arnold

By application of kinetic theory of gases to the liquid phase, Arnold (20) obtained an expression for diffusivity paralleling that obtained previously for gases:

$$D_{AB} = \frac{0.010\sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{(V_A^{1/3} + V_B^{1/3})^2} \cdot V_B$$

where D_{AB} = mutual diffusion coefficient of solute A in solvent B

M_A, M_B = molecular weights of A and B respectively

V_A, V_B = molecular volumes of A and B respectively

The three basic assumptions concerning collision rates were: (a) all collisions are binary involving only two molecules, (b) the collision rate is unaffected by the volume occupied by the molecules, and (c) intermolecular forces are absent. To account for the errors in these basic assumptions, a factor $A_A A_B V_B \eta_B^{1/2}$ (where η_B is the viscosity of the solvent) was inserted in the denominator. No adequate basis for predicting the abnormality factors A_A and A_B was developed (21).

Kinetic Theory of Eyring

Eyring and others (22, 23) have extended the theory of absolute rates to the problem of liquid diffusion and viscosity both of which phenomena are closely related. A liquid is regarded as made up of a continuum of matter interspersed with holes, and diffusion is described as a process in which molecules move from a given position into an adjacent hole in the liquid structure. The same energy is required to make a hole in the liquid the size of the molecule as the energy of vaporization per molecule. Movement of one layer of liquid relative to another requires the movement of molecules from one equilibrium position to another, for which it is necessary that a hole be available. This, in turn, requires the expenditure of energy to make the hole. These concepts lead to equations:

$$D = k e^{-E_{diff}/RT}$$

and

$$\eta = k e^{E_{vis}/RT}$$

where D = diffusion coefficient

η = viscosity

E_{diff} = energy of activation for diffusion

E_{vis} = energy of activation for viscosity

k = a constant, independent of temperature

R = gas constant

T = absolute temperature

Since k is independent of temperature, plots of log η vs. $\frac{1}{T}$ and log D vs. $\frac{1}{T}$ should give reasonably straight lines. The implication that because of the similarity of diffusion and viscosity phenomena, the energies of activation of the two processes should be the same, is not always supported by data (24, 25).

Hydrodynamic Approach

The hydrodynamic theory is based on Einstein's treatment of the Brownian movement of colloids (26), where the solute particle radius is much greater than the size of the molecule of the solvent. Assuming that Stokes' law defines the motion of the particles, we can arrive at the Stokes - Einstein equation:

$$D = \frac{k\,T}{6\pi\, r_A\, \eta}$$

where k = Boltzmann gas constant

r_A = particle radius

η = viscosity of solution

The theory is not exactly applicable because the assumption of Stokes' law which requires that the liquid through which the diffusing molecules move should be continuous, may not apply when the size of the molecules of diffusing solute actually approaches that of the solvent (21, 25).

Development from Irreversible Thermodynamics

The general equations for an irreversible process in a mixture of two components can be written as (27):

$$\vec{J}_A = L_{AA} \vec{X}_A + L_{AB} \vec{X}_B$$

$$\vec{J}_B = L_{BA} \vec{X}_A + L_{BB} \vec{X}_B$$

where $\vec{J}_A$, $\vec{J}_B$ = mass flow rates of components A and B

L_{AA}, L_{BB}, L_{AB}, L_{BA} = phenomenological constants

$\vec{X}_A$, $\vec{X}_B$ = driving forces

For the case of interdiffusion of two components, there are no cross-effects.

Therefore $\vec{J}_A = - \vec{J}_B = L_{AA} (\vec{X}_A - \vec{X}_B) = - L_{AB} (\vec{X}_A - \vec{X}_B)$

For the case with no external forces and no pressure gradients, the force difference is given by:

$$\vec{X}_A - \vec{X}_B = - \frac{1}{\omega_B} \left(\frac{\partial \mu_A}{\partial \omega_A} \right)_{T,P} \text{grad } \omega_A$$

where μ_A = chemical potential of A

ω_A, ω_B = mass fractions of A and B respectively

Comparing this with the usual diffusion equation $J = - D \text{ grad } \omega_A$, we have

$$D_{AB} = - \left(\frac{L_{AB}}{\omega_B} \right) \left(\frac{\partial \mu_A}{\partial \omega_A} \right)$$

Although phenomenological theory gives no indication of the form of L_{AB}, consideration of experimental diffusion results shows that it should be a function of concentration (27).

Engineering Correlations of Diffusion Coefficients

Several engineering correlations (28, 29, 30, 31) to estimate diffusion coefficients in dilute solutions have been suggested. They all contain one or more emperical factors evaluated from experimental data. Of these correlations, Wilke-Chang's is the one most widely used:

$$D_{AB} = \frac{7.4 \times 10^{-6} (XM)^{1/2} T}{\eta V_A^{0.6}}$$

where D_{AB} = diffusion coefficient of solute A in dilute solution in solvent B at temperature T, cm.^{2}/sec.

M = molecular weight of solvent

T = temperature, °K

η = viscosity of solution, cp

V_A = molal volume of solute at normal boiling point, cm.^{3}/g-mole

X = association parameter

Recently Reddy and Doraiswamy (32) have modified Wilke-Chang's equation. They consider two cases:

Case 1:

$$\frac{V_B}{V_A} \leq 1.5$$

$$D_{AB} = 10 \times 10^{-8} \frac{M^{1/2} T}{\eta V_A^{1/3} V_B^{1/3}}$$

Case 2:

$$\frac{V_B}{V_A} > 1.5$$

$$D_{AB} = 8.5 \times 10^{-8} \frac{M^{1/2} T}{\eta V_A^{1/3} V_B^{1/3}}$$

where V_B = molal volume of solvent at normal boiling point, $cm.^3/g\text{-mole}$.

Inspite of these several estimation methods, the predicted diffusivities vary from 30 per cent too low to as much as 100 per cent too high (33).

Effective Binary Diffusion Coefficients in Mixed Solvents

Many absorption and extraction processes employ mixed solvents instead of a pure one. The theoretical treatment of such multicomponent processes on a rigorous basis is very complicated. It is desirable to be able to define and employ an effective binary diffusion coefficient for the diffusing substance in mixed solvents by treating the mixed solvent as a pseudo pure liquid and defining the effective binary diffusion coefficient in a manner analogous to that for a binary coefficient in a pure solvent (34).

For a pure solvent, the diffusion coefficient is defined as:

$$N_A = - c D_{AB} \nabla x_A + x_A (N_A + N_B)$$

For mixed solvents:

$$N_i = - c D_{im} \nabla x_i + x_i \sum_{j=1}^{n} N_j$$

where c = molar density of solution

x = mole fraction

N_A, N_B = molar fluxes in a binary system

N_i, N_j = molar fluxes in a multicomponent system

D_{im} = effective binary diffusion coefficient in mixed solvent.

Basing his approach on the absolute rate theory, Himmelblau (35) arrived at several relations which permit the estimation of the effective binary diffusion coefficient from the binary diffusion coefficients of the solute in individual solvents:

$$D_{Am} \eta_m^{1/2} = x_B D_{AB} \eta_B^{1/2} + x_C D_{AC} \eta_C^{1/2}$$

and $$\log \left(D_{Am} \eta_m^{1/2} \right) = x_B \log \left(D_{AB} \eta_B^{1/2} \right) + x_C \log \left(D_{AC} \eta_C^{1/2} \right)$$

where D_{Am} = effective binary diffusion coefficient for diffusion of solute A in a mixed solvent

η_m = viscosity of mixed solvent

x_B, x_C = mole fractions of solutes B and C, where $x_B + x_C = 1$

η_B, η_C = viscosity of solvents B and C, respectively.

Holmes (36) suggested a relation that is very similar:

$$D_{Am} \eta_m = x_B D_{AB} \eta_B + x_C D_{AC} \eta_C$$

In case the mixed solvents form nearly ideal solutions, the following relations would also hold (34):

$$D_{Am} = x_B D_{AB} + x_C D_{AC}$$

$$\log \left(D_{Am} \right) = x_B \log \left(D_{AB} \right) + x_C \log \left(D_{AC} \right)$$

These relationships have not yet been adequately tested because of the lack of experimental data.

Effect of Temperature

The dependence of diffusion coefficient on temperature is usually related through the equation

$$\frac{D \eta}{T} = \text{constant}$$

This is suggested by Stokes - Einstein equation. The relation holds for most of the common systems but not when the viscosity is high (37). At high viscosities, the diffusivity is diminished less by increases in viscosity than predicted by this equation. The constancy of group $\frac{D\eta}{T}$ is supported by numerous data (12).

Effect of Solute Concentration

If it is assumed that the driving force for diffusion is chemical potential rather than concentration, the effect of solute concentration can be expressed as (38):

$$D = D^{\circ} \left(\frac{1 + \partial \ln f_A}{\partial \ln c_A} \right) \left(\frac{\eta_B}{\eta} \right)$$

where D = mutual diffusion coefficient in a binary system at a given composition

D° = D at infinite dilution

f_A = activity coefficient of solute A

c_A = concentration of A

η_B = viscosity of solvent B

η = viscosity of solution

If one is dealing with dilute solutions, the viscosity of the solution can be taken to be the same as that of the solvent and further $\frac{\ln f_A}{\ln c_A}$ is nearly equal to zero.

Hence $D = D^\circ$

Theory, therefore predicts that in dilute solutions, the change of diffusivity with solute concentration is not significant.

Theory of the Capillary Cell Method

In the capillary cell method, a column of deaerated liquid is confined in a capillary, one end connected to a reservoir of deaerated liquid and the other end exposed to dissolving gas. Enough time is permitted to establish a steady state. The bulk bulb is made sufficiently large so that the solute concentration in it is essentially constant. The flux of gas is measured by observing the displacement of a gas-saturated bead in the small capillary which is fused to the upper end of the large capillary. Provided no gas is transferred through the liquid bead in the small capillary, the change in volume of the gas in the cell can be directly related to the flux at the gas-liquid interface.

For the derivation of the appropriate equations, it is assumed that:

(1) The movement of the column of liquid (confined in the capillary) resulting from bulk flow is negligible i. e. volume change on absorption is very small. This was experimentally found to be true.

(2) End effects are negligible. End effects arise because of two reasons:

(a) actual interface is a curved surface whereas the flux is determined by assuming a cross-sectional area at right angles to the diffusion path.

(b) concentration of solute at the lower end of capillary may not be equal to the bulk concentration in the cell

It was seen that the end effects became negligible when the length of the diffusion path was 1.8 cm. or more. This point is discussed in greater detail in chapter IX.

Mass flux of species A relative to stationary axes is given by:

$$n_A = j_A + n\omega_A = j_A + (n_A + n_B)\,\omega_A$$

where n_A = mass flux of A relative to stationary axes, $\frac{gm_A}{(sec)(cm.^2)}$

n_B = mass flux of B relative to stationary axes, $\frac{gm._B}{(sec.)(cm.^2)}$

$n = n_A + n_B$, $\frac{\text{total gm. solution}}{(sec.)(cm.^2)}$

j_A = mass flux of A relative to mass average velocity, $\frac{gm._A}{(sec.)(cm.^2)}$

ω_A = mass fraction of A, $\frac{gm._A}{gm._{\text{solution}}}$

According to Fick's law:

$$j_A = - D_{AB} \frac{d \rho_A}{d y}$$

where ρ_A = mass concentration of A, $\frac{\text{gm. A}}{\text{cc solution}}$

y = direction of diffusion

Therefore $$n_A = - D_{AB} \frac{d\rho_A}{dy} + (n_A + n_B)\, \omega_A$$

Because there is no liquid flux at the interface, $n_B = 0$.

Hence $$n_A = - D_{AB} \frac{d\rho_A}{dy} + n_A \omega_A$$

or $$n_A (1 - \omega_A) = - D_{AB} \rho \frac{d\omega_A}{dy}$$

Where ρ = total mass concentration, $\frac{\text{gm. solution}}{\text{cm.}^3 \text{ solution}}$

Integration of this equation gives

$$D_{AB} = \frac{n_A L}{\ln \left(\frac{1 - \omega_{AL}}{1 - \omega_{A0}} \right) \cdot \rho}$$

where L = length of diffusion path, cm.

ω_{AL}, ω_{A0} = mass fractions of A in the bulk of liquid and at gas-liquid interface, respectively, $\frac{\text{gm. A}}{\text{gm. solution}}$

The concentration of solute in the cell was usually very nearly zero, but for the sake of accuracy its value could be determined by solving

the unsteady-state equation for diffusion described by Fick's second law:

$$D_{AB} \frac{\partial^2 \rho_A}{\partial y^2} = \frac{\partial \rho_A}{\partial t}$$

Boundary conditions are:

$$\rho_A (L, t) = \rho_{AL} \quad , \quad t > 0$$

$$\rho_A (0, t) = \rho_{A0} \quad , \quad t > 0$$

Initial condition is:

$$\rho_A (y, 0) = \rho_A \quad , \quad 0 < y < L$$

The total amount Q of gas, which diffuses in time t is given by (39):

$$\frac{Q}{L \rho_{A0}} = \frac{D_{AB} \cdot t}{L^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_1^{\infty} \frac{(-1)^n}{n^2} e^{-D_{AB} \cdot \frac{n^2 \pi^2 t}{L^2}}$$

where Q = amount of diffusing gas, $\frac{\text{gm. A}}{\text{cm.}^2}$

For the amount of time required to attain steady-state (about 24 hours for most of the cases, in the present investigation), even the first term of the exponential series is very small. The equation, for our purpose, therefore reduces to:

$$\frac{Q}{L \rho_{A0}} = \frac{D_{AB} \cdot t}{L^2} - \frac{1}{6}$$

The concentration of solute in the cell, ω_{AL}, can then be calculated, knowing the volume of solvent in the bulk and its density.
The solute mass fraction at the gas-liquid interface, ω_{A0}, can be deduced from a knowledge of solubilities. These have usually been reported in literature as Bunsen's or Ostwald's absorption coefficients.

SOLUBILITY

The solubility of a gas in a liquid at a fixed temperature and pressure has a definite value dependent only on the nature of the gas and the liquid. The ideal solubility can be calculated by Raoult's law and the difference between this and the actual solubility is attributed to deviations from ideal behaviour. There are very few gas-liquid pairs which form ideal solutions.

When a gas dissolves in liquid, there is an increase in the volume of the latter. It is necessary to know this change in volume on solution if one wants to express the solubility as Bunsen's or Ostwald's coefficient. To accurately evaluate the change in volume, partial molal volumes can be used provided this data is available. But this data is scarce. For moderately soluble gas-liquid pairs, where the concentration of solute in the solvent is of the order of 1 to 2 mole per cent, a correction for the increase in volume of the solvent can be made by assuming that the molar volumes of solute and solvent are additive. This has been done in this work and is considered accurate for relatively dilute solutions.

CHAPTER IV

SPECIFICATIONS AND PROPERTIES OF TEST FLUIDS

SPECIFICATIONS

The minimum specified purities for the fluids, together with the supplier are listed below.

Carbon dioxide: Carbon dioxide gas used in this research was supplied by Matheson of Canada and had a minimum purity of 99.5 per cent.

Methane: Methane gas was also supplied by Matheson of Canada and had a minimum purity of 99.0 per cent.

Ethane: Ethane gas was supplied by Matheson of Canada and had a minimum purity of 99.0 per cent.

Water: Distilled water was used as one of the liquids for diffusivity studies.

Ethanol: Ethanol was supplied by Canadian Industrial Alcohols and Chemical Limited and was 99.0 per cent pure.

Carbon tetrachloride: Carbon tetrachloride was supplied by Matheson Coleman and Bell. It was a spectroquality reagent with an ultraviolet absorption point of 265 millimicrons.

n-Hexane: n-Hexane was supplied by Matheson Coleman and Bell. It was a chromatoquality reagent with a minimum purity of 99.0 mole per cent.

n-Heptane: n-Heptane was also supplied by Matheson Coleman and Bell. It was a chromatoquality reagent with a minimum purity of 99.0 mole per cent.

FLUID PROPERTIES

The fluid properties used in the calculation of results were obtained from published sources. These properties, together with the source

from which they were obtained are shown in the following tables:

Vapor Pressure

Fluid	Temperature °C	Vapor Pressure mm Hg	Reference
Water	30	31.82	56
Carbon tetrachloride	25	114.50	57
Ethanol	30	78.06	58
n-Hexane	30	187.10	57
n-Heptane	30	58.35	57
n-Heptane	40	92.05	57

Density

Fluid	Temperature °C	Density g/cc	Reference
Water	30	0.9957	37
Carbon tetrachloride	25	1.5843	57
Ethanol	30	0.7810	58
n-Hexane	30	0.6505	58
n-Heptane	30	0.6751	58
n-Heptane	40	0.6665	58
Liquid ethane	30	0.3000	56

Viscosity

Fluid	Temperature °C	Viscosity cp	Reference
Water	30	0.8007	37
Carbon tetrachloride	25	0.8876	58
Ethanol	30	0.9910	58
n-Hexane	30	0.2780	58
n-Heptane	30	0.3640	58
n-Heptane	40	0.3330	58

Viscosities for mixed solvents were obtained by Souder's equation (25)

Molar Volumes at Normal Boiling Point

Fluid	Molar Volume cc/g-mole	Reference
Water	21	25
Carbon tetrachloride	102	25
Ethanol	63	25
n-Hexane	140	25
n-Heptane	162	25
Carbon dioxide	35	25
Methane	37.1	25
Ethane	63	25

SOLUBILITY

System	Temperature °C	Solubility Bunsen's Absp. Coeff.	Reference
Carbon dioxide-Water	30	0.664	59
Carbon dioxide-Ethanol	30	2.57	59
Methane-Carbon tetra-chloride	25	0.661	53

CHAPTER V

APPARATUS

The apparatus for measuring diffusion coefficient and for measuring solubility will be described separately.

Diffusion Apparatus (Figure 1)

The apparatus consisted of a constant temperature rectangular glass bath in which could be immersed the capillary diffusion cells. The temperature was maintained constant within $\pm$ 0.02° C by means of a thermoregulator. Heat was supplied by a heater and efficient stirring by an immersible pump. Cooling water running through an ordinary copper coil compensated for the heat generated by constant running of the pump and the heating coil used for temperature control. Gas was supplied from a high pressure cylinder. Provision was made to adjust the gas flow rate and pressure by means of a regulator, and to saturate the gas with the vapor of the liquid in a two stage bubbling device. The saturated gas passed through a gas manifold with stopcock connections to which capillary cells could be connected by pieces of tygon tubing. It was thus possible to operate either or both the cells. The gas was vented into the room through a pinchcock. The temperature of the water in the bath was read by means of a thermometer. The movement of a gas-saturated liquid bead in the capillary was measured by means of a travelling telescope.

Details of the Capillary Diffusion Cell (Figure 2)

The cell consisted of a capillary P, 0.0400 in. I.D. and about 4 cm. long, fused into a pyrex glass tee Q, the latter acting as a reservoir for deaerated liquid. The upper end of P was joined to a capillary R, 0.0130 in. I.D. and about 15 cms long. The two open ends of Q were fitted with vacuum stopcocks S and T. The volume

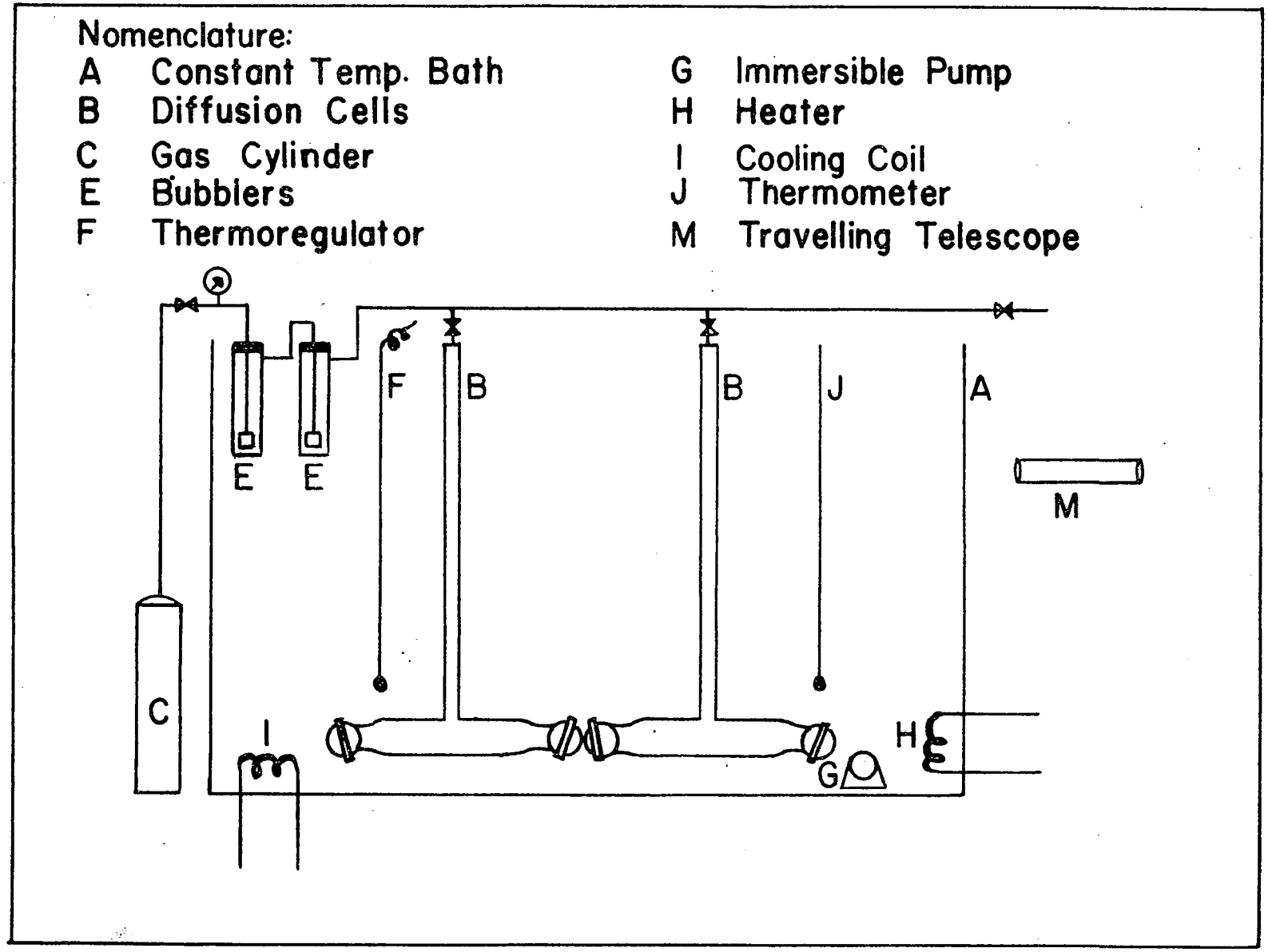

Figure 1. Apparatus for Measuring Gas-Liquid Diffusion Coefficients.

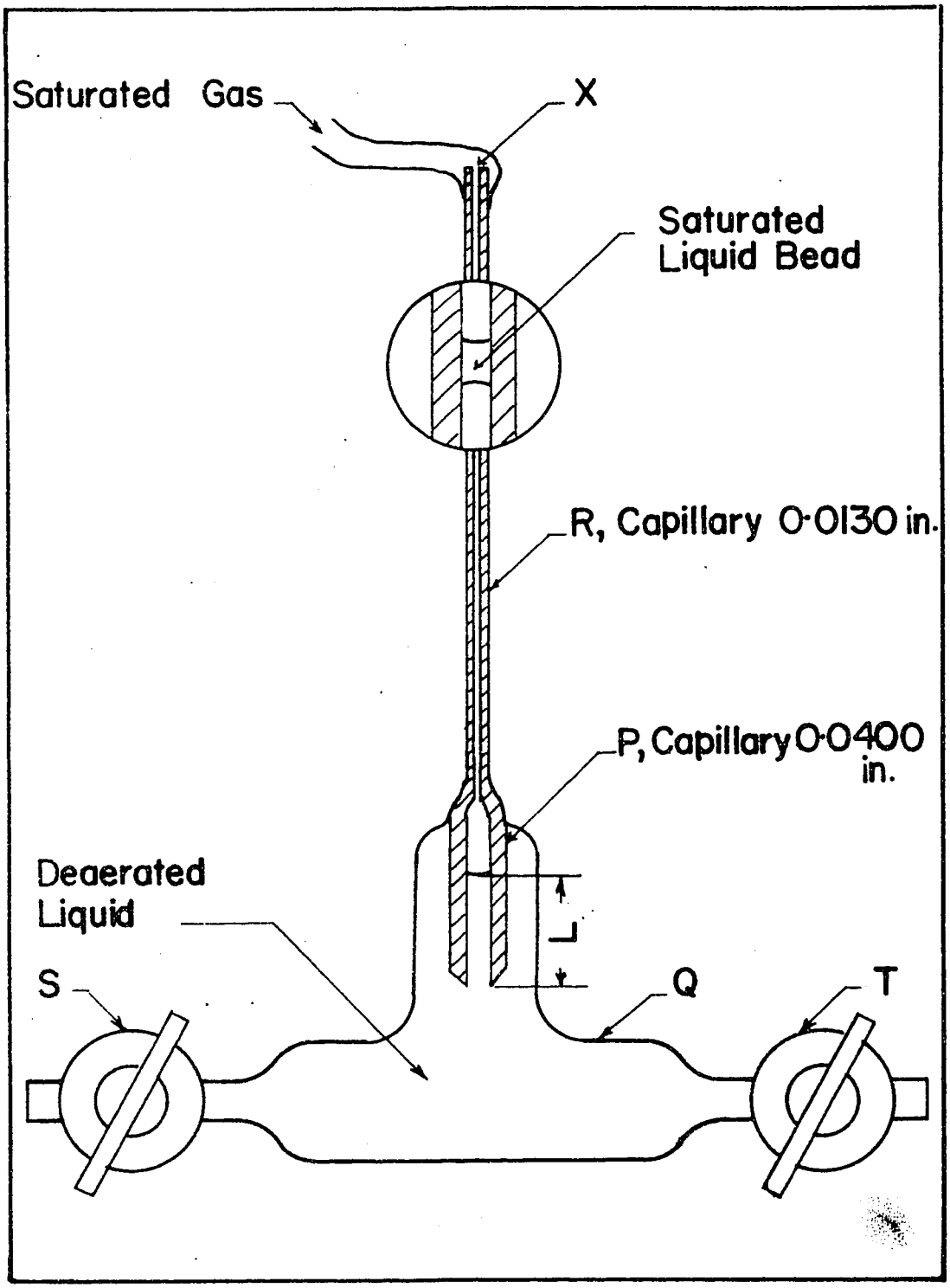

Figure 2. Capillary Diffusion Cell

enclosed by the tee was about 7 cc. This volume was arrived at with the following considerations in view:

1. Thermal equilibrium should be attained within a reasonable period of time.
2. The concentration of the solute gas in the liquid solvent should remain essentially constant over a sufficient period of time.
3. Convection caused in the confined liquid in the capillary P due to thermal expansion and contraction of the bulk liquid (i.e. thermal pumping) should be reduced, as far as possible.

The rate of movement of a gas-saturated liquid bead introduced at the top of capillary R was a measure of the flux of diffusing gas. Capillary R, with its smaller diameter, acted as a magnification device for this measurement. A comparison of the cross-sectional areas of the two capillaries shows that this magnification was about ten times, thus greatly reducing the duration of the experiment and increasing the precision of the measurements. The diameter of capillary P was not chosen more than 0.0400 in. because of the possibility of convection within the capillary. On similar lines, the diameter of capillary R was not made less than 0.0130 in. because of the possible sticking of the liquid bead to the walls of the capillary.

Deaerating Device

The deaerating device consisted of a glass column 1 in. diameter and about 5 ft. long fitted with a tubing-pinchcock combination at the lower end. The upper end of the column could be connected to a vacuum pump capable of creating an absolute pressure of 5 mm. of mercury. The lower end could be connected to the capillary cell for filling the latter.

Solubility Apparatus (Figure 3)

The apparatus used for measuring the solubilities of gases in liquids was the one recently used by Morrison and Billet (40). The suggested modification was carried out which made it suitable for use with more soluble gases (Ostwald's coefficients greater than 0.5). The apparatus was based on the flow of a liquid film through saturated gas and is much simpler to operate than the conventional Ostwald's apparatus.

The apparatus consisted of a spiral H to preheat or precool the solvent. A constriction in the form of an orifice was made at the end of the spiral, which enabled the solvent to be released drop by drop by adjusting the stopcock B. The lower end of spiral H was connected to another spiral C which was made up of nine coils of 6 mm. tubing, the coil diameter being 5 cms. This gave an effective length of about 140 cms. Preliminary work by Morrison and Billet established the fact that this length was sufficient for equilibrium between the film of liquid and gas to be established. The graduated gas burette D, of 25 cc. volume, was fused to the lower end of coil C and had a vacuum stopcock T at the bottom. The other burette E, also of 25 cc. was fused just above the spiral at point F, and its lower end was connected to the mercury levelling tube G, about 0.6 mm. diameter. The upper end of G was open to atmosphere and the lower end was connected to the mercury reservoir J which could be raised very gradually at an adjustable rate by means of a mechanical-screw device K, driven by a variable-speed motor. The whole apparatus, except the reservoir J, was enclosed in a water jacket R. Water from the constant temperature bath L flowed continuously through this jacket.

Gas from high pressure cylinder P, controlled by regulator Q

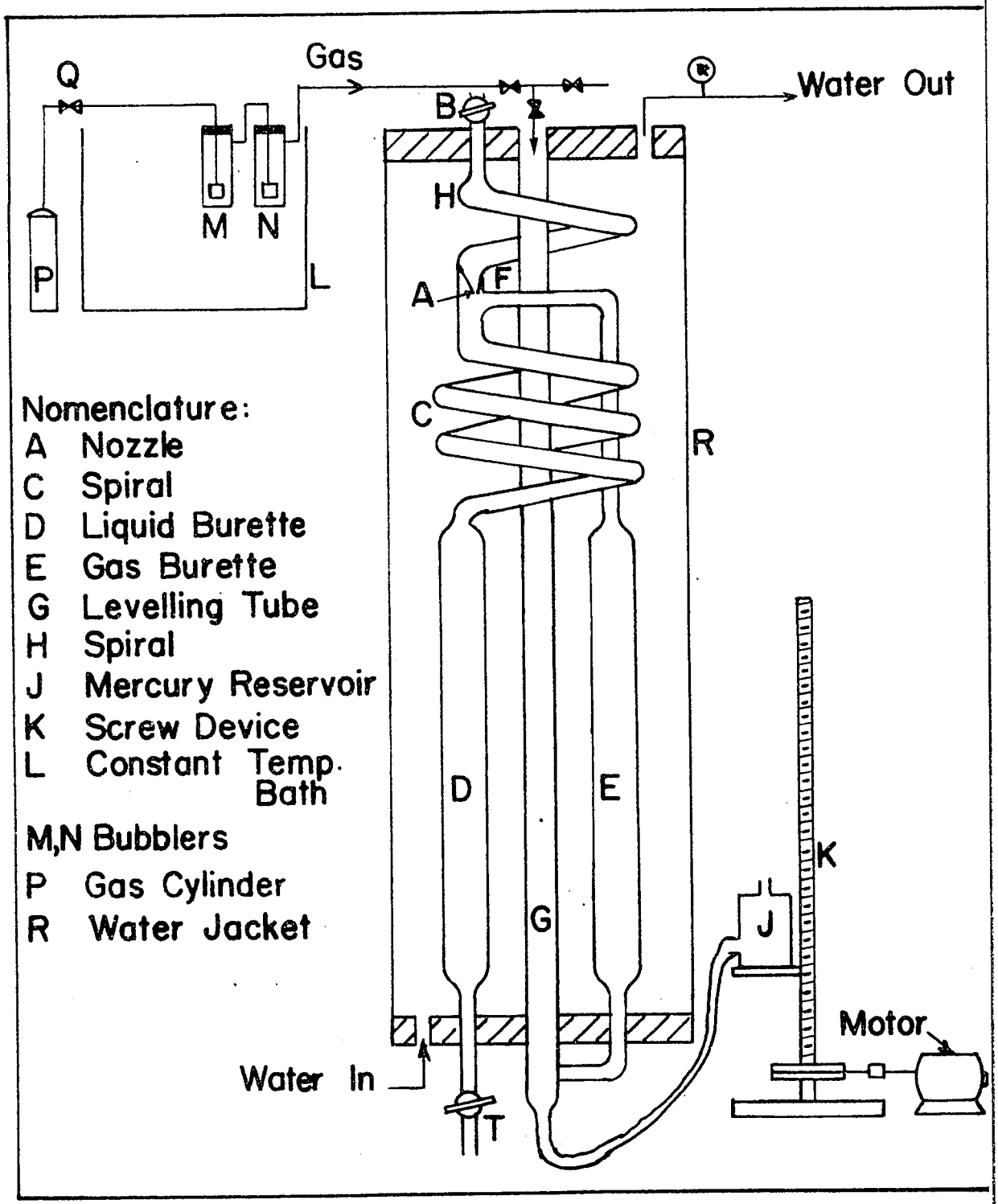

Figure 3. Solubility Apparatus

could enter the top of tube G after being saturated with the vapor of the liquid in the bubblers M and N.

Materials of Construction

The solubility apparatus, the capillary cell, the gas manifold, the bubblers, the deaeration column as well as the stopcocks were all made of pyrex glass. All connecting tubing was of tygon.

CHAPTER VI

PROCEDURE

A. PROCEDURE FOR THE MEASUREMENT OF DIFFUSIVITY:

The procedure for measuring diffusion coefficients is described in three sections. In the first section, the procedure is described for pure solvents, in the second for the special case of water as the solvent and in the third for a solvent composed of a mixture of hexane and heptane.

General Procedure for Pure Solvents

Prior to use, the capillary cell was cleaned by means of chromic acid solution and was then flushed several times with water to ensure that all the chromic acid was washed away. Finally it was rinsed with acetone and dried with gas.

A stream of gas from the high pressure cylinder was passed through the bubblers for a sufficient period of time to drive out the air. Because the rate was low, it could be expected that the outcoming gas was saturated with the vapor of the liquid. The capillary of the cell was fitted with a piece of tygon tubing and a pinch-clamp. The cell was thoroughly purged by allowing saturated gas to flow into one stopcock and out of the other, and subsequently out through the capillary, while the outlet stopcock was kept closed. This operation took about ninety minutes. The pinch-clamp and the stopcock were then closed to confine the gas within the cell.

The solvent was deaerated by boiling in the glass column at an absolute pressure of about 5 mm. of mercury. The height of the liquid in the glass column was about four feet. Water was deaerated for about 90 minutes, while the organic liquids were deaerated for about 45 minutes. Slight heating of the liquid was provided by wrapping a

heating tape around the deaerating column. At the end of boiling period, the top surface of liquid was exposed to atmosphere. Since the height to diameter ratio of the column was considerable (about fifty), it would take a long time for air to diffuse through an appreciable depth of the liquid and hence the liquid at the bottom of the column was considered to be essentially gas-free for the duration of the filling operation.

The capillary cell was filled with the liquid by connecting it to the bottom of the deaerating column and allowing the liquid to flow into it by gravity. Care was taken to see that no gas bubble was entrapped along the cell walls. The pinchcock at X was kept closed, otherwise liquid would flow all the way down the capillary and would wet the walls. The extent of wetting might not be the same each time, causing irreproducibility of results. When the cell was full of the solvent, 150 cc more (about twenty times the cell volume) of the latter were allowed to flow through, which ensured that the ultimate liquid confined in the cell was essentially gas-free. The stopcocks were then closed in such a manner that a suitable length of the solvent liquid was confined in capillary P. This length depended on the expected contraction or expansion of the liquid column due to the difference in the room temperature and the temperature of the experiment. Once filled, the cell was disconnected from liquid supply and the upper end of capillary R was immediately connected to the gas manifold. The capillary cell was next immersed in the bath. The height of the liquid column in the capillary was adjusted to become about 2 cms by draining out some of the liquid through one of the stopcocks. This was a delicate operation because only a fraction of a drop had to be drained.

A small stream of liquid-saturated gas was permitted to flow continually through the gas manifold to maintain an atmosphere of saturated gas at the end of the capillary. It was seen that the thermal equilibrium was attained within a couple of hours, as evidenced by the lack of any further expansion of the liquid. However, it took several hours for getting a steady-state concentration profile along the diffusion path. The approximate time required could be estimated by the relation $\frac{Dt}{L^2} = 0.45$, where D is the diffusion coefficient, t the time and L the length of the diffusion path (39). In practice, 1.25 times the above period was allowed before proceeding further with the experiment. A small quantity of the gas-saturated solvent was then extracted from the bubbler E in a syringe and a bead (about 1.5 mm. long) of this liquid was introduced at the top of the capillary. As the diffusion of the gas into the liquid proceeded, this bead moved and its movement was noted with time by means of the travelling telescope. Movement of the bead was plotted against time and a straight line resulted. From its slope and the cross-sectional area of the capillary, the flux of gas could be calculated.

The length of the diffusion path was measured both before and after the experiment. No change was observed, which showed that the volume change on mixing in the liquid was negligible. This was to be expected because the amount of solute gas absorbed was really very small.

Modification of the Procedure for Water as the Solvent

It was observed that when a water bead was introduced into the capillary, it tended to stick and did not move easily, probably due to the high surface tension of water. Addition of a small amount of a surface active agent (n-butanol) did not produce an appreciable

improvement. Hence it was decided to use a liquid whose surface tension was smaller and whose vapor pressure at the temperature of the experiment was negligible. Secondary octyl alcohol, with a surface tension of 27.53 dynes per cm. at 20° C and a vapor pressure of 1 mm. of mercury at 32.8° C answered these requirements well. The bead of liquid was, as usual, saturated with the gas before being introduced into the capillary. Because of the low vapor pressure of secondary octyl alcohol, its bead had no tendency to evaporate. Nor did any appreciable amount of water diffuse into the bead, as deduced from the fact that the length of the bead remained constant throughout its travel along the capillary length.

Modification of the Procedure for Mixtures of Hexane and Heptane as Solvents

If the general procedure for saturating the gas with the vapor of pure solvent was followed for mixed solvents, the composition of the liquid (and consequently the vapor as well) would change continually because of the faster evaporation of the more volatile component. Therefore, for mixed solvents, the bubbler liquid was prepared in such a way that it was richer in the more volatile component as compared to the liquid to be confined in the capillary cell. Hence when the purging ended, the gas mixture confined in the capillary was approximately of the right composition. An analysis of the bubbler liquid before and after the experiment showed a change of about 8 mole-per cent.

B. PROCEDURE FOR THE MEASUREMENT OF SOLUBILITY:

The solubility apparatus was initially evacuated to remove air and then saturated gas was allowed to flow from the bubblers through the apparatus for a period of about one hour. A small amount of

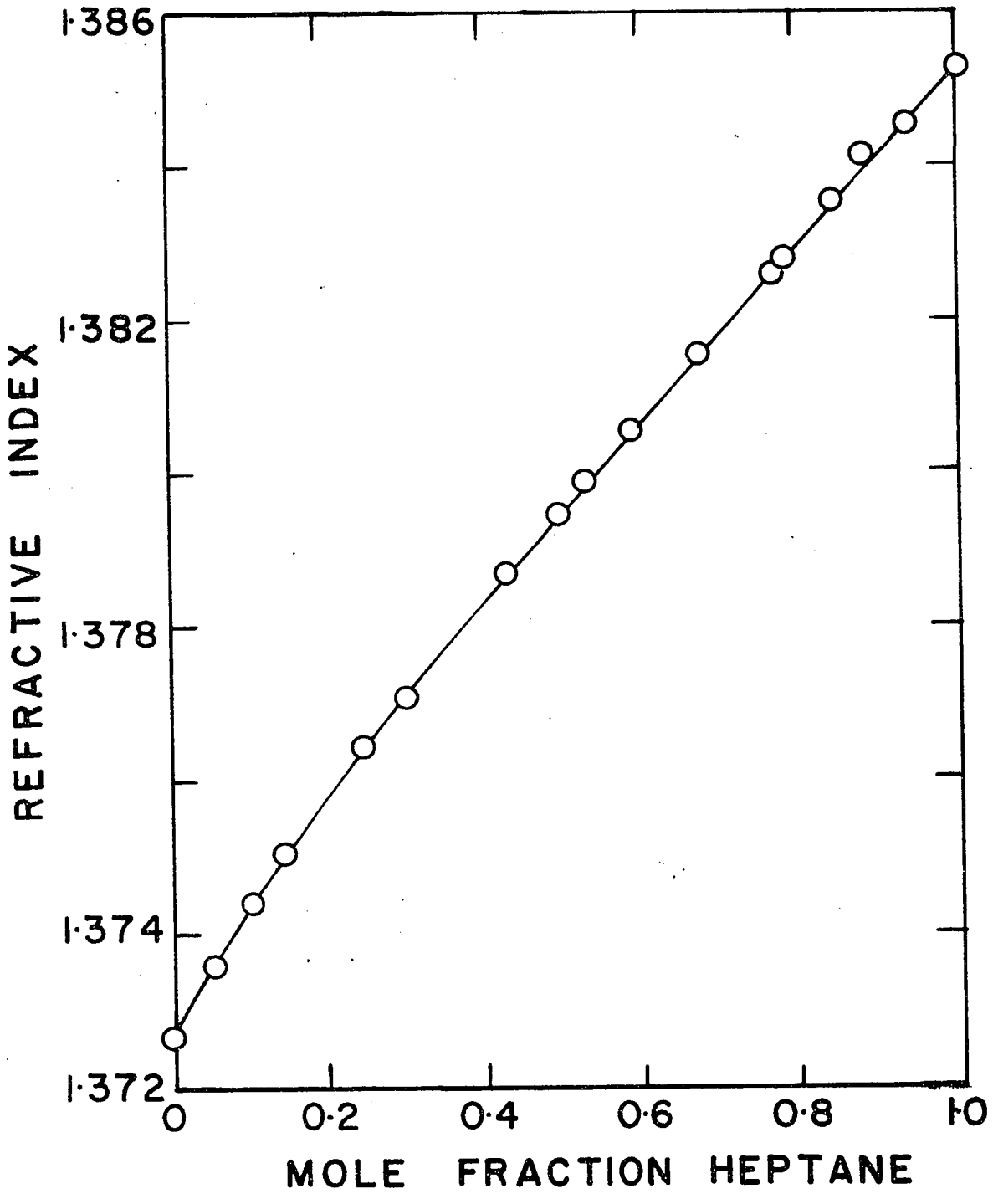

Figure 4. Calibration Curve for n-Hexane, n-Heptane Mixtures.

deaerated liquid was flushed through the spiral and drained through stopcock T. Then the liquid flow through the orifice was adjusted to about 0.05 cc per minute, the stopcock T was closed, the pressure of the gas in the apparatus was adjusted to atmospheric and was kept constant by raising the mercury reservoir by means of the mechanical-screw device. The speed of the motor was adjusted so that the mercury in the levelling tube and the gas burette always remained at equal level, within 1 mm. The mercury level in E and the level of collected liquid in D were recorded at regular intervals and a graph was plotted between the two. Its slope, after appropriate correction, gave the solubility in terms of cc of gas per cc of solution.

C. PROCEDURE FOR ANALYSIS OF MIXTURES OF HEXANE AND HEPTANE:

Refractive index was the basis for determining the composition of hexane-heptane mixtures. The refractive indices of hexane-heptane mixtures of known composition were measured at 25° C using Bausch and Lomb Abb-3 precision refractometer. A calibration curve drawn from these measurements was used for subsequent analyses and is shown in Figure 4. This corresponds to the data given in Appendix I.

CHAPTER VII

TREATMENT OF DATA

DIFFUSIVITY MEASUREMENTS

The slope of the plot of bead travel vs. time enables one to find the flux of solute gas, n_A. A typical plot is shown in Figure 5.

Making use of the ideal gas law, the flux of gas through the gas-liquid interface could be calculated from the following equation:

$$n_A = \frac{A_1 \, h \, p_A \, M}{A_2 \, RT}$$

where n_A = flux of gas, $\frac{\text{gm.}}{(\text{cm.}^2)(\text{sec.})}$

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

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

h = rate of movement of liquid bead, cm./sec.

p_A = partial pressure of gas, atmospheres

M = molecular weight of gas

R = gas constant, (cc) (atmosphere)/(g-mole)(°K)

T = temperature of the experiment, °K

If α is the Bunsen's absorption coefficient, the solubility, w_{A0}, expressed in mass fraction was given by:

$$w_{A0} = \frac{\frac{p_A \, \alpha \, M}{T° \, R}}{\rho_+ \frac{p_A \, \alpha \, M}{T° \, R}} \qquad \frac{\text{gm. solute}}{\text{gm. solution}}$$

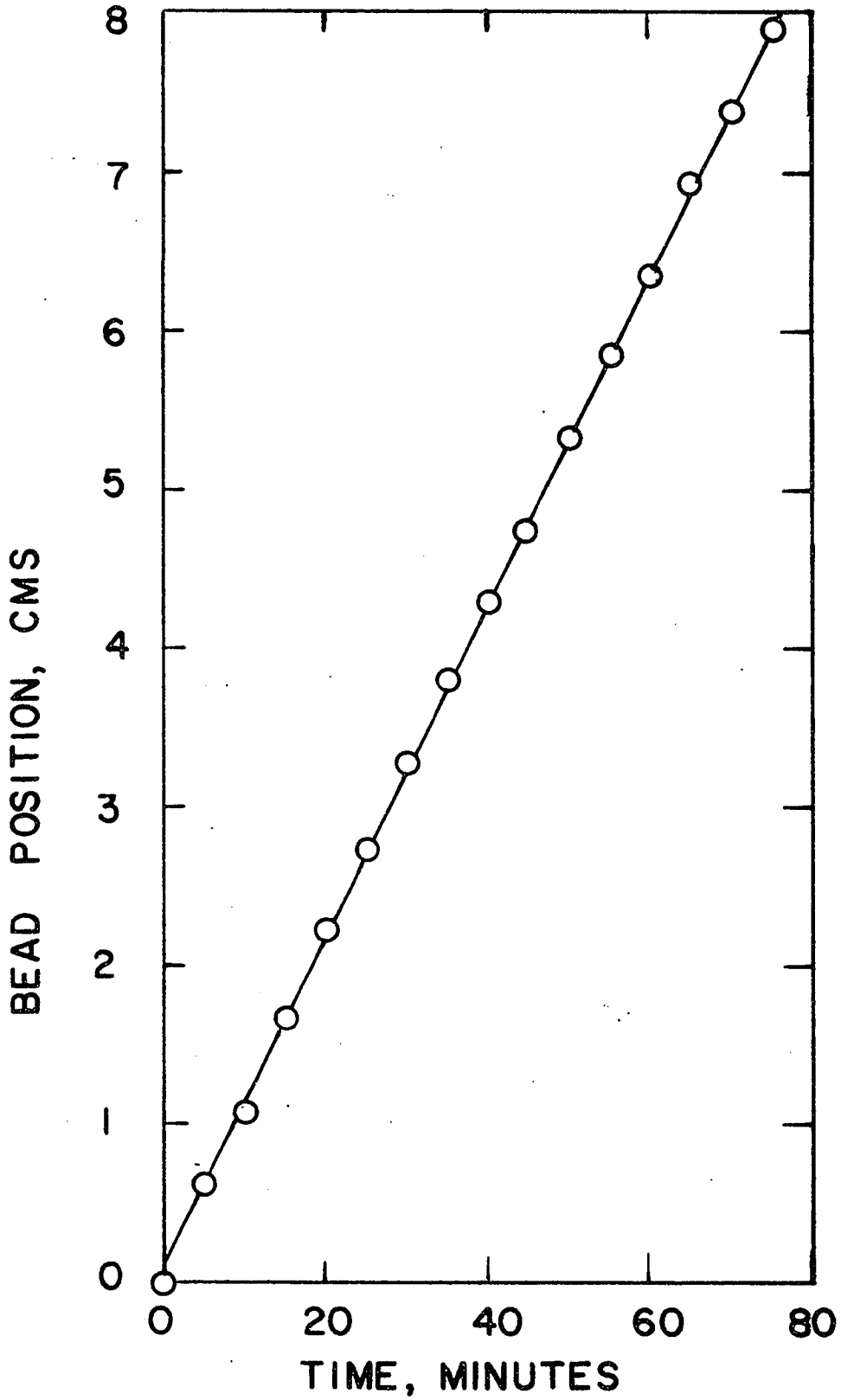

Figure 5. Change of Bead Position With Time.

where T° = Standard temperature, 273.15°K

ρ = density of pure solvent, $\frac{gm.}{cm.^3}$

Necessary modifications of this relation could be made when solubility data was available either as Ostwald's coefficient or in the units of solute volume dissolved per cc of solution.

The partial pressure of the gas was calculated from the total pressure and estimated vapor pressure of the solvent. The vapor pressure of the solvent was calculated using Raoult's law allowing for the relatively small (maximum 1 to 2 per cent) solute content of the solution. For most solutions, the vapor pressure of the solvent in the solution was essentially equivalent to that of a pure liquid. Thus the gas partial pressure was given by

$$p_A = P - x_B P^\circ_B$$

where p_A = partial pressure of the gas

P = barometric pressure

x_B = mole fraction of the solvent

P_B° = vapor pressure of the pure solvent

The diffusion coefficient was calculated from the flux at the gas-liquid interface and the equilibrium solubility. The equation was as follows:

$$D_{AB} = \frac{n_A L}{\ln \left(\frac{1-\omega_{AL}}{1-\omega_{A0}} \right) \cdot \rho}$$

In the first trial, π_{AL} (solute mass fraction in the bulk of the liquid), was assumed to be zero, which was nearly but not exactly true. The diffusivity value so calculated could then be used in the solution of the unsteady-state diffusion equation to calculate π_{AL} by the relation:

$$\pi_{AL} = \frac{\left(L\rho_{\pi_{A0}}\right)\left(\frac{Dt}{L^2} - \frac{1}{6}\right)A_2}{(7)(\rho)}$$

where t = time during which the unsteady-state diffusion occurs, seconds

7 = volume of the solvent contained in the capillary cell, cc

This value of π_{AL} was used to calculate the corrected diffusivity.

Treatment of Hexane-Heptane Mixtures as Solvents

Since hexane-heptane mixtures contained considerable quantities of both, activity coefficients were used to calculate the correct partial pressures. These were calculated by means of Benedict's equation (60)

$$\gamma_B = \frac{y_B P_t}{x_B p_B} e^{\frac{(p_B - p_t)(V_B - B_B)}{RT}}$$

where γ_B = activity coefficient for the liquid B

y_B = mole fraction of component B in vapor phase

x_B = mole fraction of component B in liquid phase

p_t = total pressure

p_B = vapor pressure of liquid B

V_B = molal volume of liquid B

B_B = second virial coefficient of the equation of state for component B

$= \left(\frac{RT}{p_t}\right)\left(Z_B - 1\right)$, Z_B = compressibility factor

The following results for activity coefficients were obtained:

$$\gamma_{\text{hexane}} = 0.9904$$

$$\gamma_{\text{heptane}} = 0.9982$$

These results do confirm the fact reported in literature that hexane and heptane form very nearly ideal mixtures. However, activity coefficient corrections were applied to calculations involving hexane-heptane mixtures as solvents.

SOLUBILITY MEASUREMENTS

A typical plot of volume of gas dissolved vs. the corresponding volume of liquid solution accumulated is shown in Figure 6.

Ostwald's coefficient is based on the gas volume dissolved per unit volume of the solvent. In the apparatus used, data was obtained in terms of gas volume dissolved per unit volume of the solution. To convert the latter into the former, dissolved ethane was considered to exist in the condensed phase and its contribution towards the solution volume was determined from a knowledge of its mass and liquid-state

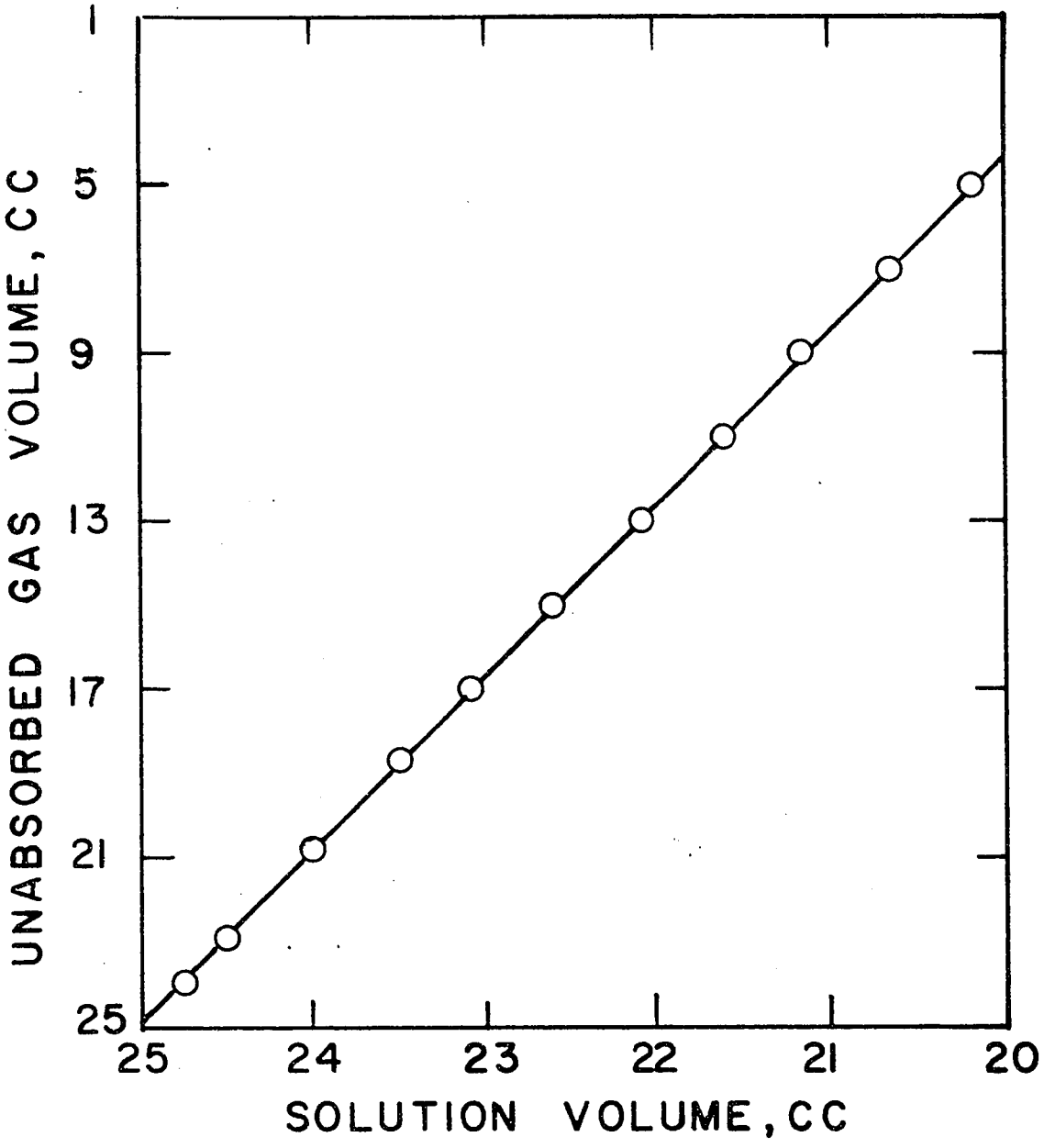

Figure 6. Plot of Unabsorbed Gas Volume vs. Accumulated Solution Volume.

density. Ostwald's coefficient was then calculated by the equation:

$$\text{Ostwald's coefficient} = \frac{V}{\left(1 - \frac{m}{d_l}\right)} \qquad \frac{\text{cm.}^3 \text{ gas}}{\text{cm.}^3 \text{ solvent}}$$

where V = c. c. of gas dissolved per c. c. of solution

m = mass of gas dissolved, gm.

d_l = density of liquid ethane, gm./cm.^{3}

CHAPTER VIII

EXPERIMENTAL RESULTS

In this chapter, the experimental results for diffusion coefficients and solubilities are presented. The raw experimental data from which these results were computed is given in Appendix II and III. All the measurements were taken at atmospheric pressure. Sample plots incorporating the raw data for diffusivity and solubility are shown in Figures 5 and 6 respectively. These respectively correspond to the data of runs D-5 (Appendix II) and H-1 (Appendix III).

DIFFUSION COEFFICIENTS

Figure 7 shows the effect of the length of diffusion path on the value of diffusion coefficient for the system ethane, n-heptane.

Table I shows the diffusion coefficients for various systems. In computing the mean value, of course only those experimental runs were selected where the length of diffusion path was of the right order. This point is discussed in chapter IX. For purposes of comparison, experimental results are compared with those obtained from Wilke-Chang equation and Reddy's modifications of it, all of which are given hereunder as equations (1), (2) and (3) respectively:

$$D_{AB} = \frac{7.4 \times 10^{-6} (XM)^{1/2} T}{\eta V_A^{0.6}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$D_{AB} = \frac{10 \times 10^{-8} (M)^{1/2} T}{\eta V_A^{1/3} V_B^{1/3}}, \quad \text{when} \quad \frac{V_B}{V_A} \leq 1.5 \quad \ldots\ldots\ldots (2)$$

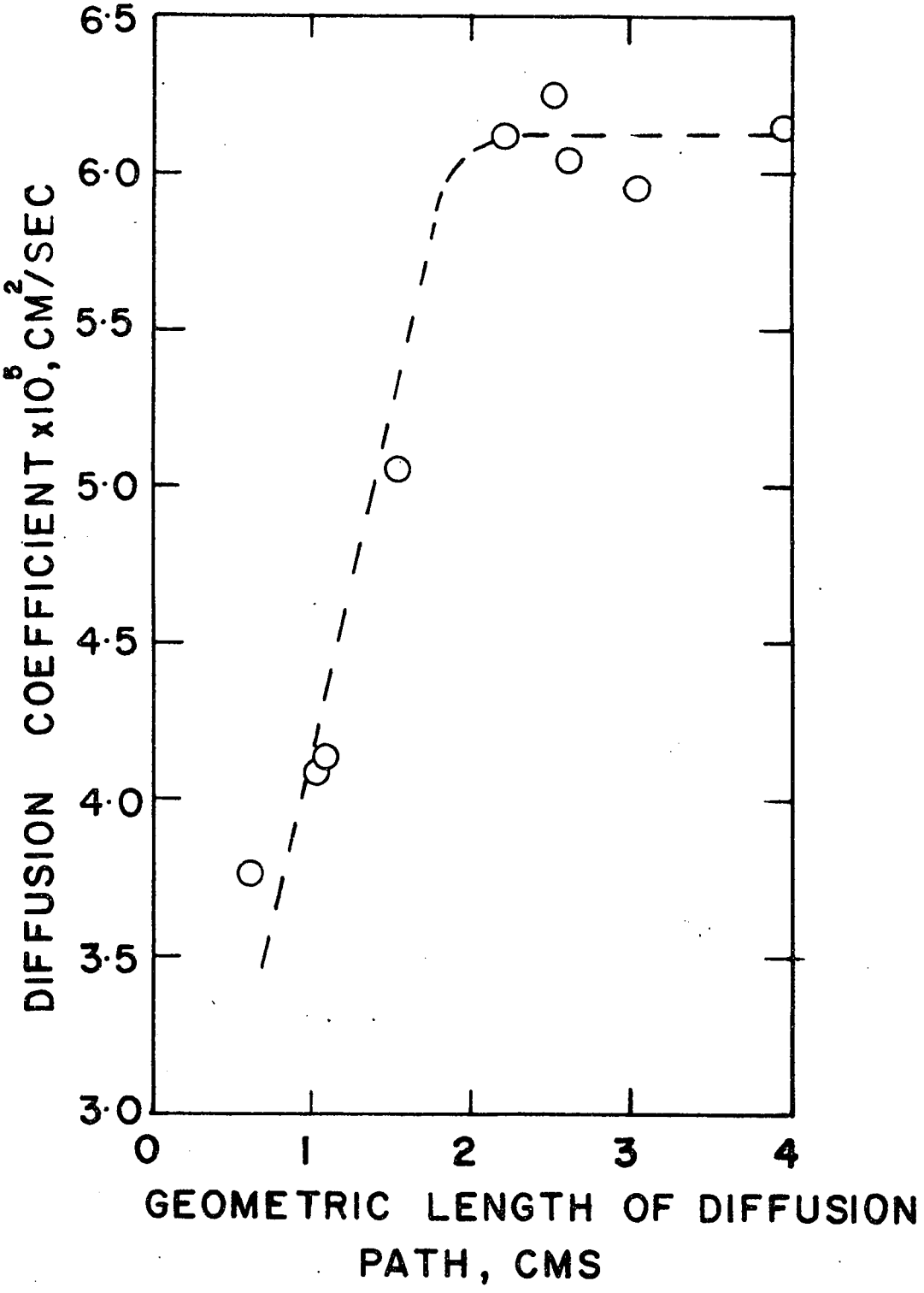

Figure 7. Effect of the Geometric Length of Diffusion Path on Diffusion Coefficient.

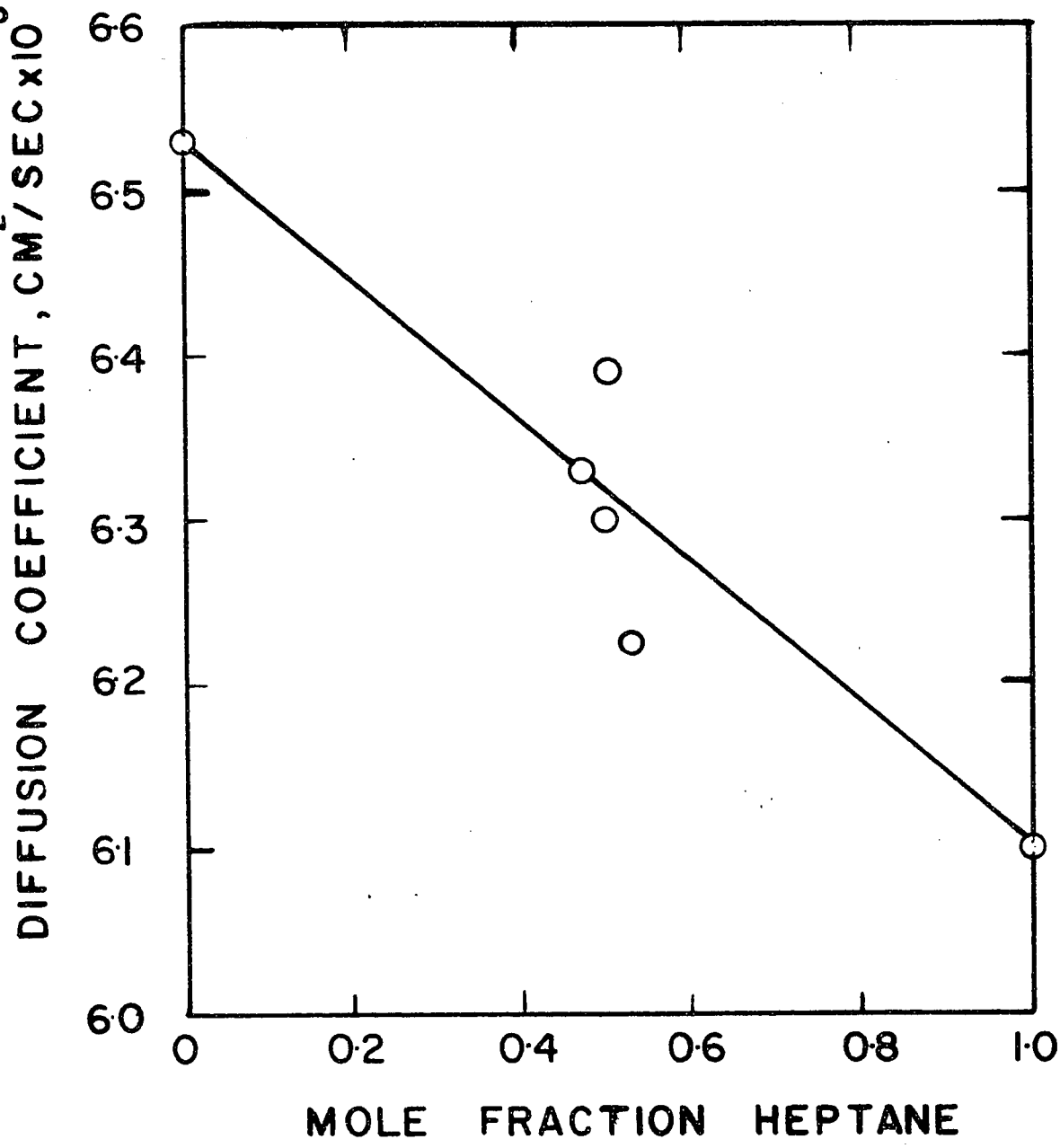

Figure 8. Effect of Solvent Composition on Diffusion Coefficient.

$$D_{AB} = \frac{8.5 \times 10^{-8} (M)^{1/2} T}{\eta V_A^{1/3} V_B^{1/3}}, \quad \text{when } \frac{V_B}{V_A} > 1.5 \quad \ldots\ldots\ldots\ldots (3)$$

where the symbols have their usual significance.

Table II shows the variation of the group $\frac{D\eta}{T}$ with temperature for the system ethane, n-heptane.

Figure 8 shows the effect of solvent composition (when mixed solvents are used) on diffusion coefficients. This is summarized in Table III and a comparison is made with the predicted diffusivity obtained using Wilke-Chang equation.

Table IV compares the experimental diffusion coefficients in mixed solvents with the ones computed from the following correlations suggested by Himmelblau:

$$D_{Am} = x_B D_{AB} + x_C D_{AC} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$D_{Am} \eta_m = x_B D_{AB} \eta_B + x_C D_{AC} \eta_C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$D_{Am} \eta_m^{1/2} = x_B D_{AB} \eta_B^{1/2} + x_C D_{AC} \eta_C^{1/2} \quad \ldots\ldots\ldots\ldots (6)$$

$$\log\left(D_{Am} \eta_m^{1/2}\right) = x_B \log\left(D_{AB} \eta_B^{1/2}\right) + x_C \log\left(D_{AB} \eta_C^{1/2}\right) \ldots (7)$$

Graphs of log D vs. $\frac{1}{T}$ and log η vs. $\frac{1}{T}$ are plotted in Figure 9

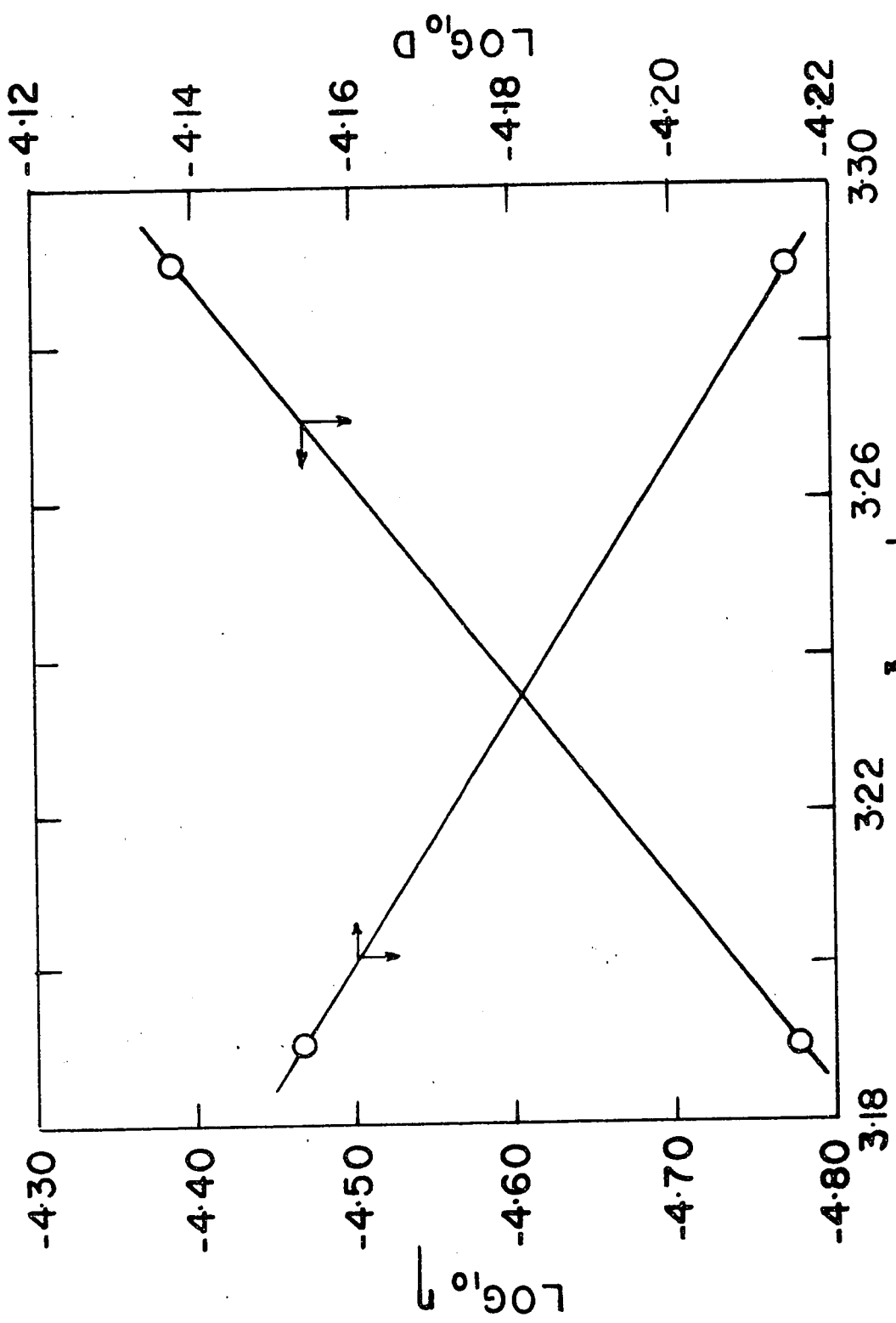

Figure 9. Plots of Log D vs $\frac{1}{T}$ and Log η vs $\frac{1}{T}$

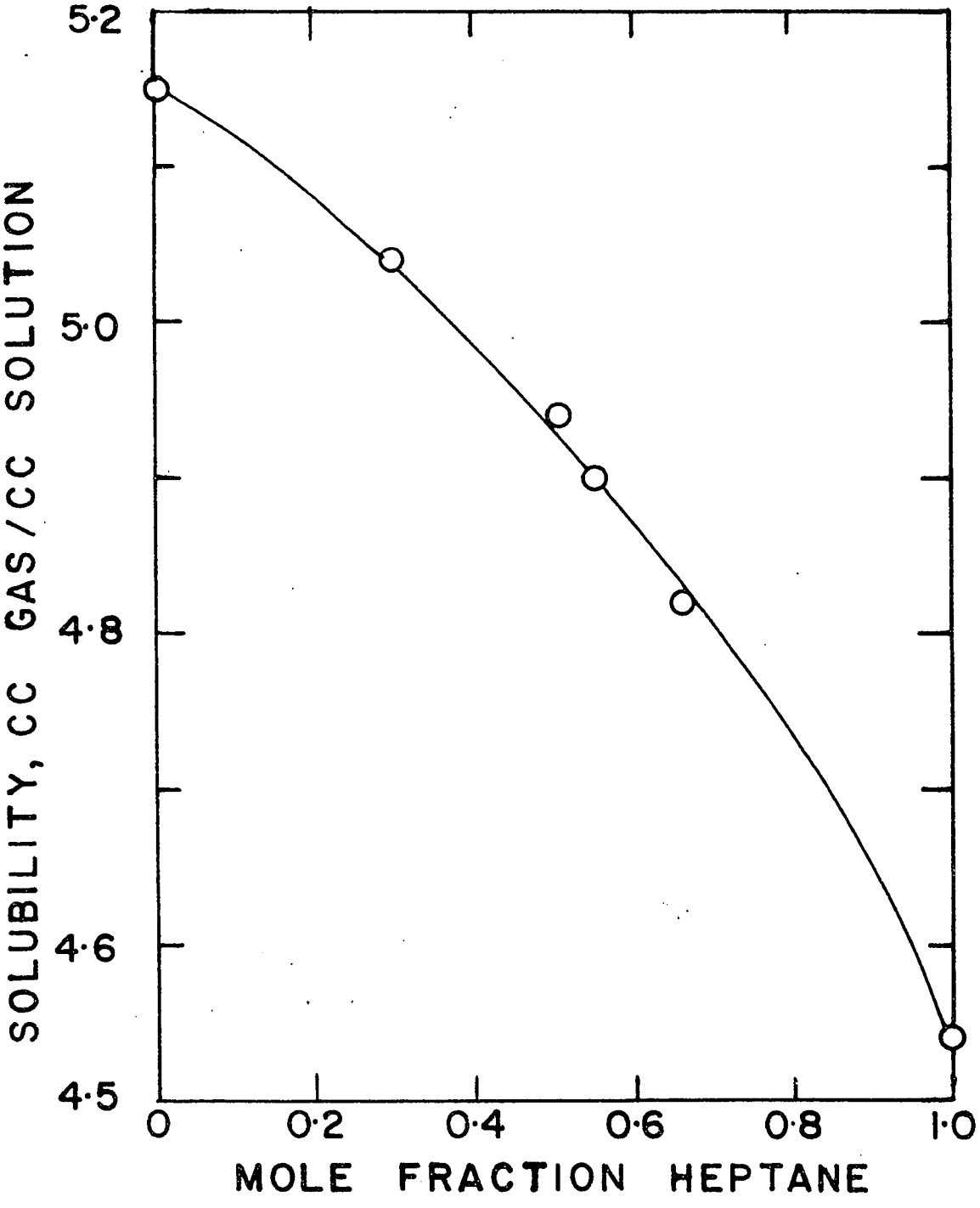

Figure 10. Effect of Solvent Composition on Solubility.

and the energies of activation due to diffusion and viscosity for n-heptane calculated from the slopes of these plots are reported in Table V.

SOLUBILITY

The solubilities of ethane in n-hexane and in n-heptane are reported as Ostwald's coefficients in Table VI.

In Figure 10 is reported the variation of solubility with solvent composition. This corresponds to data of Table VII.

TABLE I

Experimental and Predicted Diffusion Coefficients

System	Temp. °C	Number of Exptl. Runs	Mean Diff. Coeff. $D_{AB} \times 10^5$ cm.^{2}/sec.	Standard Deviation	Predicted $D_{AB} \times 10^5$, cm.^{2}/sec. Eq. (1)	Eq. (2)	Eq. (3)
Carbon dioxide, Water	30	4	2.20	0.022	2.27	1.78	
Methane, Carbon tetrachloride	25	4	2.92	0.066	3.53		2.27
Carbon dioxide, Ethanol	30	4	3.67	0.036	5.75		1.36
Ethane, n-Hexane	30	5	6.53	0.086	6.69		4.33
Ethane, n-Heptane	30	5	6.10	0.110	5.51		3.40
Ethane, n-Heptane	40	5	7.03	0.093	6.23		3.84

TABLE II

Variation of $D\eta/T$ With Temperature

System	Temperature, °C	$D\eta/T \times 10^9$
Ethane, n-Heptane	30	0.73
Ethane, n-Heptane	40	0.74

TABLE III

Variation of Diffusion Coefficient With Solvent Composition

System	Temp. °C	Mole Fraction Heptane	Exptl. $D \times 10^5$ cm.^{2}/sec.	Predicted $D \times 10^5$ (Eq. 1) cm.^{2}/sec.
Ethane and		0.470	6.33	6.01
Mixtures of	30	0.496	6.30	5.97
Hexane and		0.500	6.39	5.97
Heptane		0.525	6.23	5.79

TABLE IV

Predicted Values of D by Means of Equations (4),(5),(6) and (7) Using Experimental Values of D for Each of the Pure Solvents

System	Temp. °C	Mole Fraction Heptane	Exptl. $D \times 10^5$ $cm.^2/sec.$	Predicted $D \times 10^5$, $cm.^2/sec.$ Eq.(4)	Eq.(5)	Eq.(6)	Eq.(7)
Ethane and		0.470	6.33	6.33	6.22	6.25	6.25
Mixtures of	30	0.496	6.30	6.32	6.22	6.25	6.24
Hexane and		0.500	6.39	6.31	6.23	6.26	6.25
Heptane		0.525	6.33	6.30	6.25	6.27	6.27

TABLE V

Energies of Activation of n-Heptane

Activation Energy Due to Diffusion, cal/g-mole	Activation Energy Due to Viscosity, cal/g-mole
1224	768

TABLE VI

Solubility (Ostwald's Coefficient) of Gases in Pure Solvents

System	Temp., °C	Number of Exptl. Runs	Mean Ostwald's Coefficient	Standard Deviation
Ethane, n-Hexane	30	3	5.23	0.012
Ethane, n-Heptane	30	3	4.62	0.025
Ethane, n-Heptane	40	3	4.40	0.006

TABLE VII

Solubility (cc gas per cc solution) of Gases in Mixed Solvents

System	Temp., °C	Mole Fraction Heptane	Solubility
Ethane and Mixtures of Hexane and Heptane	30	0	5.15
		0.295	5.04
		0.505	4.94
		0.550	4.90
		0.660	4.82
		1.000	4.54

CHAPTER IX

DISCUSSION

The discussion in this chapter is divided into two parts. The first deals with diffusion coefficients and the second with solubilities.

DIFFUSION COEFFICIENTS

In a variety of experimental techniques for measuring diffusivities in the liquid state, the analysis of the diffusion process has been done by several analytical methods such as optical, radioactive, chromatographic and mass spectrographic. The calibration of the equipment together with the complexity of the analytical methods can cause a decrease in the accuracy of experimental results. The fact that even after innumerable experiments with the carbon dioxide-water system, there is no certain agreement about the correct value of diffusivity emphasizes this point. Similarly, the diffusivities for ethanol-water reported by two groups of investigators (41, 42) differ by about a hundred per cent. Thus the magnitude of experimental uncertainty can hardly be overemphasized.

In the steady-state capillary cell technique, analytical methods for measuring concentrations were not used; instead volume changes were measured by noting the linear change in position of the bead at regular intervals of time. The maximum deviation in the value of diffusion coefficient about the mean, for any set of experimental runs, never exceeded 2.29 per cent.

Validity of the Steady-State Capillary Cell Technique for Measuring Diffusion Coefficients

It is now proposed to establish that the results obtained by the capillary cell technique used in this work are comparable to those

obtained by other methods. For this purpose, the system carbon dioxide-water was selected because the diffusion coefficient for this system has been more or less established as a result of the investigations of various workers (5, 7, 9, 17, 43, 44, 45). The diffusion coefficients, at 30° C, obtained for this system by several investigators are reported hereunder:

Worker	$D_{AB} \times 10^5$, cm.^{2}/sec.
Peaceman	2.29
Davidson and Cullen	2.25
Tang and Himmelblau	2.15
Ringbom	2.06
Nijsing and Kramers	2.26
Vivian and King	2.27 (extrapolated from 25° C)
Thomas and Adams	2.21 (extrapolated from 25° C)

The diffusion coefficient obtained by the present technique was 2.20×10^{-5} cm.^{2}/sec., which compares well with these values.

As a further confirmation of the validity of this method, the system methane-carbon tetrachloride was also studied. At 25° C, the value of diffusion coefficient reported in literature (19) is 2.89×10^{-5} cm.^{2}/sec. compared to 2.92×10^{-5} cm.^{2}/sec. obtained in this work.

The diffusion coefficient for carbon dioxide-ethanol was also determined and was found to be 3.67×10^{-5} cm.^{2}/sec. at 30° C. This does not compare favourably with a value of 4.06×10^{-5} cm.^{2}/sec. obtained by extrapolating the data of Onda and Okamato (46) but is quite close to a diffusivity of 3.78×10^{-5} cm.^{2}/sec. obtained by extrapolating the very recent data of Davis, Ponter and Craine (47).

Therefore it can be concluded that the results obtained by the steady-state capillary cell method are reliable. The method does not require measurement of gas flow rates nor any analyses, which is a distinct advantage over other methods. Moreover, it is simple and inexpensive.

Effect of the Length of Diffusion Path

An error that can occur in the capillary cell technique is the so called "Δl effect", which arises because the actual length of the diffusion path may differ from the geometric length owing to a concentration build up at the mouth of the capillary (48). Although slight temperature fluctuations of the order of 0.01° to 0.02° C are sufficient for good mixing in the bulk of the liquid (19), a small "Δl effect" might persist all the same. The difference between the actual length of the diffusion path and the geometric length becomes negligible above a certain length. The relation between diffusion path length and diffusion coefficient has already been shown in Figure 7. From this graph, it is evident that the geometric length of the diffusion path beyond which "Δl effects" become negligible is 1.80 cm. This minimum length was adhered to in all experiments.

Convection in Liquid Confined in the Capillary

Confining a liquid in a capillary is a general way of eliminating convection. Extensive experiments with the capillary cell technique developed by Wang and others (48, 49, 50) have shown that convection is absent when the diameter of the capillary is about 1 mm. or less.

The capillary used in the present investigation had an internal diameter of 0.04 in. (1.016 mm.).

Degree of Mixing in the Bulk of the Liquid

Although the convection currents in the liquid confined in the capillary should be suppressed, there should be sufficient convection within the cell to distribute the dissolved gas uniformally. Berne and

Well (51) performed a series of preliminary experiments to investigate the influence of stirring on the measured value of diffusivity. No difference was observed, inside the limits of the error of the method, whether the solution was stirred mechanically or when a slight thermal convection was established. This is confirmed in a later investigation by Hildebrand (19). Thus it is concluded that the convection caused in the bulk liquid due to cyclic changes of temperature provided good mixing.

Bulk Motion Caused by Volume Change on Mixing

In the present investigation, volume change due to solution of the gas in the liquid was not significant. However, if there is significant bulk motion due to solution, an appropriate term for it must be introduced in the fundamental diffusion equation. The solution to such an equation is:

$$D_{AB} = \frac{n_A \cdot L}{\ln\left(\frac{1 + w_{A0}}{1 + w_{AL}}\right) \cdot \rho} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where the symbols have their usual meaning. We have already seen that the solution neglecting the volume change on mixing is:

$$D_{AB} = \frac{n_A \cdot L}{\ln\left(\frac{1 - w_{AL}}{1 - w_{A0}}\right) \cdot \rho} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Thus it is possible to describe both the situations mathematically.

However, it can be readily seen that the difference between (1) and (2) is very small for dilute solutions.

Effect of Temperature

According to Stokes-Einstein equation, the group $\frac{D\eta}{T}$ is independent of temperature. In this work, for the system ethane-normal heptane, the value of this group at 30° C and 40° C deviated by 1.36 per cent about the mean value. Considering the precision of the measurements, it is concluded that the group $\frac{D\eta}{T}$ remains constant with temperature. It is recognized that this temperature range is too narrow to conclusively study the effect of temperature.

Energy of Activation

The energy of activation due to diffusion is compared with that due to viscosity to study Eyring's suggestion that the two should be equal. The value of the former was determined as 1224 cal/g-mole while that of the latter was 768 cal/g-mole. This is an appreciable difference. Probably the presence of ethane in n-heptane effects the activation energy. It is also conceivable that the mechanism of diffusion is somewhat different from that of viscosity.

Validity of Wilke-Chang Equation

Of the emperical correlations tested for predicting diffusivities, the Wilke-Chang correlation showed least deviation from measured values for systems ethane-hexane and ethane-heptane. For these pure liquids, the error introduced by using this correlation varied from + 2.45 per cent to -11.38 per cent, and for mixed solvents the error lay between -4.13 per cent and -6.57 per cent.

Reddy and Doraiswamy's modifications of Wilke-Chang equation (equations 2 and 3, Chapter VIII) gave results no closer than -33.69 per cent of the experimental.

Himmelblau's Relations for Predicting Effective Binary Diffusion Coefficients in Mixed Solvents

As already pointed out in chapter VIII, Himmelblau has suggested four relationships for predicting diffusivities in mixed solvents. The following table gives the extent of the errors introduced by using relations (1), (2), (3) and (4) of chapter VIII for the system (ethane), (hexane + heptane):

Relationship	Span of Error, Per cent
(1)	-1.26 to + 4.13
(2)	-2.50 to + 2.80
(3)	-2.03 to + 3.30
(4)	-2.19 to + 3.14

From this, it is not possible to say as to which of the four is better. Perhaps, whenever the solvents form a nearly ideal mixture, one correlation would be as good as another. Solvents which form non-ideal mixtures are a better test for arriving at a reasonable conclusion.

Two points are worth mentioning. In these correlations, the experimental values were used for the diffusivity of solute in each of the pure solvents. Therefore the predicted diffusivity in the mixed solvent would necessarily be better than that predicted by Wilke-Chang equation. The other point is that in the four experimental runs studied, the liquid composition was nearly the same in all cases -0.470 mole fraction heptane to 0.525 mole fraction heptane. This was done deliberately so that the points formed a cluster close to one another. The precision of the present experimental technique was not high enough as to be of use in determining diffusivity at

several widely varying compositions of the solvent mixture. This was especially true when the diffusivities of ethane in each of the pure solvents were so close to each other (6.53×10^{-5} cm.^{2}/sec. for n-hexane and 6.10×10^{-5} cm.^{2}/sec. for n-heptane).

SOLUBILITIES

The Ostwald's coefficients, at 30° C, for ethane in n-hexane and ethane in n-heptane have been found to be 5.23 and 4.62 respectively, compared with McDaniel's (52) values of 3.1842 and 4.4200. It may be well to point out that McDaniel's are the only values known for this system. Horiuti (53) also compared his values with McDaniel's for several other systems and found the latter's values to be consistently lower.

Solubility of Ethane in Mixed Solvents:

O'Connell and Prausnitz (54) have derived the following equation for the solubility of a gas in mixed solvents:

$$\ln H_{2,\ \text{mixed solvent}} = x_1 \ln H_{2,1} + x_3 \ln H_{2,3} - \alpha_{1,3} x_1 x_3$$

where $H_{2,\ \text{mixed}}$ = Henry's constant for solute in mixed solvent

$H_{2,1}$ = Henry's constant for solute in pure solvent 1

$H_{2,3}$ = Henry's constant for solute in pure solvent 3

$x_1,\ x_3$ = mole fractions of solvents

$\alpha_{1,3}$ = Margule's constant

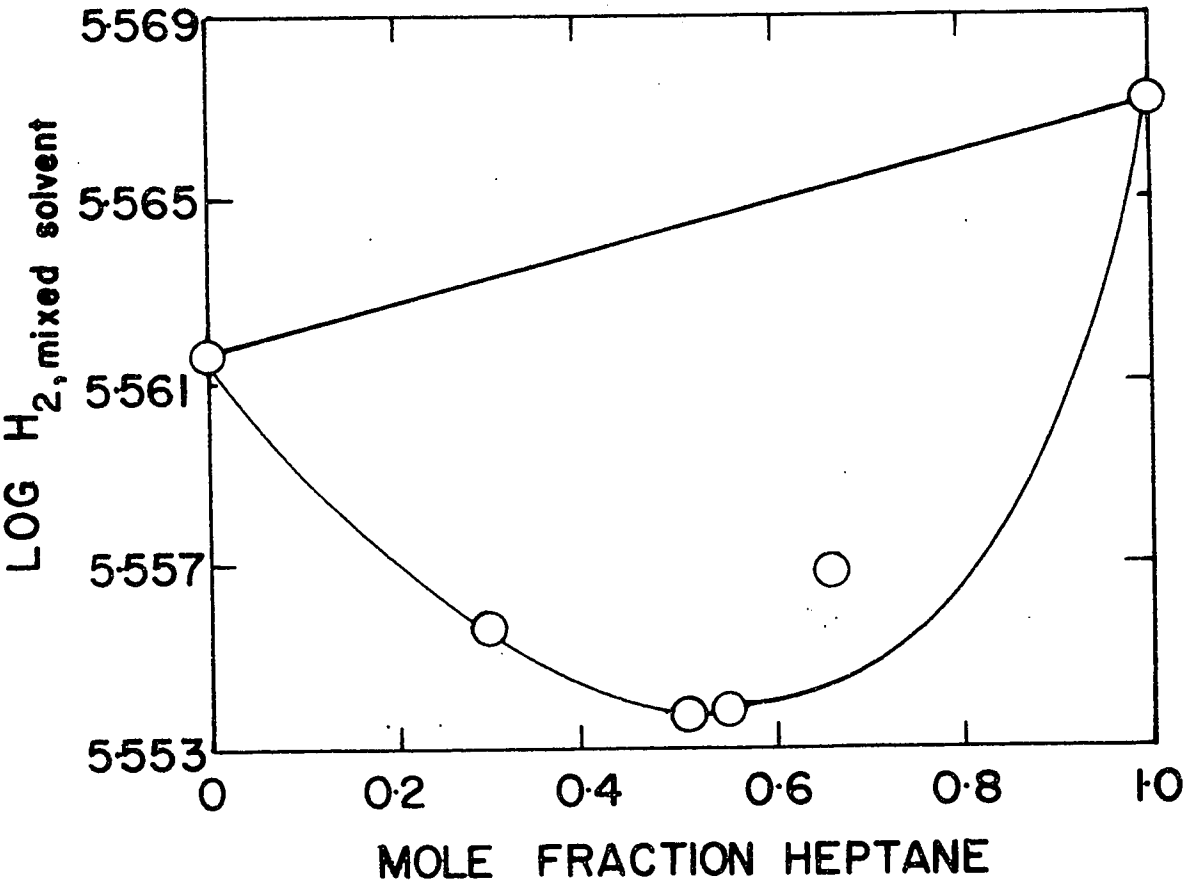

Figure 11. Effect of Solvent Composition on Henry's Law Constant.

Margule's constant approaches zero when the solvents form a nearly ideal mixture.

According to this equation, a plot of log $H_{2,\ \text{mixed solvent}}$ vs. x, should give a straight line. This graph was plotted in Figure 11, which corresponds to data given in Appendix III, and it was not found to be a straight line. The deviation from a straight line relationship can be taken to represent the extent of non-ideality.

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APPENDIX I

CALIBRATION CURVE DATA FOR ANALYSIS OF HEXANE-HEPTANE MIXTURES AT 25°C

Mole Fraction Heptane	Refractive Index
0.000	1.37264
0.055	1.37358
0.105	1.37440
0.145	1.37505
0.245	1.37641
0.300	1.37712
0.426	1.37870
0.493	1.37930
0.525	1.37988
0.584	1.38054
0.670	1.38156
0.766	1.38259
0.780	1.38280
0.840	1.38356
0.880	1.38415
0.934	1.38455
1.000	1.38528

APPENDIX II

RAW EXPERIMENTAL DATA FOR DIFFUSION COEFFICIENT DETERMINATIONS

Run No.: A-1
System: CO_2, H_2O
Temperature: 30° C
Bar. Pressure: 763.1 mm Hg
Diffusion Path Length: 0.800 cm.

Time min.	Bead Position cm.
0	0.00
30	0.31
60	0.52
90	0.78
120	1.04
165	1.44
235	2.08
305	2.77
395	3.68
420	3.88
450	4.22
500	4.60
560	5.21
600	5.55
700	6.50

$D = 1.72 \times 10^{-5}$ cm.^{2}/sec.

Run No.: A-2
System: CO_2, H_2O
Temperature: 30° C
Bar. Pressure: 760.3 mm Hg
Diffusion Path Length: 1.933 cm.

Time min.	Bead Position cm.
0	0.00
50	0.20
100	0.52
150	0.75
200	1.04
300	1.46
400	1.90
500	2.40
600	2.87
700	3.33
800	3.82
900	4.28

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

Run No.: A-3
System: CO_2, H_2O
Temperature: 30° C
Bar. Pressure: 762.6 mm Hg
Diffusion Path Length: 1.869 cm.

Time min.	Bead Position cm.
0	0.00
45	0.29
100	0.58
135	0.75
180	0.93
220	1.14
270	1.41
400	2.00
500	2.50
610	3.03
1160	5.75
1255	6.22
1310	6.47
1355	6.72
1400	6.92

$D = 2.19 \times 10^{-5}$ cm.^{2}/sec.

Run No.: A-4

System: CO_2, H_2O

Temperature: 30° C

Bar. Pressure: 754.0 mm Hg

Diffusion Path Length: 1.810 cm.

Time min.	Bead Position cm.
0	0.00
30	0.11
60	0.21
135	0.59
240	1.15
360	1.73
410	2.03
490	2.45
555	2.80
645	3.30
700	3.54
790	4.00
850	4.32

$D = 2.21 \times 10^{-5}$ cm.^{2}/sec.

Run No.: A-5

System: CO_2, H_2O

Temperature: 30° C

Bar. Pressure: 758.9 mm Hg

Diffusion Path Length: 2.752 cm.

Time min.	Bead Position cm.
0	0.00
30	0.11
65	0.23
100	0.35
160	0.53
250	0.82
300	0.98
355	1.18
400	1.30
550	1.81
740	2.35
1440	4.77
1520	5.03
1570	5.13
1660	5.47

$D = 2.17 \times 10^{-5}$ cm.^{2}/sec.

Run No.: B-1

System: CH_4, CCl_4

Temperature: 25° C

Bar. Pressure: 757.0 mm Hg

Diffusion Path Length: 1.706 cm.

Time min.	Bead Position cm.
0	0.00
60	0.29
90	0.39
120	0.67
150	0.78
180	1.01
210	1.10
240	1.42
270	1.56
300	1.80
330	2.05
360	2.28
390	2.49
420	2.70
450	2.86
480	3.12
510	3.34

$D = 2.96 \times 10^{-5}$ cm.^{2}/sec.

Run No.: B-2

System: CH_4, CCl_4

Temperature: 25° C

Bar. Pressure: 765.0 mm Hg

Diffusion Path Length: 3.169 cm.

Time min.	Bead Position cm.
0	0.00
120	0.15
180	0.33
210	0.53
270	0.70
330	0.90
400	1.14
460	1.38
520	1.65
580	1.82
640	2.02
700	2.26
760	2.50
940	3.16

$D = 2.83 \times 10^{-5}$ cm.^{2}/sec.

Run No.: B-3

System: CH_4, CCl_4

Temperature: 25° C

Bar. Pressure: 766.6 mm Hg

Diffusion Path Length: 2.248 cm.

Time min.	Bead Position cm.
0	0.00
60	0.05
120	0.22
190	0.53
260	0.98
310	1.30
400	1.73
500	2.17
600	2.82
700	3.40
800	3.90
850	4.17

$D = 2.92 \times 10^{-5}$ cm.^{2}/sec.

Run No.: B-4

System: CH_4, CCl_4

Temperature: 25° C

Bar. Pressure: 763.8 mm Hg

Diffusion Path Length: 2.212 cm.

Time min.	Bead Position cm.
0	0.00
100	0.25
150	0.50
200	0.80
300	1.35
400	1.87
500	2.41
550	2.74
600	3.05
700	3.54
800	4.12

$D = 2.98 \times 10^{-5}$ cm.^{2}/sec.

Run No.: C-1

System: CO_2, C_2H_5OH

Temperature: 30° C

Bar. Pressure: 754.2 mm Hg

Diffusion Path Length: 2.798 cm.

Time min.	Bead Position cm.
0	0.00
40	0.77
80	1.30
120	2.24
160	2.89
200	3.80
240	4.36
280	5.50
320	6.33
360	7.13
400	8.00

$D = 3.65 \times 10^{-5}$ cm.^{2}/sec.

Run No.: C-2

System: CO_2, C_2H_5OH

Temperature: 30° C

Bar. Pressure: 757.6 mm Hg

Diffusion Path Length: 3.120 cm.

Time min.	Bead Position cm.
0	0.00
40	0.83
90	1.70
120	2.30
160	3.00
200	3.77
240	4.52
280	5.22
320	6.03
350	6.60
380	7.18
410	7.65

$D = 3.66 \times 10^{-5}$ cm.^{2}/sec.

Run No.: C-3

System: CO_2, C_2H_5OH

Temperature: 30° C

Bar. Pressure: 756.7 mm Hg

Diffusion Path Length: 2.481 cm.

Time min.	Bead Position cm.
0	0.00
20	0.48
40	0.88
60	1.45
80	1.92
100	2.52
160	3.90
180	4.33
200	4.85
220	5.30
240	5.80
260	6.28
280	6.76

$D = 3.72 \times 10^{-5}$ cm.^{2}/sec.

Run No.: C-4

System: CO_2, C_2H_5OH

Temperature: 30° C

Bar. Pressure: 762.6 mm Hg

Diffusion Path Length: 3.916 cm.

Time min.	Bead Position cm.
0	0.00
30	0.43
60	0.89
95	1.41
120	1.85
150	2.22
180	2.63
340	4.82
360	5.38
390	5.81
430	6.42
480	7.20
540	8.12

$D = 3.64 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-1

System: C_2H_6, n-C_6H_{14}

Temperature: 30° C

Bar. Pressure: 756.8 mm Hg

Diffusion Path Length: 1.290 cm.

Time min.	Bead Position cm.
0	0.00
10	1.36
20	2.64
30	4.10
40	5.63
50	6.90
60	8.25
70	9.63
80	11.00
85	11.71

$D = 6.03 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-2

System: C_2H_6, n-C_6H_{14}

Temperature: 30° C

Bar. Pressure: 755.0 mm Hg

Diffusion Path Length: 2.404 cm.

Time min.	Bead Position cm.
0	0.00
10	1.05
20	1.83
30	2.65
40	3.39
50	4.18
60	4.92
70	5.85
100	8.05
110	8.82

$D = 6.39 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-3

System: C_2H_6, n-C_6H_{14}

Temperature: 30° C

Bar. Pressure: 759.6 mm Hg

Diffusion Path Length: 1.968 cm.

Time min.	Bead Position cm.
0	0.00
5	0.56
10	1.02
15	1.38
20	2.03
25	2.41
30	2.90
35	3.35
40	3.85
45	4.30
50	4.80
55	5.29
60	5.78
65	6.27
70	6.71

$D = 6.55 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-4

System: C_2H_6, n-C_6H_{14}

Temperature: 30° C

Bar. Pressure: 759.7 mm Hg

Diffusion Path Length: 4.350 cm.

Time min.	Bead Position cm.
0	0.00
10	0.43
20	0.83
30	1.26
40	1.72
50	2.09
60	2.58
70	2.96
80	3.38
90	3.80
100	4.30
110	4.63
120	5.04
130	5.44
140	5.90

$D = 6.53 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-5

System: C_2H_6, n-C_6H_{14}

Temperature: 30° C

Bar. Pressure: 749.2 mm Hg

Diffusion Path Length: 1.890 cm.

Time min.	Bead Position cm.
0	0.00
5	0.63
10	1.08
15	1.65
20	2.23
25	2.74
30	3.27
35	3.79
40	4.28
45	4.71
50	5.31
55	5.82
60	6.33
65	6.91
70	7.37
75	7.90

$D = 6.64 \times 10^{-5}$ cm.^{2}/sec.

Run No.: D-6

System: C_2H_6, n-C_6H_{14}

Temperature: 30° C

Bar. Pressure: 755.0 mm Hg

Diffusion Path Length: 2.630 cm.

Time min.	Bead Position cm.
0	0.00
15	1.04
25	1.69
35	2.55
45	3.29
55	4.01
65	4.70
75	5.50
85	6.25
95	7.00
105	7.71

$D = 6.64 \times 10^{-5}$ cm.^{2}/sec.

Run No.: E-1

System: C_2H_6, n-C_7H_{16}

Temperature: 30° C

Bar. Pressure: 756.0 mm Hg

Diffusion Path Length: 0.525 cm.

Time min.	Bead Position cm.
0	0.00
10	1.68
20	3.55
30	5.49
40	7.28
50	9.10
60	10.95

$D = 3.75 \times 10^{-5}$ cm.^{2}/sec.

Run No.: E-2

System: C_2H_6, n-C_7H_{16}

Temperature: 30° C

Bar. Pressure: 761.4 mm Hg

Diffusion Path Length: 1.045 cm.

Time min.	Bead Position cm.
0	0.00
10	0.95
20	1.84
30	2.86
40	3.95
50	4.90
60	5.92
70	6.90
80	7.96
90	8.92

$D = 4.08 \times 10^{-5}$ cm.^{2}/sec.

Run No.: E-3

System: C_2H_6, n-C_7H_{16}

Temperature: 30°C

Bar. Pressure: 746.6 mm Hg

Diffusion Path Length: 1.090 cm.

Time min.	Bead Position cm.
0	0.00
10	0.99
20	2.00
30	2.95
40	4.12
50	4.94
60	5.75
70	6.78
80	7.77
90	8.70

$D = 4.13 \times 10^{-5}$ cm.^{2}/sec.

Run No. : E-4

System: C_2H_6, n-C_7H_{16}

Temperature: 30°C

Bar. Pressure: 765.0 mm Hg

Diffusion Path Length: 1.545 cm.

Time min.	Bead Position cm.
0	0.00
10	0.70
20	1.63
30	2.53
40	3.15
50	3.95
70	5.60
80	6.38
90	7.20
100	8.19
110	8.81
120	9.65

$D = 5.05 \times 10^{-5}$ cm.^{2}/sec.

Run No. : E-5

System: C_2H_6, n-C_7H_{16}

Temperature: 30°C

Bar. Pressure: 754.6 mm Hg

Diffusion Path Length: 2.198 cm.

Time min.	Bead Position cm.
0	0.00
10	0.67
20	1.51
30	2.12
40	2.82
50	3.58
60	4.30
70	5.05
80	5.75
90	6.58
100	7.22
110	7.99
120	8.70
130	9.42

$D = 6.12 \times 10^{-5}$ cm.^{2}/sec.

Run No.: E-6

System: C_2H_6, n-C_7H_{16}

Temperature: 30° C

Bar. Pressure: 754.6 mm Hg

Diffusion Path Length: 2.602 cm.

Time min.	Bead Position cm.
0	0.00
10	0.46
20	1.18
30	1.60
50	2.90
60	3.38
70	3.98
80	4.60
90	5.20
110	6.38
120	6.99
130	7.67
140	8.17
150	8.72

$D = 6.04 \times 10^{-5}$ cm.^{2}/sec.

Run No.: E-7

System: C_2H_6, n-C_7H_{16}

Temperature: 30° C

Bar. Pressure: 755.2 mm Hg

Diffusion Path Length: 3.880 cm.

Time min.	Bead Position cm.
0	0.00
10	0.40
20	0.80
40	1.61
80	3.24
100	4.03
120	5.00
140	5.75
160	6.50
200	8.12
220	8.95

$D = 6.15 \times 10^{-5}$ cm.^{2}/sec.

Run No.: E-8

System: C_2H_6, n-C_7H_{16}

Temperature: 30° C

Bar. Pressure: 756.3 mm Hg

Diffusion Path Length: 2.448 cm.

Time min.	Bead Position cm.
0	0.00
10	0.60
20	1.34
30	1.91
50	3.22
60	3.84
70	4.52
80	5.27
90	6.07
110	7.28
120	7.85
130	8.60
140	9.31
150	9.79

$D = 6.25 \times 10^{-5}$ cm.^{2}/sec.

Run No.: E-9

System: C_2H_6, n-C_7H_{16}

Temperature: 30° C

Bar. Pressure: 756.3 mm. Hg

Diffusion Path Length: 3.020 cm.

Time min.	Bead Position cm.
0	0.00
10	0.68
20	1.71
30	2.20
40	2.80
70	4.19
80	4.70
90	5.32
100	5.68
110	6.15
120	6.68
130	7.14
140	7.81
150	8.12
160	8.60
170	9.10

$D = 5.96 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-1

System: C_2H_6, n-C_7H_{16}

Temperature: 40° C

Bar. Pressure: 753.0 mm Hg

Diffusion Path Length: 2.032 cm.

Time min.	Bead Position cm.
0	0.00
10	0.83
20	1.41
30	2.21
40	3.10
70	5.65
80	6.50
90	7.36
100	8.21

$D = 7.17 \times 10^{-5}$ cm.^{2}/sec.

Run No.: F-2

System: C_2H_6, n-C_7H_{16}

Temperature: 40° C

Bar. Pressure: 751.8 mm Hg

Diffusion Path Length: 2.591 cm.

Time min.	Bead Position cm.
0	0.00
10	0.48
20	1.18
30	1.90
40	2.45
70	4.38
80	5.03
90	5.68
100	6.32
110	6.99

$D = 6.93 \times 10^{-5}$ cm.^{2}/sec.

Run No. : F-3

System : C_2H_6, n-C_7H_{16}

Temperature: 40° C

Bar. Pressure: 754.8 mm Hg

Diffusion Path Length: 3.155 cm.

Time min.	Bead Position cm.
0	0.00
10	0.57
20	1.18
30	1.65
40	2.19
50	2.73
60	3.26
70	3.81
80	4.35
90	4.90
130	7.09
140	7.66
150	8.17
160	8.72
170	9.28

$D = 6.96 \times 10^{-5}$ cm.^{2}/sec.

Run No. : F-4

System: C_2H_6, n-C_7H_{16}

Temperature: 40° C

Bar. Pressure: 759.2 mm Hg

Diffusion Path Length: 2.226 cm.

Time min.	Bead Position cm.
0	0.00
10	0.77
20	1.52
30	2.28
40	3.02
50	3.79
60	4.54
70	5.26
80	6.08
90	6.80
100	7.55
110	8.32

$D = 7.04 \times 10^{-5}$ cm.^{2}/sec.

Run No. : F-5

System: C_2H_6, n-C_7H_{16}

Temperature: 40° C

Bar. Pressure: 761.8 mm Hg

Diffusion Path Length: 2.896 cm.

Time min.	Bead Position cm.
0	0.00
10	0.48
20	1.09
30	1.70
40	2.30
50	2.89
60	3.52
70	4.08
80	4.71
90	5.26
100	6.00
110	6.50

$D = 7.03 \times 10^{-5}$ cm.^{2}/sec.

Run No.: G-1

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.504 mole fr. n-C_6H_{14}
0.496 mole fr. n-C_7H_{16}

Temperature: 30°C

Barometric Pressure: 754.8 mm Hg

Diffusion Path Length: 2.527 cm.

Time min.	Bead Position cm.
0	0.00
10	0.83
20	1.49
30	2.23
40	2.90
50	3.65
60	4.36
70	4.98
80	5.78
90	6.46
100	7.18

$D = 6.30 \times 10^{-5}$ cm.^{2}/sec.

Run No.: G-2

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.475 mole fr. n-C_6H_{14}
0.525 mole fr. n-C_7H_{16}

Temperature: 30°C

Barometric Pressure: 762.8 mm Hg

Diffusion Path Length: 2.738 cm.

Time min.	Bead Position cm.
0	0.00
10	0.63
20	1.03
30	1.80
40	2.42
50	3.08
60	3.67
70	4.22
80	5.00
90	5.58
100	6.20

$D = 6.25 \times 10^{-5}$ cm.^{2}/sec.

Run No.: G-3

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.500 mole fr. n-C_6H_{14}
0.500 mole fr. n-C_7H_{16}

Temperature: 30°C

Barometric Pressure: 758.8 mm Hg

Diffusion Path Length: 1.922 cm.

Time min.	Bead Position cm.
0	0.00
10	0.94
20	1.86
30	2.73
40	3.78
50	4.64
60	5.56
70	6.47
80	7.35

$D = 6.39 \times 10^{-5}$ cm.^{2}/sec.

Run No.: G-4

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.530 mole fr. n-C_6H_{14}
0.470 mole fr. n-C_7H_{16}

Temperature: 30°C

Barometric Pressure: 759.6 mm Hg

Diffusion Path Length: 3.127 cm.

Time min.	Bead Position cm.
0	0.00
10	0.57
20	1.10
30	1.64
40	2.10
50	2.73
60	3.28
70	3.91
80	4.33
90	4.90
100	5.45
110	6.00

$D = 6.33 \times 10^{-5}$ cm.^{2}/sec.

APPENDIX III

RAW EXPERIMENTAL DATA FOR SOLUBILITY DETERMINATIONS

Run No.: H-1
System: C_2H_6, n-C_6H_{14}
Temperature: 30°C
Bar. Pressure: 760.9 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
24.00	24.75
23.00	24.50
20.80	24.00
18.70	23.50
17.00	23.10
15.00	22.62
13.00	22.10
11.00	21.63
9.00	21.17
7.00	20.68
5.00	20.20

Solubility = 5.15 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: H-2
System: C_2H_6, n-C_6H_{14}
Temperature: 30°C
Bar. Pressure: 762.7 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
23.40	22.58
21.30	22.00
20.00	21.68
18.00	21.40
16.00	20.73
14.00	20.35
13.00	20.00
12.00	19.77
11.00	19.53
10.00	19.28
9.00	19.00

Solubility = 5.17 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: H-3
System: C_2H_6, n-C_6H_{14}
Temperature: 30°C
Bar. Pressure: 760.0 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
24.00	24.00
23.00	23.68
22.00	23.50
20.00	23.03
18.00	22.58
16.00	22.09
14.00	21.55
12.00	21.05
10.00	20.56
8.00	20.06
6.00	19.57
4.00	19.07

Solubility = 5.14 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: I-1

System: C_2H_6, n-C_7H_{16}

Temperature: 30°C

Bar. Pressure: 758.1 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
22.80	22.00
20.00	21.42
19.26	21.00
18.00	20.65
17.00	20.25
16.00	20.07
14.60	19.61
14.00	19.52
13.00	19.25
12.00	18.96
11.00	18.68
10.00	18.40

Solubility = 4.54 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: I-2

System: C_2H_6, n-C_7H_{16}

Temperature: 30°C

Bar. Pressure: 758.1 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
22.00	22.51
21.10	22.25
20.30	22.00
18.00	21.38
17.00	21.11
16.00	20.82
15.12	20.50
14.00	20.25
13.00	20.00
12.00	19.70
11.00	19.42
10.00	19.13
8.70	18.75

Solubility = 4.56 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: I-3

System: C_2H_6, n-C_7H_{16}

Temperature: 30°C

Bar. Pressure: 765.0 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
22.80	23.00
21.00	22.48
20.00	22.20
18.00	21.64
16.00	21.03
15.00	20.78
14.00	20.35
12.00	19.94
10.00	19.37

Solubility = 4.51 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: J-1

System: C_2H_6, n-C_7H_{16}

Temperature: 40°C

Bar. Pressure: 753.9 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
22.90	23.00
22.00	22.74
20.00	22.15
18.00	21.55
17.00	21.25
16.00	21.00
15.00	20.65
14.00	20.35
13.00	20.04
12.00	19.75

Solubility = 4.34 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: J-2

System: C_2H_6, n-C_7H_{16}

Temperature: 40°C

Bar. Pressure: 761.1 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
22.60	22.90
21.00	22.43
19.00	21.83
17.85	21.49
15.65	20.85
12.00	19.74
11.00	19.46
10.00	19.15

Solubility = 4.34 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: J-3

System: C_2H_6, n-C_7H_{16}

Temperature: 40°C

Bar. Pressure: 761.1 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
23.25	23.10
21.20	22.50
19.50	21.98
18.00	21.54
16.00	20.95
14.00	20.35
12.00	19.75
10.00	19.16
8.00	18.83
7.00	18.27

Solubility = 4.35 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: K-1

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.705 mole fr. n-C_6H_{14}
0.295 mole fr. n-C_7H_{16}

Temperature: 30° C

Barometric Pressure: 759.2 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
24.00	23.70
23.00	23.46
22.00	23.15
21.00	22.95
20.00	22.73
19.00	22.48
18.00	22.23
17.00	21.99
16.00	21.75
15.00	21.50
14.00	21.25
13.00	21.00
12.00	20.75

Solubility = 5.04 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: K-2

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.495 mole fr. n-C_6H_{14}
0.505 mole fr. n-C_7H_{16}

Temperature: 30° C

Barometric Pressure: 759.2 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
21.00	23.50
19.00	23.00
18.00	22.73
17.00	22.42
16.00	22.22
15.00	21.97
14.00	21.71
12.00	21.21
11.00	20.95
10.00	20.71
9.00	20.45

Solubility = 4.94 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: K-3

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.450 mole fr. n-C_6H_{14}
0.550 mole fr. n-C_7H_{16}

Temperature: 30° C

Barometric Pressure: 757.7 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
23.90	23.85
23.00	23.65
22.50	23.50
22.00	23.40
20.00	22.87
18.00	22.36
16.00	21.85
15.00	21.50
14.00	21.33
12.40	21.00
12.00	20.83
11.00	20.57
10.00	20.32

Solubility = 4.90 $\frac{\text{cc gas}}{\text{cc solution}}$

Run No.: K-4

System: C_2H_6, n-C_6H_{14} and n-C_7H_{16}

Solvent Composition: 0.340 mole fr. n-C_6H_{14}
0.660 mole fr. n-C_7H_{16}

Temperature: 30° C

Barometric Pressure: 757.7 mm Hg

Unabsorbed Gas Volume cc	Solution Volume cc
20.00	24.00
19.00	23.75
18.00	23.55
16.00	23.01
14.00	22.49
12.00	21.96
11.00	21.70
10.00	21.43
9.00	21.16
8.00	20.90
7.00	20.63

Solubility = 4.82 $\frac{\text{cc gas}}{\text{cc solution}}$

Table Showing Variation of Henry's Law Constant With Solvent Composition

System: Ethane, Mixtures of n-Hexane and n-Heptane

Temperature: 30° C

Mole Fraction Heptane	H Ethane, Mixed Solvent atm.	log H
0	36.47	5.5617
0.295	35.95	5.5557
0.505	35.79	5.5538
0.550	35.80	5.5539
0.660	36.05	5.5569
1.000	36.91	5.5672