

A STUDY OF DIFFUSION COEFFICIENTS IN

BENZENE-CYCLOHEXANE MIXTURES

By

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December, 1962

Submitted to the Faculty of the Graduate School of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
August, 1965

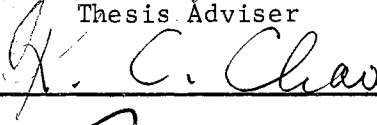
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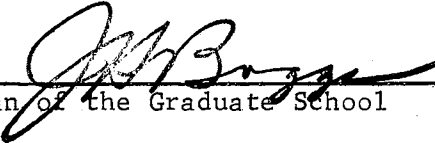
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PREFACE

Experimental data on diffusion coefficients, viscosities, and densities for Benzene-Cyclohexane mixtures are presented in this study. The data were collected over the complete concentration range at 30°C and 55°C. The porous diaphragm cell technique was used to determine the diffusion coefficients.

I wish to express my thanks to my adviser, Dr. John B. West, for his able guidance, patience and useful advice in every phase of this work. I am grateful to the faculty of the School of Chemical Engineering and to my fellow graduate students for valuable discussion. I am thankful to Dr. K. J. Bell for making available some financial assistance under the Leidenfrost Project of the Army Research Office. My thanks are due to Dr. John H. Erbar for helping me in my work.

I am especially grateful to my parents, brothers and sisters for their patience, help and inspiration.

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CHAPTER I

INTRODUCTION

A knowledge of diffusion coefficients is very important in the design of mass transfer equipment as well as in the study of liquid solutions. Experimental data on the diffusion coefficients of liquid solutions are necessary for the testing and modification of various theoretical correlations proposed for the prediction of diffusion coefficients.

The theory of liquid state is complex and yet in its infancy. Although a number of workers have proposed theories attempting to explain liquid solution behavior, yet most of these theories either lack accuracy in their basic assumptions, or are too complex to be of any practical use. At present, the rigorous theories of liquid solutions have limited application unless drastic simplifications are made. From a practical standpoint, it is convenient to propose models, which can be based on simplifying assumptions and can be treated mathematically despite the fact that they are known to be inexact. These models offer promise of partial success.

A detailed review of the liquid state theory is beyond the scope of this thesis. A brief review, of the theories of diffusion and of the correlations based on them is presented later in the thesis. There have been a large number of these correlations for the prediction of diffusion coefficients proposed. Unfortunately, a lack of experimental

data has hindered extensive testing of these correlations.

In the last few years, a number of studies have been reported on a wide range of systems. Models for predicting the behavior of ideal systems have been well established. As for the case of non-ideal systems, the attempts to test correlations have, invariably, met with failure. The reasons for this failure seem quite obvious; a **general lack of data, and a lack of understanding of the solution behavior.**

The system Benzene-Cyclohexane offers a typical example of non-ideal, non-associating class of solutions. The system had been studied previously but there was some difference in opinion regarding its behavior (34, 13). Another reason for the choice of this particular system was the availability of the activity data and self-diffusion coefficients.

This study presents an experimental investigation of the diffusion coefficients of Benzene-Cyclohexane mixtures using the porous diaphragm cell technique. The diaphragm cell method has been highly recommended by Stokes (55), Dullien (17) and Robinson (52). The method is capable of reasonable accuracy and offers promise at high temperatures (35).

Diffusion coefficients for Benzene-Cyclohexane mixtures were determined over the complete concentration range at 30°C and 55°C. Viscosities and densities were also measured and are reported. Differential diffusion coefficients were calculated from the diaphragm cell integral coefficients using Gordon's equations. Diffusion coefficients were activity-corrected and the dependence of D_{μ} product on concentration was evaluated. The dependence of diffusion coefficients on concentration was studied in the light of Hartley-Crank

theory. The results were also compared with the diffusion coefficients calculated employing the theories of Prager, and Lamm.

CHAPTER II

A SURVEY OF LITERATURE

Extensive work has been done since the beginning of the century on the theoretical as well as the experimental aspects of liquid diffusion. Johnson and Babb (35), Robinson (52), and Himmelblau (31), have given excellent reviews of theories of liquid diffusion. An exhaustive treatment of the subject is beyond the scope of this work. A review of the literature pertinent to the present study is the purpose of this chapter.

A brief summary of the various diffusion theories is followed by the hydrodynamic development of diffusion coefficients on the basis of the Hartley-Crank theory. The correlations of Lamm (37) and Prager (50) for the calculation of mutual diffusion coefficients from self-diffusion coefficients are compared to experimental data next. Lastly, a few remarks, regarding the diffusion in non-ideal liquid solutions, are made.

Theories of Liquid Diffusion

The previous attempts to propose a liquid diffusion theory have been based on four principal approaches; the hydrodynamic, kinetic, thermodynamic, and statistical mechanical theories (35, 52).

Hydrodynamic.

The classical hydrodynamic development was made by Einstein (35), who equated the driving force to the frictional resistance term and showed that

$$D = RT/\sigma\mu rN \quad (\text{II-1})$$

where

r = radius of the diffusing molecule

μ = viscosity of the medium

N = Avogadro's number

R = gas constant

T = absolute temperature

The frictional resistance term, $\sigma\mu r$, was derived from Stokes' Law. Equation II-1 is commonly known as the Stokes-Einstein equation.

The Equation II-1 has been shown to apply accurately (35) to the particles of colloidal size but generally its accuracy decreases as the particle size decreases. This is conceivable as the frictional resistance term, $\sigma\mu r$, is derived from Stokes Law which is based on the premise that solvent is a continuum. This premise is no longer true when the solute particles approach the size of the solvent particles. Also, the viscosity considered is that of the solvent, this further restricts the use of Equation II-1 to dilute solutions.

Kinetic.

Kinetic approach to the diffusion problem is based on the Reaction Rate Theory and is primarily due to Eyring and co-workers (22, 23, 26). The development is based on the hole theory concept of the liquid state

theory. This theory visualizes the liquid as a lattice type structure in which molecules move from a given position to an adjacent hole in the structure. Although, the holes in the liquids are considered to be similar in behavior to the gas molecules, yet the partition function for the holes in the liquids is taken less than that for the gases (35).

Eyring and co-workers (22) applied the absolute rate theory to diffusion by assuming that the activation energy for the diffusion process, is that energy which is required to form an extra space in the liquid to allow the molecules to move. Assuming the flux of a component is proportional to λ , the distance between the equilibrium positions of a molecule, and assuming the rate constant to be identical for forward and reverse motion, the following equation is given for an ideal solution (30, 35)

$$D = \lambda^2 K \quad (\text{II-2})$$

where

K = rate constant

A similar treatment of viscous flow yields,

$$\mu = \frac{\lambda_1 \bar{K} T}{\lambda_2 \lambda_3 \lambda^2 K} \quad (\text{II-3})$$

where

\bar{K} = Boltzmann's constant

λ_1 = distance between successive layers of molecules

λ_2 = distance between molecules in the same layer, perpendicular to direction of flow

λ_3 = distance between molecules in the direction of flow

Combining the corresponding parameters in the equation of diffusion and viscous flow, we obtain

$$D = \frac{\lambda_1}{\lambda_2 \lambda_3} \frac{\bar{K}T}{\mu} \quad (\text{II-4})$$

Introducing the basic form of the expression for the rate of reaction and further considering that only degree of freedom as the translational one, Eyring showed that

$$D = \frac{\lambda^2}{V_f^{1/3}} \left(\frac{\bar{K}T}{2\pi m} \right)^{1/2} \text{Exp} \left(\frac{-\Delta E_{\text{VAP}}}{nRT} \right) \quad (\text{II-5})$$

where

V_f = free volume of the liquid

ΔE = energy of vaporization per mole

$$n = \frac{\Delta E_{\text{VAP}}}{\Delta E_{\text{DIFF}}}$$

m = reduced mass of A and B

For ideal systems, Eyring develops two forms, as follows:

$$D = \frac{\lambda_1}{\lambda_2 \lambda_3} \frac{\bar{K}T}{\mu} \frac{d \ln a_A}{d \ln X_A} \quad (\text{II-6})$$

$$D = D^0 \frac{d \ln a_A}{d \ln X_A} \quad (\text{II-7})$$

where $D^0 = D$ for the ideal mixtures, Equation II-4. The above Equations II-2 to II-7 have been found to give only order of magnitude correspondence with experimental results (9).

Thermodynamic.

The thermodynamic approach has been used by Prigogine (52), deGroot (15), Dunlop (2), Laity (36), and Lisianskii (40). Using the methods of irreversible thermodynamics, relations for the diffusion coefficient

in terms of phenomenological coefficients are deduced. This gives a valuable view of the diffusion process without regard to the mechanism of transport. However, no prediction of the diffusion coefficient or the phenomenological coefficients is possible without recourse to molecular hypothesis. This method has been shown to give reasonably good agreement with the experimental measured values of diffusion coefficients in the few cases where it has been tested (40).

Statistical Mechanical.

A statistical approach consists in formulation of diffusion coefficients by considering the interactions between molecular pairs. No rigorous solutions have been obtained. Bearman and Kirkwood (35) have overcome the problems of rigorous solution by a semi-phenomenological approach. Even after these simplifications, it is not possible to apply the results for the actual prediction of diffusion coefficients.

Hartley-Crank Theory

This is the most widely used relation for diffusion in non-ideal binary mixtures of non-electrolytes. The wide spread use of the Hartley-Crank equation is due to the ease of application and the availability of physical data required for its use. Equation II-11 has been shown to fail in predicting the behavior of non-ideal systems (11, 28). The reasoning in the derivation is quite similar to that used in the derivation of Stokes-Einstein equation. Hartley and Crank (29) extended the reasoning to non-ideal solutions. The following is an adaptation from the derivation of Hartley and Crank (35).

Considering that in a real solution the driving force is the

activity gradient rather than the concentration gradient, they empirically designated the resistance terms, σ 's, which were to be functions of solution composition. The σ 's were introduced to take care of the effect of the velocity of molecules, due to a change in concentration, on the randomness of the molecular motion. They obtained the following two expressions for what they called, the intrinsic diffusion coefficients.

$$D_A = \frac{RT}{N\sigma_{A\mu}} \left(\frac{N_A}{V_B C_A} \right) \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A} \right) \quad (\text{II-8})$$

$$D_B = \frac{RT}{N\sigma_{B\mu}} \left(\frac{N_B}{V_A C_B} \right) \left(1 + \frac{\partial \ln \gamma_B}{\partial \ln N_B} \right) \quad (\text{II-9})$$

where

D_A, D_B = intrinsic diffusion coefficients

σ = parameter with the dimensions of length

γ = activity coefficient

V = molal volume

μ = viscosity

C = concentration

N_A, N_B = number of moles of A and B, respectively

subscripts A and B refer to the components A and B. Hartley and

Crank (29) have further shown that under constant volume conditions

mutual diffusion coefficient can be defined by

$$D_{AB} = V_A C_A (D_B - D_A) + D_A \quad (\text{II-10})$$

where V_A and V_B are assumed to be independent of concentration. This relation when combined with the Gibbs-Duhem equation, yields an expression for the mutual coefficient for a non-ideal binary solution.

$$D_{AB} = \frac{RT}{N} \frac{\partial \ln a_A}{\partial \ln N_A} \left[\frac{N_B}{\sigma_{A\mu}} + \frac{N_A}{\sigma_{B\mu}} \right] \quad (\text{II-11})$$

Although the resistance factors are functions of composition, yet the practice has been to assume σ 's independent of concentration and determine the values of σ 's from the diffusivities at the two limits of concentrations (34). The behavior of D at intermediate concentrations can then be predicted.

The intrinsic coefficients of Hartley and Crank have aroused considerable interest as well as controversy. Carman and Stein (10), first reported a difference in the values of D_A and D_B . Bearman (6) was the first to cast doubts on the independence of D_A and D_B . He showed that

$$D_A = D V/V_A \quad (\text{II-12})$$

and

$$D_B = D V/V_B \quad (\text{II-13})$$

Mills (45) contradicted Bearman's arguments and using intuitive arguments showed that

$$D_A = D_B = D \quad (\text{II-14})$$

Robinson (52) closely studied the equations and arrived at essentially the same results as Mills (45). He attributed the controversy due to a misinterpretation on the part of Bearman and found that relation II-10 was trivial. Thereby, he reached the conclusion that the intrinsic diffusion coefficients are not fundamentally independent quantities and that they need not be considered separately from the mutual diffusion coefficient D .

Relation Between Mutual Diffusion and Self-Diffusion

The self-diffusion coefficient differs from the true mutual

diffusion coefficient in that its measurement does not require the existence of any over all chemical concentration gradient, thus giving the nearest approach possible to observing the magnitudes of actual molecular motion in a gross sense. At first glance it might appear that the measurement of self-diffusion rates yields, true differential diffusion coefficients. But the recent experimental evidence indicates that considerable differences may exist between the two kinds of diffusion coefficients for the same average solution concentration (35). The following is a review of two of the theoretical contributions to the problem.

Prager (50) presented the viewpoint that the mutual diffusion coefficient, corrected for activity, should have the same value as the self-diffusion coefficient. Prager considered that the driving force for diffusion is the gradient of chemical potential and which becomes effectively equal to the gradient of isotopic concentration, even in the case of non-ideal solutions, when the self-diffusion of one component is occurring. By considering that the difference in the effective gradient would alter the random motion of the molecules, he derived the following equation:

$$D_{12}/D_{22} = D_{12}/D_{11} = \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln X_1}\right) \quad (\text{II-15})$$

where D_{12} is the mutual diffusion coefficient and D_{11} and D_{22} are the self-diffusion coefficients of the respective components.

Lamm (38) developed the second relationship between the two types of diffusion coefficient on a more logical basis. He considered that the mechanism acting between the interchange of A molecules is different from the mechanism acting between the exchange of A and B

molecules in a binary solution of A and B. The development has a hydrodynamic basis, with the notion of one force acting between the tagged molecules and the chemically identical non-tagged molecules and another force acting between the tagged molecules and the chemically dissimilar molecules.

By considering diffusion in a system of three components 1, tagged A; 1', untagged A; 2, untagged B; Lamm derived the following expression for the relation between the self and the mutual diffusion coefficient (38),

$$\frac{D_{12}}{D_{11}} = \frac{\phi'_{11} \left[\frac{1}{n_1 + n_{1'}} \right] + \phi_{12} \left[\frac{1}{n_1} + \frac{1}{n_{1'}} \right]}{\phi_{12} \left[\frac{1}{n_1 + n_{1'}} + \frac{1}{n_2} \right]} \left(1 + \frac{\partial \ln \gamma_2}{\partial \ln N_2} \right) \quad (\text{II-16})$$

where

ϕ_{12} = frictional resistance per cc, between components 1 and 2

ϕ'_{11} = frictional coefficient for the interaction of tagged
and untagged A, per cc

n_1 = molar concentration of 1

n_2 = molar concentration of 2

Equations II-15 and II-16 are similar except that Lamm introduced an additional coefficient for the case of self diffusion.

Lamm further developed a simplified form of the relation II-16 by assuming that the addition of component 2 does not alter the specific frictional properties of component 1, thus allowing the frictional factors to be evaluated on a volume basis. This simplified form is shown below:

$$\frac{1}{D_{11}} - \frac{n_1 V_1^0}{D_{11}^0} = \frac{N_2}{D_{12}} \left(1 + \frac{\partial \ln \gamma_2}{\partial \ln N_2} \right) \quad (\text{II-17})$$

where V_1^0 is the molar volume of pure 1 and D_{11}^0 is the self diffusion coefficient of pure 1. Lamm emphasized that the above relation should only be approximately true as the specific frictional properties of a component may be a function of concentration.

The relationships discussed above have been found to fail in many cases (35). It has been reported that the relation of Prager was without experimental justification while the more general relation of Lamm was shown to be approximately true in the case of ideal solutions. The behavior of non-ideal systems could be rationalized if the forces were considered to vary with solution composition.

Comments on Diffusion in Non-ideal Solutions

The basic motion of molecules is more complicated in non-ideal solutions due to the presence of force fields which cause the motion to become not strictly random. The theories mentioned in the preceding pages have a number of factors in common but the end results are different from one another.

From the common features, it turns out that the product, $D\mu$, should be linear in concentration. The activity correction term

$$\frac{\partial \ln a_A}{\partial \ln X_A}$$

for non-ideality is also common.

Despite these common features, the equations do not compare directly with the more complicated relations developed from absolute rate theory and the random walk treatment (35). Bearman (6) has demonstrated that the results of most of the above mentioned theories may be obtained from statistical mechanical approach under the assumption

of regular solutions. Therefore, it becomes apparent that the correlations have an indirectly implied assumption of applicability to regular solutions.

It seems to the author that the problem of predicting the diffusion coefficients theoretically, remains unresolved.

CHAPTER III

EXPERIMENTAL APPARATUS

A detailed description of the apparatus employed for experimental measurements of diffusion rates, viscosities, and densities is presented in this chapter. The apparatus used was identical to that used by Robinson (52).

Porous Diaphragm Cell Equipment

I. Diffusion Cells

The cell used for the experiments is shown in Figure 1. The cell is a modification of that used by Dullien (17) and similar to one used by Burchard and Toor (8). The same set of cells as that of Robinson was employed for the purpose of this study.

The cell consists of a cylindrical vessel separated into two compartments by a porous diaphragm. The capillary legs provide the outlets from the two compartments. The cell body, legs and diaphragm were made of pyrex glass. The dimensions of the cell are as follows:

Cylinder diameter = 35mm

Diaphragm diameter = 30mm

Diaphragm thickness = 2.5mm

Height of each compartment = 70mm

Capillary tube size, i.d. = 0.75mm

Over all height of cell and legs = 48cm

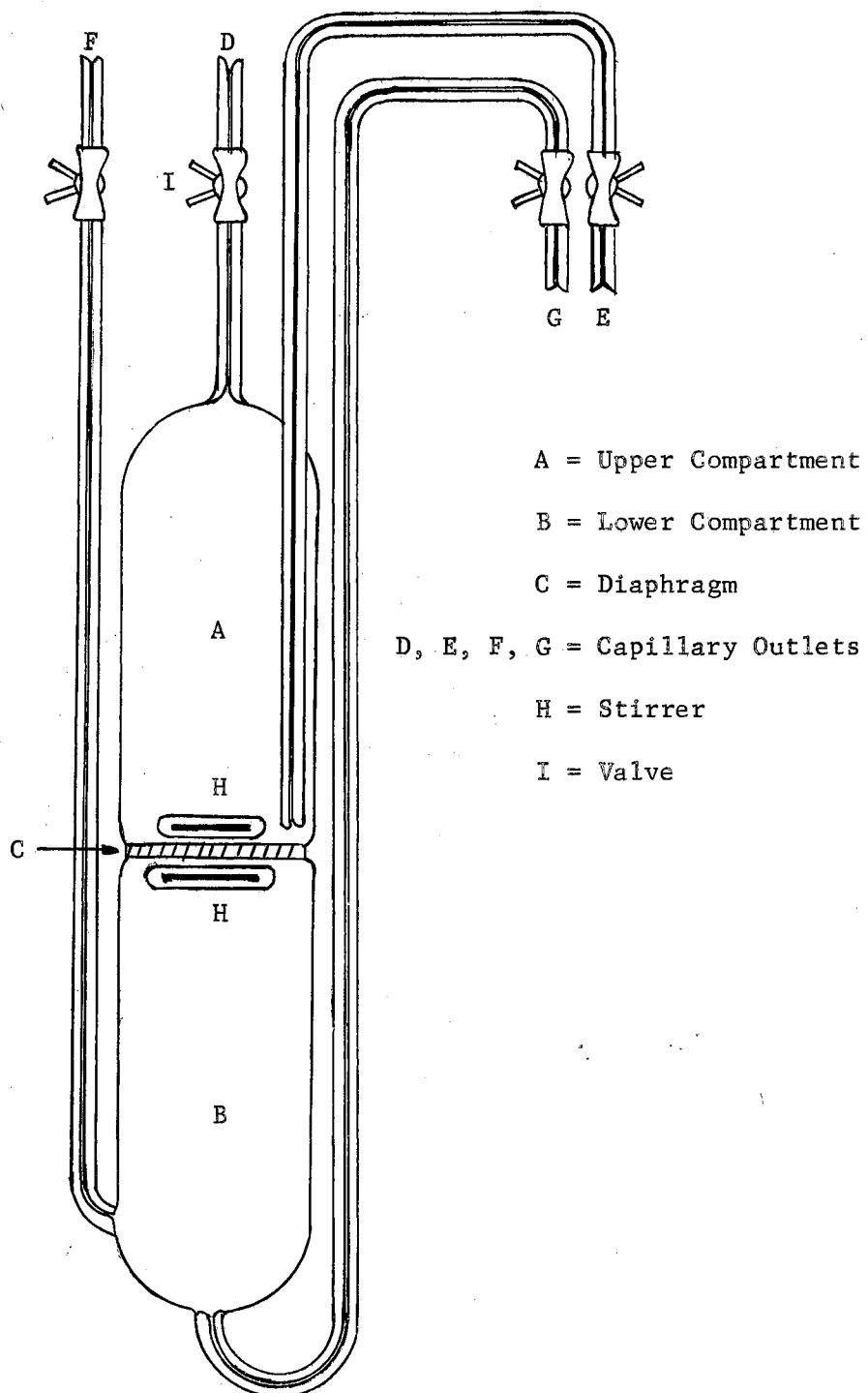


Figure 1. Porous Diaphragm Diffusion Cell.

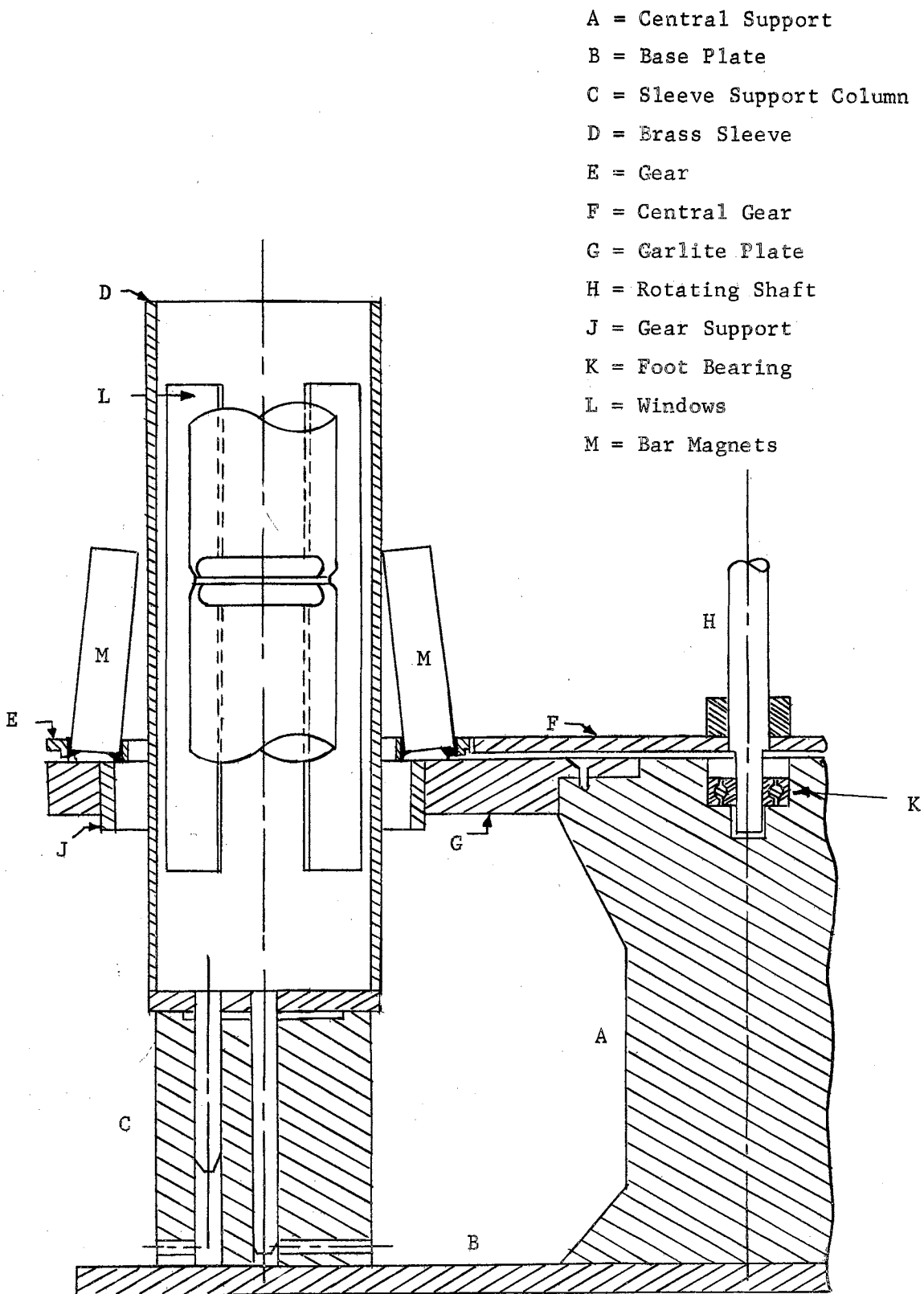


Figure 2. Cell Support and Stirring Device.

Volume of each compartment = 50cc, approximately

The diaphragm used in the work was F (fine) grade (Fisher Catalog, Item II-136) with pore sizes in the range of 2-5 microns, as has been recommended by Gordon (27). Porous diaphragms have been known to allow bulk streaming between the compartments if the pore sizes are larger than 2-5 microns. The use of lower porosities and different materials seems to have no effect (27).

Each compartment has a cylindrical stirrer made of iron wire sealed in soft glass. The length of the stirrer was slightly less than the diaphragm diameter. Densities of the stirrers were adjusted to make them rest against the faces of the diaphragm by inclusion of air. The stirrers were rotated by externally mounted bar magnets.

The capillary outlets from the two cell compartments were provided with valves made of polyethylene tubing fitted with commercial screw clips. The polyethylene tubing was joined to the capillary by application of heat and subsequently, sealing with epoxy. The polyethylene tubing was heated and flattened with pliers. The screw clips were seated on this flattened portion. Screw clips were reinforced with solder at their joints, and heavy wire handles were attached to facilitate tightening. In Figure 1, the capillary legs are shown on the opposite sides of the cell for clarity. Actually, these legs are side by side and are in contact with the wall of the cell. The legs were fastened to the body of the cell and to each other by electrical insulating tape. This reinforcement imparts sturdiness to the cell, lessening the chance of a breakage. Since diaphragm cell experiments take a long time, six cells were used at a time.

II. Cell Support and Stirring

The apparatus to support six cells and provide stirring for the magnets was the same as described elsewhere by Robinson (52). Six brass sleeves like the one shown in the Figure 2, were arranged in a hexagonal pattern. Each sleeve holds one diffusion cell. The sleeves have three cut out sections, to allow free circulation of bath fluid. The sleeve has two brass dowells that fit into holes drilled in a solid brass supporting column. These six brass columns were brazed to a common brass plate. The above arrangement provides a sturdy cell support, while allowing any cell and surrounding sleeve to be removed as desired.

The cells were supported within the brass sleeve by a cylindrical polyethylene block machined to fit into the bottom of each sleeve. The upper face of the block was concave to seat the hemispherical base of the cell and the block had slots cut into it to seat the capillaries at the base of the cell. These slots were sufficiently narrow to allow minimum margin for rotation of cell within the sleeve. Near the top of each sleeve, between the three cut out sections, three small bolts were threaded through the sleeve to level the diaphragm.

Stirring in the cells was accomplished by a pair of bar magnets whose poles were at the level of the diaphragm. Some care was required in aligning the diaphragms and the magnets to assure that the stirrers were not drawn away from the faces of the diaphragm. The two magnets were seated into the face of a gear with epoxy. The bottom face of the gear was attached to a cylindrical shell of mild steel, which rested in a closely machined hole in a large plate of "Garlite" (a linen-laminated phenol-formaldehyde resin).

The six gears, so arranged in a hexagonal pattern, were driven by a central gear. This central gear was mounted on a drive-shaft coupled to a variable speed motor (Gerald K. Heller Co., Model 6T60-20). The motor speed was controlled by a motor controller (Gerald K. Heller Co., Model C-25). The central gear was securely positioned by a foot-bearing attached to the base of the drive shaft. The foot-bearing rested in a receptacle in the central supporting structure.

III. The Constant Temperature Bath

The constant temperature bath was a rectangular vessel of galvanized sheet metal, lagged with two inches of cork-board, supported in a wooden housing. The bath fluid was a petroleum absorber oil fraction.

Heat was supplied to the oil by two ring heaters rated at 300 watts and 500 watts. The 300 watt heater was connected through an autotransformer and was used as a constant heat supply. The 500 watt heater was connected directly through a relay (Fisher Catalog, Item 13-99-65V2). The relay was activated by a mercury-in-glass thermostat (Fisher Catalog, Item 15-180-5) placed in the bath.

Cooling was provided by circulating cooling water through a copper coil in the bath. Temperature of the cooling water was maintained 15°C below the bath temperature by a Blue M Cooling Unit, Model PCC-IA. No cooling was used when making runs at 55°C . The bath fluid was stirred with a variable speed mixer (Lightening Mixer, Model F). Rotation of the bar magnets, gears and stirring apparatus aided in the stirring. Temperature control varied from ± 0.03 at 30°C to ± 0.08 at 55°C . Temperatures were measured with a calibrated Precision thermometer having a range of 19°C to 31°C in divisions of $1/100$ of a degree. At 55°C , the temperatures were measured with a NBS calibrated

thermometer having a range of 0°C to 100°C in divisions of $1/10$ of a degree. A Beckman differential thermometer with divisions of $1/100$ of a degree was used along with the thermometer described above.

Refractometer

A Bausch and Lomb Precision refractometer (Fisher Catalog, Model 33-45-03-02) having a stated precision of 0.00003 units of refractive index was used for the analysis of samples. The refractometer was fitted with a General Electric Lab Arc as light source. A precision temperature controller made by Precision Scientific Co., Model 33-45-88, was used for temperature control of the prisms as well as the samples. The temperature control was maintained within $\pm 0.03^{\circ}\text{C}$ of a degree.

Viscosity Apparatus

Viscosities were measured using standard Ostwald viscometers (Aloe Scientific Catalog, Item V82000). The viscometers were suspended in a water bath. Temperature control of the bath varied from $\pm 0.03^{\circ}\text{C}$ to $\pm 0.05^{\circ}\text{C}$ depending upon the temperature at which the experiment was being run. Flow times were measured with a stop watch.

Density Apparatus

Densities were determined using modified Sprengel pycnometers (Fisher Catalog, Item 3-290). The pycnometers were supplied with ground glass caps for each leg to prevent evaporation losses. The pycnometers were modified to obtain increased accuracy (17). One of the capillary legs was heated at the tip to almost close the opening. Care was taken to leave a portion of the ground glass fitting undamaged

so that the cap could still be seated. A portion of the other leg was drawn out to form a very narrow constriction in the leg. A hash mark was placed with a file at this point. The bath used for the density measurements was the same as the one used for the viscosity measurements.

Materials

The organic chemicals used in this work were from the following sources:

<u>Material</u>	<u>Minimum Stated Purity</u>	<u>Source</u>
Benzene	99 mole %	J. T. Baker Chemical Co.
Cyclohexane	99 mole %	J. T. Baker Chemical Co.
Potassium Chloride	99.9 wt. %	J. T. Baker Chemical Co.

The chemicals were used as received. It has been reported that small amounts of impurities do not effect the diffusion rate (45). The purity of the chemicals was checked by density and refractive index determinations. The results, with corresponding literature values, are given below.

<u>Chemical</u>	<u>Refractive Index 30°C</u>		<u>Density, gm/cc 30°C</u>	
	<u>Exptl.</u>	<u>Lit. (61)</u>	<u>Exptl.</u>	<u>Lit. (61)</u>
Benzene	1.49357	1.4948	0.86849	0.86836
Cyclohexane	1.420778	1.4212	0.76916	0.76914

The water used was deionized and distilled.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The experimental procedure employed in obtaining the data is outlined below. Most of the techniques were devised by Robinson (40) and Dullien (14).

Volumetric Data of the Diaphragm Cells.

The Volumes for the two cell compartments and the diaphragm were required for the present study. Volumes were taken from the data of Robinson (52).

Leveling the Diaphragm.

Before starting a diffusion experiment, each cell was assigned a specific sleeve in the supporting apparatus. The cells were placed in their respective sleeves and leveled.

The Garlite table of the supporting apparatus was leveled first; this served as the reference for future checks on leveling. The three leveling bolts were tightened to touch the cell and they were adjusted until the diaphragm was horizontal. Robinson had previously checked that cells were vertical when the diaphragms were horizontal by testing with glass beads placed on the diaphragm. Two of the three leveling bolts were fixed in position by tightening them to the sleeve with nuts. The third bolt was adjustable to allow entry and removal of the cell. Using the above method, the cells had to be leveled only once. Each time a cell was returned to its sleeve and the adjustable

screw tightened, it was automatically leveled.

This care in leveling had to be exercised since the system is stable with respect to gravity only when the diaphragm is horizontal and the less dense solution is in the upper compartment. Stokes (57) experimentally showed that the mass transfer rate increases as an approximately quadratic function of the angle of departure from the horizontal position of the diaphragm.

Stirring Rate.

The need for stirring in the cells has been demonstrated (17, 56). Stirring assures homogeneity in the individual compartments and more important, eliminates any stagnant layers at the diaphragm. Stagnant layers increase the effective path length for diffusion.

Diaphragm cell results have been reported to vary with the speed of stirring when this speed is below some critical value. Above the critical speed, results are independent of stirrer speed. Unfortunately, there seems to be no agreement on the critical stirring rate. Critical stirring rates from one to one hundred rpm have been reported. Following the recommendation of Robinson (52), rates of 80 rpm were used.

Preparation of Solutions.

Solutions of known compositions were prepared for each diffusion run. The solutions for the upper compartments had to be prepared very accurately. Solution for the lower compartments were not so accurately prepared since the composition of the lower compartment was calculated by material balance. Solutions of known composition were prepared gravimetrically, by mixing weighed portions of the two components forming the mixture. Refractive indices were measured as

a further check on the composition. Solutions for lower compartments were made by mixing predetermined volumes of two components. The volumes were delivered by pipettes. The concentration differences were kept small to avoid effects of volume changes during diffusion.

Filling the Cells.

To start an experiment, the lower cell was filled as follows: With valves E and F closed, a shallow beaker was placed at the mouth of leg G and aspirator vacuum was applied at D. Solution was drawn into the cell till the lower compartment was filled and an inch of solution covered the diaphragm. Suction was removed from D, valve F opened, and suction applied to F until that leg filled above the valve. Valve F was then closed and the aspirator vacuum removed. Valve G was then closed. After filling the lower compartment, the cell was immersed to a point just below the diaphragm in a beaker filled with Dow-Corning silicone oil. The beaker was placed on a hot plate, and the beaker was heated until the contents of the cell boiled under a mild aspirator vacuum.

During the heating, the solution first expanded to increase the liquid level above the diaphragm, then a vapor space formed beneath the diaphragm, and finally boiling began in the lower compartment. The rapid boiling forced the vapors through the diaphragm at a high rate. The vapors condensed in the upper compartment. Boiling the solution served two purposes. First, it degassed the solution in the lower compartment, and second, it flushed out any entrapped air from the diaphragm pores. The effectiveness of the air displacement was evident by the disappearance of the pea size bubble which remained in the lower compartment after filling.

After degassing, the lower cell was placed in the sleeve and seated in the bath. The bath fluid covered the upper compartment by one inch. The cell was allowed to remain in the bath for 30 minutes to establish thermal equilibrium. No stirring was used to avoid the uptake of air by the degassed solution. After the cell had attained bath temperature, the solution in the upper cell was removed by opening valve E and applying compressed air at D. Since leg E terminates a few millimeters above the diaphragm, a small amount of remaining liquid was always removed by inserting a very fine capillary through D and applying aspirator vacuum. By bringing the tip of capillary very near the diaphragm, the last few drops of the liquid could be removed. The upper compartment was rinsed with the solution to be filled in it. The compartment was then filled with the solution of the desired composition. All solutions filled in the upper compartment were kept at the bath temperature in an auxiliary bath.

Degassing the Solutions.

All solutions had to be degassed in order to avoid possible bubble formation in the diaphragm. The lower compartment solutions were degassed by boiling as described earlier. Upper solutions were degassed by boiling and subsequent cooling to the bath temperature when using water, and by freezing and melting under a slight vacuum when using organic solutions. Freezing was done with ice-acetone mixtures.

Preliminary Diffusion.

The diffusion coefficient calculated from the experimental results of the diaphragm cell is based on the assumption of "quasi-steady state." As previously mentioned, this assumption is less in error

if a concentration gradient exists at the beginning of an experiment. Therefore, a short period of diffusion was employed before starting an actual run. The preliminary diffusion was conducted as follows. Approximately 20cc of the upper solution was filled in the upper compartment. Low stirring rates were employed to minimize air absorption. Duration of the preliminary diffusion was estimated by the relation suggested by Gordon (27).

At the end of preliminary diffusion, the upper compartment was emptied, fresh solution filled and the actual run started. Timing of the actual run began at this stage. A small but significant change occurred in the concentration of the lower solution. However, since the initial concentration was calculated by material balance, this effect was taken into account.

Sampling the Cells.

Sampling from the upper compartment was done by applying compressed air at D and opening the valve E. The first few drops from E were discarded and the remainder of the sample was collected in the sampling bottle with screw-on caps. This point marked the end of diffusion time. The lower compartment was then emptied by applying compressed air at F. Before opening the valve G and actually sampling, several air bubbles were forced into the lower compartment. This air forced some of the lower solution into the diaphragm. Valve G was then opened, the first few drops discarded and the sample collected.

The lower sample contained about 0.2cc of the solution which was essentially at the initial concentration and had to be taken into account. This represented the portion of the solution below the valve F.

Sampling time depended on the viscosity and hence on the bath temperature. This time ranged from a few seconds to a few minutes. Sampling time was relatively insignificant compared to the total diffusion time.

Calibration of the Cells.

The effective length and total cross-sectional area for each diaphragm must be known. These quantities are always calculated by performing an actual experiment with a system whose diffusion coefficients are accurately known. All cells were calibrated using KCl-H₂O system as the standard. The integral diffusion coefficients were taken from the data of Stokes (57). This system is the most widely used standard for diaphragm cell experiments.

Analytical Technique.

I. The KCl-H₂O Runs.

The aqueous KCl samples were analyzed by evaporating known volumes of sample to dryness and weighing the residue. Each sample concentration was analyzed in duplicate. Considerable care was taken in this analytical technique. The bottles were thoroughly washed and rinsed in distilled water. The bottles were then placed in the oven (Fisher Catalog, Item 696) at 100°C to dry. The temperature was later increased to 280°C. After cooling the bottles were covered with a glass bell to shield them from dust.

The empty bottles were weighed on a Chain-a-matic balance. The bottles were wiped with a moist chamois and placed, four at a time, inside the balance housing. Approximately 30 minutes were allowed for the bottles to reach the temperature of the balance. A standard bottle which was similar to the ones used for the samples was placed inside the

housing. The standard bottle was used to obtain bouyancy corrections.

The four empty bottles were weighed three times each by a rotating procedure. The procedure was to place the first bottle on the pan, then moved the second, third, and fourth bottle into the position vacated by the preceding one. The first bottle was then weighed and placed in the position vacated by the fourth one. The average weight of each bottle was recorded. This procedure was used to reduce the effect of radiated body heat.

Bottles were filled with 20cc of samples delivered from a calibrated pipet. A three-way pipet bulb (Fisher Catalog, Item 13-681-50) was used for positioning the meniscus. The pipet was calibrated with water.

The filled sample bottles were placed in the oven along with standard bottle on a porcelain tray. The samples were left in the oven to dry. After the samples had dried, the temperature was raised to 280°C to remove the last traces of moisture. On removal from the oven, the bottles were capped and covered with the plastic sheet. The gross weights were determined in a manner similar to the one described above.

The weight of KCl residue was calculated from the equation

$$W_r = W' - \frac{W}{W_s} (W'_s - W_s) - W \quad (\text{IV-1})$$

where

W_r = weight of KCl residue, gms

W, W' = weight of sample bottle, tare and gross, respectively,
gms

W_s, W'_s = weight of standard bottle at time weights W and W' ,
respectively were taken, gms

II. The Organic Runs

The organic samples were analyzed by refractometer described in Chapter III. Temperature control on the refractometer was within $\pm .03^{\circ}\text{C}$. The refractometer was standardized before actual use. A standard prism provided with the refractometer was used for this purpose. Sample bottles were placed in an auxiliary bath maintained at the same temperature as the refractometer. This reduced any errors due to temperature gradients. The prisms were wiped with lint free paper, cleaned with ethyl alcohol, and again wiped with lint free paper. The sample was dropped by means of droppers which had been previously cleaned with acetone. The cross wires were rapidly moved till a sharp dividing line was obtained. To sharpen the dividing line the light source had to be moved occasionally. The mixture composition changes very rapidly due to evaporation. So the first reading was exploratory to locate the approximate vicinity in which the actual reading will fall. The prisms were re-cleaned as before and a few drops of the sample dropped as before. The procedure was repeated. The second and third readings were within $\pm .02$ of the first reading. In this manner the effects of change in composition during the time a reading was being taken were eliminated. The readings were converted to refractive indexes by conversion tables (Series 945).

The refractive indexes, determined above were converted to concentrations, from experimentally determined $N_D - x_A$ and $x_A - \rho_A$ relations. Solutions of known composition were prepared gravimetrically and their refractive indexes determined. These gave the desired relation of refractive index to concentration.

Density Measurements.

Densities were measured by pycnometry. Four 20cc pycnometers of the type described in Chapter III were calibrated with distilled water. Precision of volumes was .05%.

The pycnometers and caps were wiped with a chamois, and the caps were put in place. The caps were secured to the pycnometers by looping each cap with a fine wire and joining the opposite ends of the two wires. The pycnometers were placed in two wire supporting frames beside the balance. The air density was taken at the room temperature. For every weighing the room temperature was taken. The pycnometers were weighed using a rotating scheme on the wire supporting frames. A wire hook was used to suspend the pycnometer during weighing.

After the pycnometers had been weighed three times the hook was weighed. The weights of the pycnometers and the hook were recorded. The pycnometers were then filled with samples. Each sample was run in duplicate. The pycnometers were filled through the leg with the constricted tip by applying very slight aspirator vacuum to the opposite leg. Each pycnometer was filled to a point just past the mark on the hash mark leg, then suspended in the water bath. After 20 minutes the meniscus was carefully adjusted to the hash mark by touching the opposite filled leg with a blotting paper. A very thin roll of the paper was then inserted into the unfilled portion of the leg with the hash mark to remove traces of solution clinging to the walls. The pycnometer was then removed from the bath, the ground glass joints wiped, and the caps immediately replaced.

Gross weights were determined by a procedure similar to that used for the tare weights. The weight of the pycnometer was determined from the relation

$$W^0 = W \left[1 + \rho_{aw} \left(\frac{1}{\rho} - \frac{1}{\rho_W} \right) \right] \quad (\text{IV-2})$$

where

W^0 = weight, in vacuo, of the pycnometer and contents if any, gms

ρ_{aw} = air density, gm/cc

ρ = density of pycnometers and contents if any, gm/cc

W = weight, in air, of the pycnometer and contents if any, gms

ρ_W = density of the weights used in the balance, gm/cc

The difference in the values for W^0 for the filled and empty pycnometer gave the sample weight, in vacuo; the ratio of sample weight to pycnometer volume gave the sample density.

Viscosity Measurements.

The viscosity measurements were made using Ostwald viscometers. The viscometers were cleaned with cleaning solution and acetone in a manner identical to that used for pycnometers. Each viscometer was then filled with sample and placed in the water bath for 20 minutes. A 5cc pipet was used to deliver samples to the viscometers.

The viscometers were calibrated with water. Samples of known composition were then investigated. Flow times were measured three times for each sample. The viscosity was calculated as shown in the Appendix D.

CHAPTER V

RESULTS AND DISCUSSION

Diffusion coefficients for Benzene-Cyclohexane solutions at 30°C and 55°C are listed in Tables I and II. The data are illustrated in Figures 3 and 4. In Tables I and II, the column headed 'Identification' gives the serial number and the cell number. The column headed ' ρ_{Avg} ' gives the average concentration and the column headed ' ρ_A ' gives the concentration at which \bar{D} is equal to D . Each entry is the result of one experimental determination. Data show a maximum deviation of 1.8% and 3.0% from the smoothed curves of Figures 3 and 4. Differential diffusion coefficients are illustrated in Figures 5 and 6.

Differential diffusion coefficients were calculated by the procedure recommended by Gordon (27). The procedure is discussed briefly in Appendix A. The calculations were performed graphically. Dullien and Schemilt (19) have discussed the relative merits of graphical and analytical methods of calculating differential diffusion coefficients from the integral diffusion coefficient data. They held that the error involved in fitting an arbitrary function to the data and extrapolating it to the two axis of concentration to get the diffusivities at infinite dilution can be considerable. They recommended the use of graphical methods. Robinson (52) also discussed the relative merits of the two methods and agreed with Dullien and Schemilt (19) regarding the amount of error involved in using the analytical method.

TABLE I
 DIFFUSION COEFFICIENTS FOR BENZENE-CYCLOHEXANE
 MIXTURES AT 30°C

Identification	$\bar{D} \times 10^5, \text{ cm}^2/\text{sec.}$	ρ Avg. gm/cc	ρ_A
1. VI	2.221	0.099	0.091
2. IV	2.368	0.144	0.089
3. V	2.586	0.319	0.345
4. V	2.610	0.369	0.413
5. IV	2.614	0.489	0.486
6. III	2.563	0.550	0.57
7. I	2.475	0.635	0.65
8. III	2.345	0.707	0.725
9. I	2.365	0.695	0.73
10. VI	2.350	0.741	0.74

TABLE II
 DIFFUSION COEFFICIENTS FOR BENZENE-CYCLOHEXANE
 MIXTURES AT 55°C

Identification	$\bar{D} \times 10^5, \text{ cm}^2/\text{sec.}$	ρ Avg. gm/cc	$\rho_A, \text{ gm/cc}$
1. V	3.261	0.079	0.085
2. III	3.303	0.089	0.096
3. I	3.328	0.088	0.096
4. II	3.625	0.226	0.235
5. II	3.661	0.241	0.25
6. IV	3.742	0.290	0.31
7. IV	3.791	0.309	0.33
8. VI	3.875	0.375	0.376
9. IV	3.946	0.462	0.466
10. VI	3.969	0.465	0.49
11. II	3.69	0.662	0.67
12. III	3.577	0.709	0.72
13. III	3.545	0.722	0.73
14. IV	3.448	0.777	0.78

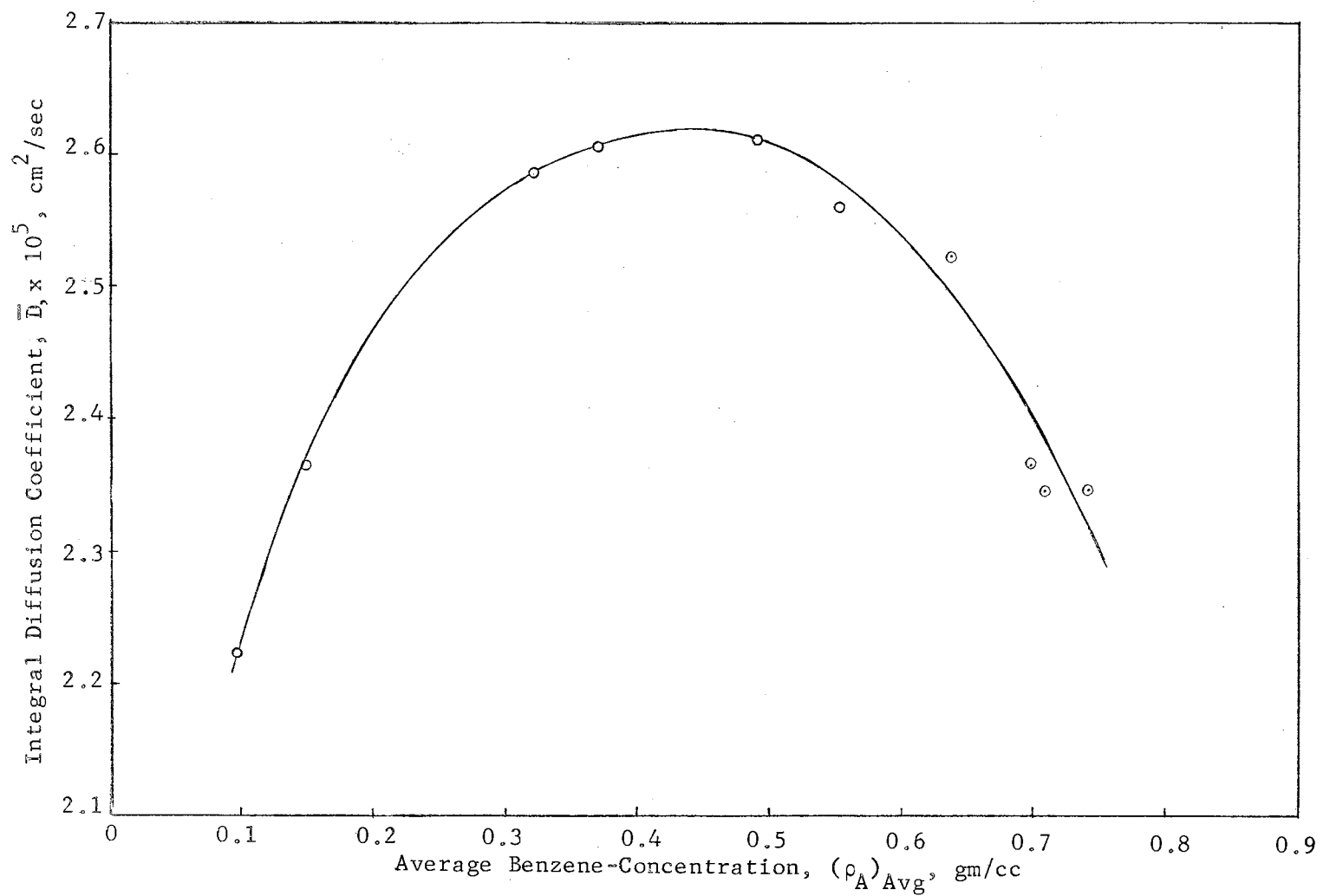


Figure 3. Integral Diffusion Coefficients at 30°C.

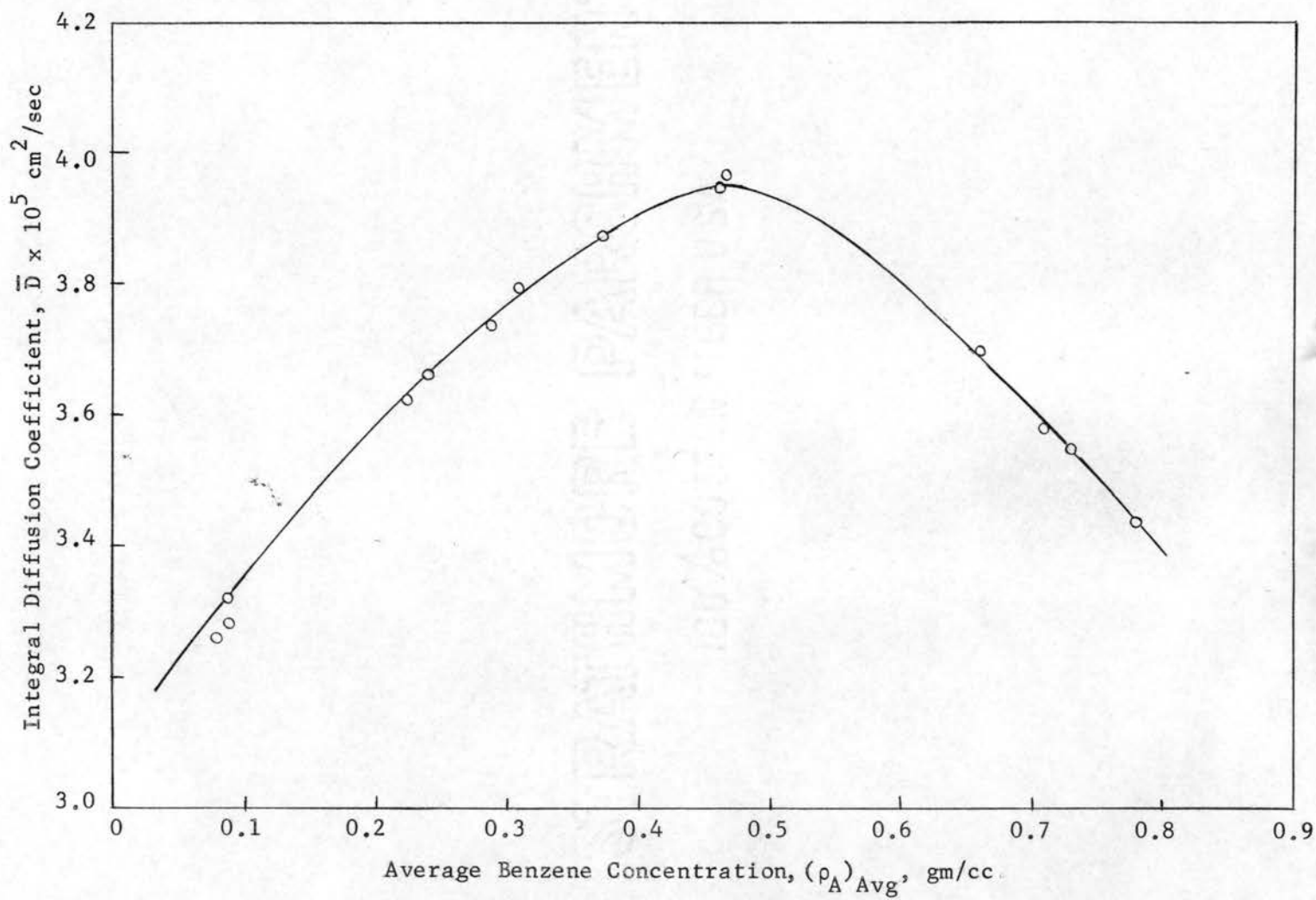


Figure 5. Integral Diffusion Coefficients at 55°C.

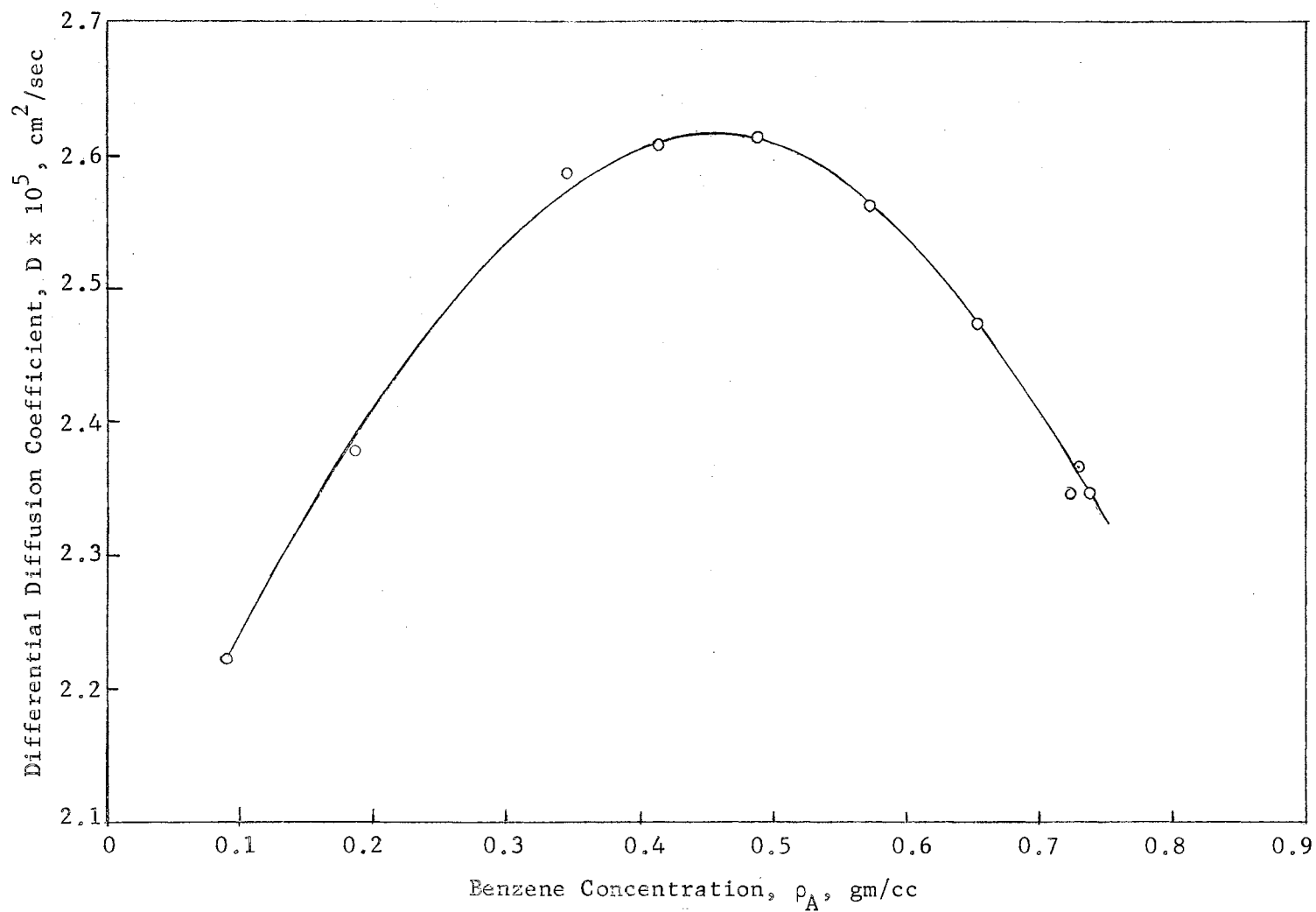


Figure 4. Differential Diffusion Coefficients at 30°C.

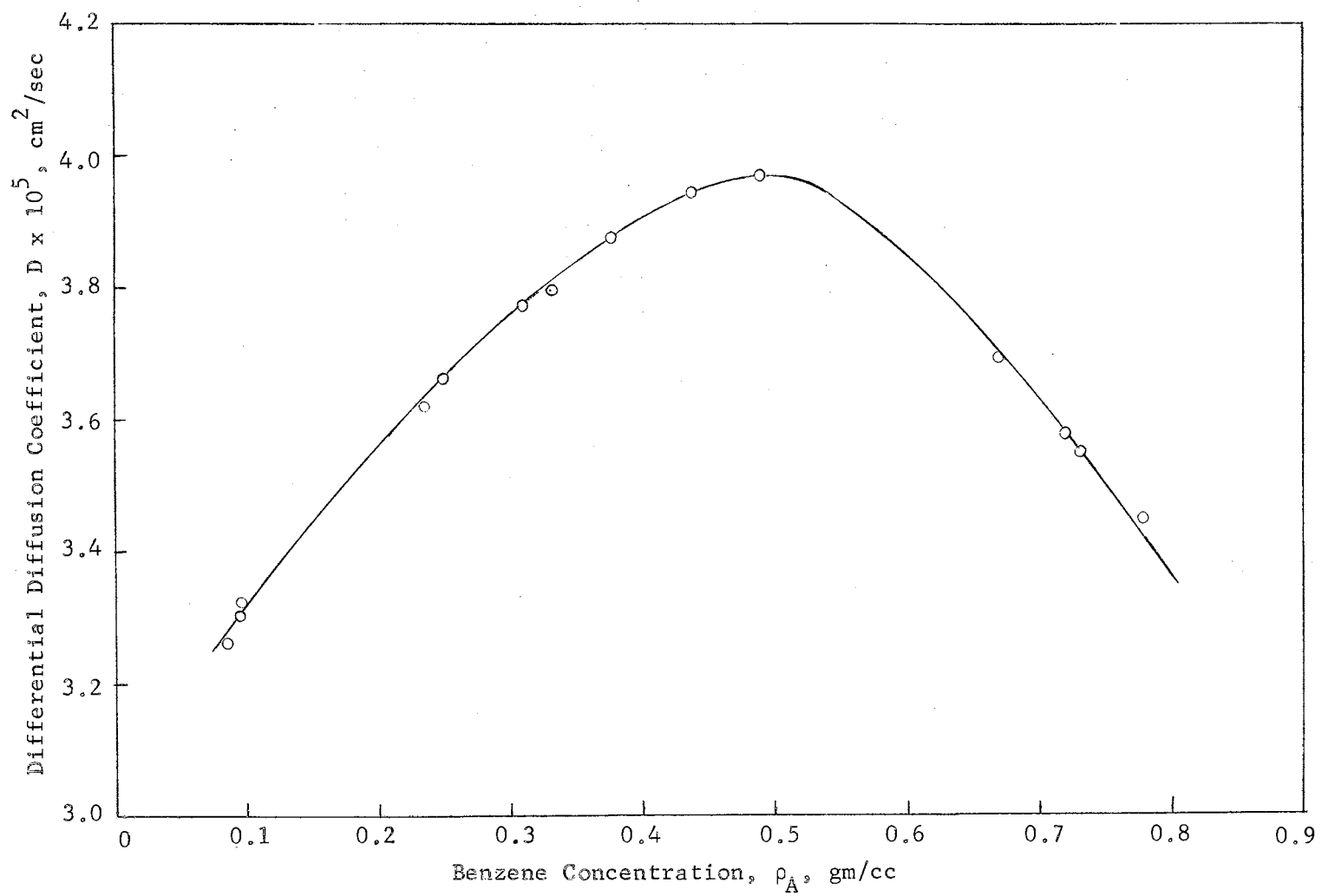


Figure 6. Differential Diffusion Coefficients at 55°C.

A major source of error in using the Gordon's equations can be the assumption of no volume changes during the diffusion. Equations which take into account the effect of volume changes have been proposed and the subject is discussed in Appendix A. Robinson (52) tested his proposed equations which involve no assumption regarding the volume changes for the Ethanol-Water mixtures. Comparing the diffusion coefficients calculated by his own equations with those calculated by Gordon's equations, he found no significant differences in the results calculated by the two methods. He also compared his results with those of Dullien and Shemilt (19) which were calculated using a graphical technique and discovered very good agreement in the diffusion coefficients. Although, the system Ethanol-Water exhibits a volume change of 3% yet there were no significant differences reported in the diffusion coefficients by using Gordon's equations. Robinson attributed the cause to the small concentration differences employed in the experiments. There seems to be general agreement among the workers that if the concentration differences employed are small, the error involved in using Gordon's equations will not be significant (27, 35).

Benzene-Cyclohexane solutions show a maximum volume change of 0.6% at equimolar composition (53). The concentration differences employed in this study were small. Therefore, it was inferred that no significant error will be involved in using Gordon's equations for the calculation of differential diffusion coefficients from the integral diffusion coefficients.

Harned (34) has reported the data of Lyons and Rodwin for Benzene-Cyclohexane mixtures at 25°C. He reported a minimum in the diffusion coefficient at a molal concentration of 0.5. The order of magnitude

TABLE III
 VISCOSITY DATA FOR BENZENE-CYCLOHEXANE
 MIXTURES AT 30°C

Mass Fraction Benzene	Mole Fraction Benzene	Viscosity, cp
0.0	0.0	0.811
0.141	0.150	0.742
0.352	0.369	0.648
0.495	0.514	0.593
0.608	0.626	0.564
0.841	0.851	0.550
0.911	0.915	0.55
0.955	0.958	0.561
1.0	1.00	0.567

TABLE IV
 VISCOSITY DATA FOR BENZENE-CYCLOHEXANE
 MIXTURES AT 55°C

Mass Fraction Benzene	Mole Fraction Benzene	Viscosity, cp
0.0	0.0	0.561
0.141	0.150	0.532
0.352	0.369	0.497
0.495	0.514	0.469
0.608	0.626	0.456
0.841	0.851	0.448
0.911	0.915	0.452
0.955	0.958	0.458
1.0	1.0	0.461

of the diffusion coefficient reported by him ranged from 21.01×10^{-5} to 18.3×10^{-5} . The units of the diffusion coefficients are not clearly stated in the work of Harned (34). Takamatsu (59) has recently reported a diffusion coefficient of $1.6 \times 10^{-5} \text{ cm}^2/\text{sec.}$ at 20°C . Collins and Watts (13), in their study on the self-diffusion coefficients in Benzene-Cyclohexane mixtures, expressed doubts about the data of Harned. They report a maximum in self-diffusion coefficient at a mole fraction of 0.6. The data of present study show a maximum in diffusion coefficient at a mole fraction of about 0.6. This seems to be in agreement with the conclusion of Collins and Watts (13) that both self and mutual diffusion coefficients should go through a maximum at a mole fraction of 0.6. It would seem, therefore, that the data of Lyons and Rodwin is in error by a factor of ten.

The self-diffusion data of Collins and Watts (13), the mutual diffusion data of this work, and the mutual diffusion data of Lyons and Rodwin (34) are illustrated in Figure 13. In plotting the data of Lyons and Rodwin, it was presumed, that a decimal was misplaced by the workers, and that the units are same as those of this work, $\text{cm}^2/\text{sec.}$

Viscosity data for the system is listed in Tables III and IV and illustrated in Figure 7. The viscosity shows a minimum at a mole fraction of 0.76 approximately. Collins and Watts (13) and Harned (34) have also reported a minimum in viscosity at a mole fraction of 0.76. The viscosity data show very good agreement with the data of Collins and Watts (13) over the complete concentration range at 30°C . No viscosity data over the complete concentration range were available in the literature at 55°C , and so, no comparison could be made. The

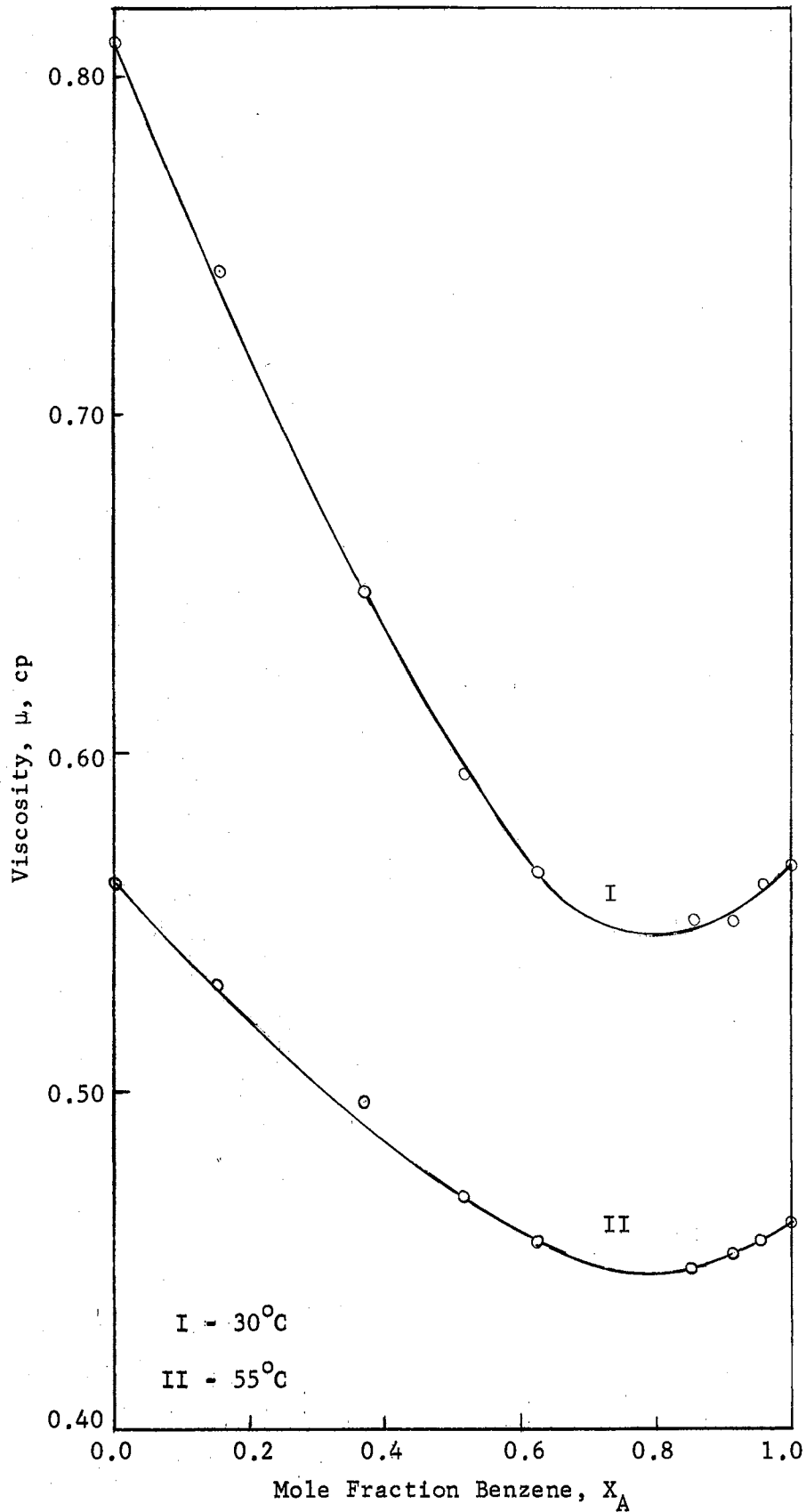


Figure 7. Viscosities of Benzene-Cyclohexane Mixtures.

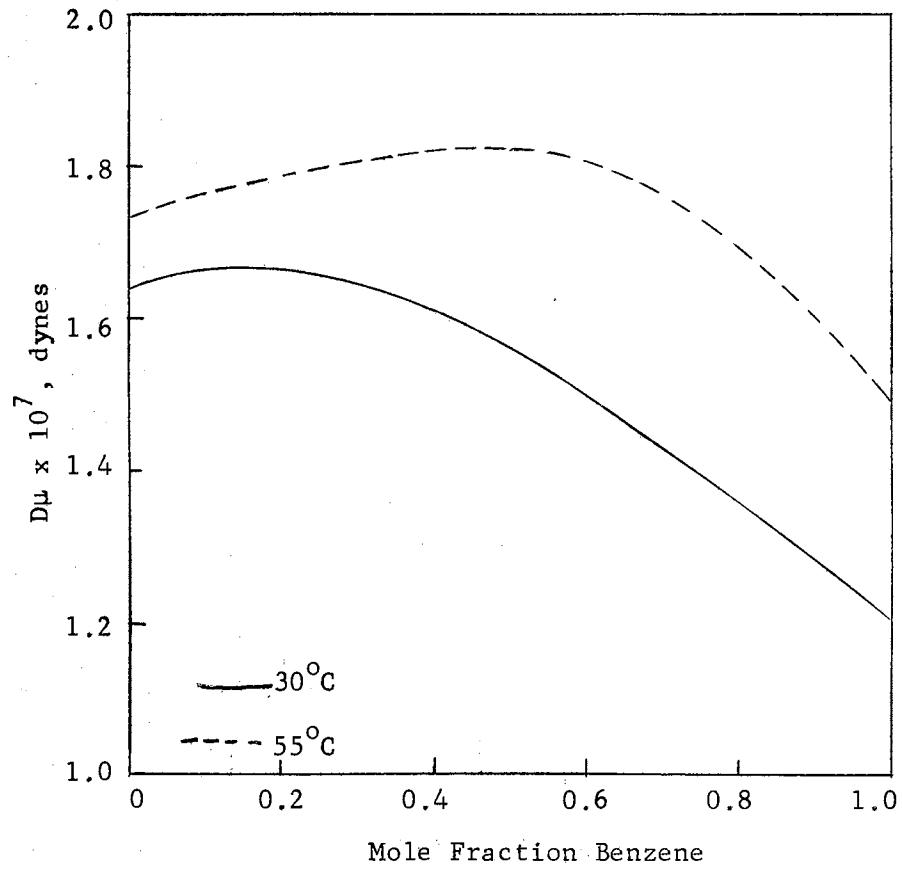


Figure 8. Concentration Dependence of $D\mu$.

data shown in Figure 7 shows a deviation from mean of 0.05%. Each data point is the mean of three experimental observations.

As mentioned earlier, Benzene-Cyclohexane mixtures show a maximum volume change of 0.6% (58). The heat of mixing is also maximum at a mole fraction of 0.5. This implies that energy of interaction between a benzene and a cyclohexane molecule is less than that between two benzene and two cyclohexane molecules (13). Therefore, there should be maximum in diffusion coefficient and a minimum in viscosity. This is borne out by the data of this work. At first glance, the minimum in viscosity appears to be at a different composition. Defining an excess viscosity as the difference between the viscosity of the solution minus the viscosities of the two components, Collins and Watts (13) showed that the minimum in this excess viscosity did occur at the same mole fraction as the maximum in diffusion coefficient.

The values for diffusion coefficients can be corrected for activity by dividing the diffusion coefficient by the quantity $d \ln a / d \ln x$. The activity correction is discussed in Appendix B. Activity-corrected diffusion coefficients along with the smoothed diffusion coefficients are listed in Tables V and VI.

The quantity D_{12} is of special interest since it appears in the equations developed from different theoretical approaches (23, 30, 35). D_{12} product dependence on concentration is illustrated in Figure 8. There seems to be a general agreement among the workers that the D_{12} product should be a linear function of concentration for ideal solutions (3, 9, 13, 35, 52). It is evident from Figure 8, that as expected, D_{12} is not a linear function. Another convenient way of treating the activity correction is to study the concentration dependence

TABLE V

SMOOTHED AND ACTIVITY-CORRECTED DIFFUSION DATA FOR
BENZENE-CYCLOHEXANE MIXTURES AT 30°C

Mole Fraction Benzene, x_A	$D \times 10^5$, $\text{cm}^2/\text{sec.}$	$D/(d \ln a/d \ln x)$
0.0	2.04*	2.04
0.1	2.19	2.28
0.2	2.33	2.48
0.3	2.44	2.62
0.4	2.53	2.72
0.5	2.60	2.77
0.6	2.61	2.75
0.7	2.57	2.65
0.8	2.44	2.49
0.9	2.29	2.30
1.0	2.16*	2.16

*extrapolated value

TABLE VI

SMOOTHED AND ACTIVITY-CORRECTED DIFFUSION DATA FOR
BENZENE-CYCLOHEXANE MIXTURES AT 55°C

Mole Fraction Benzene, x	$D \times 10^5$, $\text{cm}^2/\text{sec.}$	$D/(d \ln a/d \ln x)$
0.0	3.06*	3.06
0.1	3.23	3.32
0.2	3.42	3.52
0.3	3.59	3.72
0.4	3.74	3.87
0.5	3.87	3.99
0.6	3.96	4.06
0.7	3.93	3.99
0.8	3.74	3.77
0.9	3.58	3.59
1.0	3.24 *	3.24

*extrapolated value

TABLE VII

COMPARISON BETWEEN EXPERIMENTAL DIFFUSION DATA
AND THEORETICAL RESULTS AT 30°C

Mole Fraction, Benzene, X_A	$D \times 10^5, \text{ cm}^2/\text{sec.}$		
	Observed	Prager	Lamm
0.0	2.04	1.98	1.98
0.2	2.33	2.09	2.16
0.3	2.44	2.21	2.33
0.4	2.54	2.32	2.46
0.5	2.60	2.46	2.60
0.6	2.61	2.56	2.67
0.7	2.57	2.54	2.61
0.8	2.44	2.51	2.50
0.9	2.29	2.46	2.45
1.0	2.16	2.37	2.37

of $D_{\mu}/(d \ln a/d \ln x)$. Figure 9 shows the plots of $D_{\mu}/(d \ln a/d \ln x)$ vs. the mole fraction at 30°C and 55°C. Eyring proposed that D_{μ} should become more linear after the activity correction (22). Unfortunately, the previous attempts to get a more linear behavior of $D_{\mu}/(d \ln a/d \ln x)$ have not been successful (6). Anderson and Bidlack (3) have reported success in their study on diffusion coefficients of hexane-hexadecane in obtaining a linear behavior of $D_{\mu}/(d \ln a/d \ln x)$. As is evident from the plots of figure 9, the system benzene-cyclohexane does not give a linear behavior of $D_{\mu}/(d \ln a/d \ln x)$ with concentration. No explanation is forwarded as to why there is no significant tendency toward linearity in this system.

It has been suggested that there is a tendency for the activity to overcorrect, sometimes, by as much as several hundred per cent (28). This tendency to overcorrect has been observed for both negatively and positively deviating systems (3). Eyring and co-workers have ascribed some of the difference to rotational terms which are neglected in the partition function ratio (26).

Diffusion coefficients were also calculated from the self-diffusion data of Collins and Watts (13). Correlations of Prager (50), and Lamm (38) were used for the purpose. These correlations are discussed in Chapter II. The results from the two correlations along with smoothed data of this work are listed in Table 7 and are illustrated in Figure 10. The self-diffusion data at 30°C were obtained by interpolation between the data at 25°C and at 35°C. No self-diffusion data were available at 55°C, and so no comparison could be made at this temperature. The average deviation of calculated data from the observed data is about 1.0%. Although the average deviation

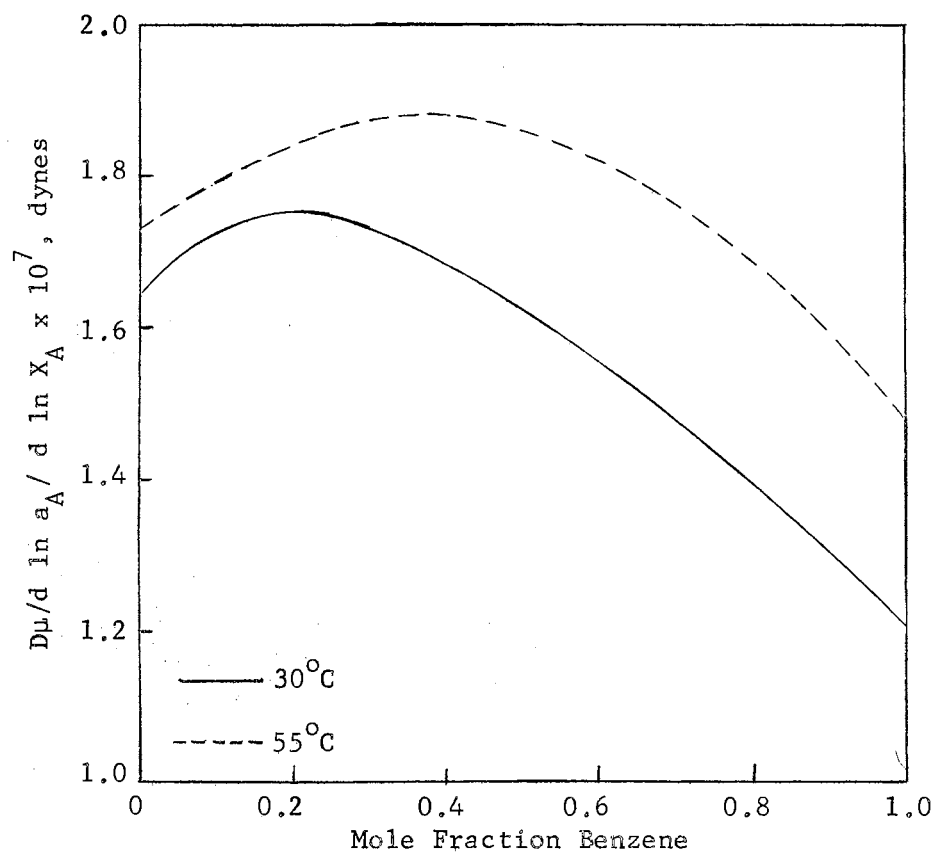


Figure 9. Concentration Dependence of Activity-Corrected $D\mu$.

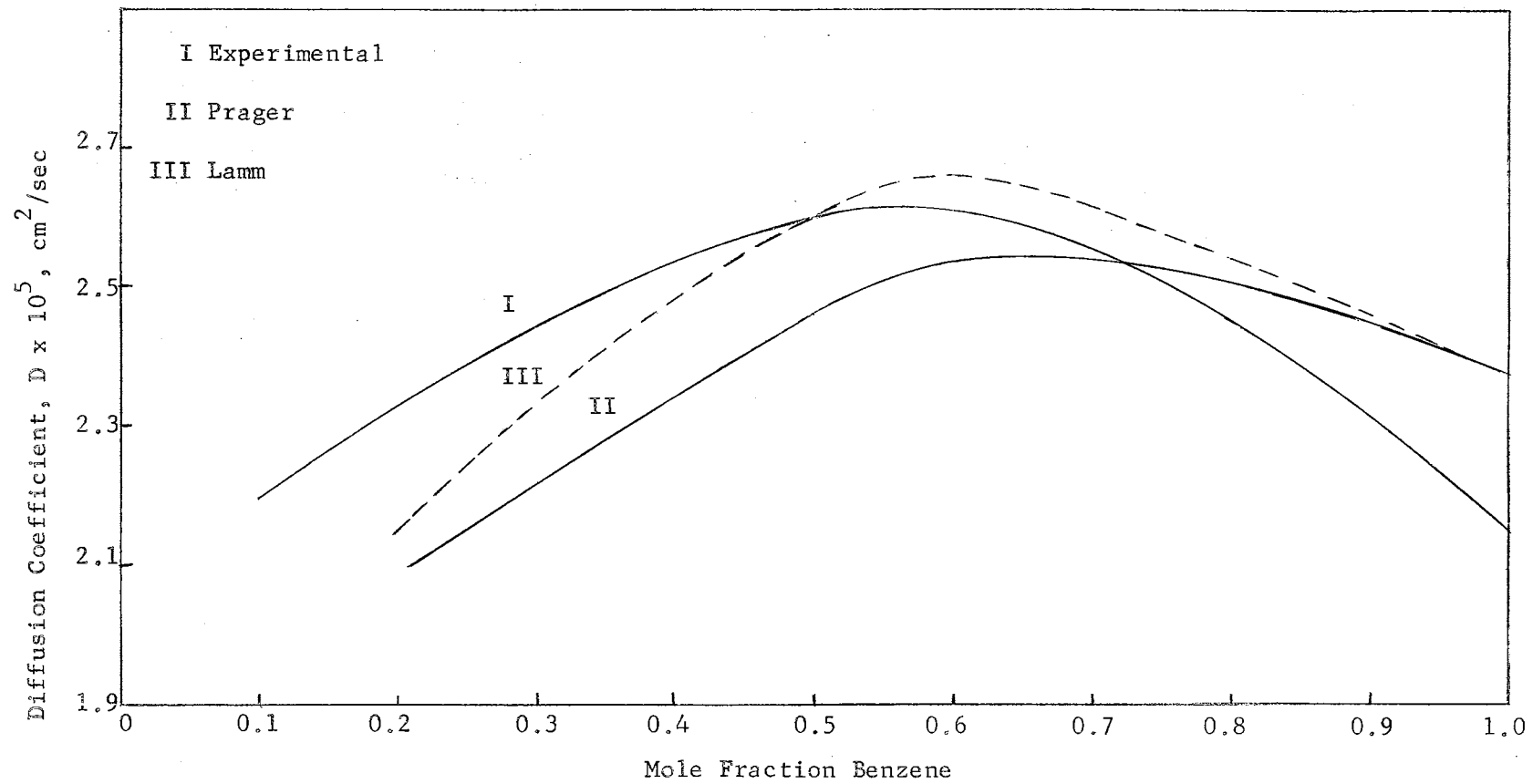


Figure 10. Comparison of Results with Diffusivities From Lamm and Prager at 30°C.

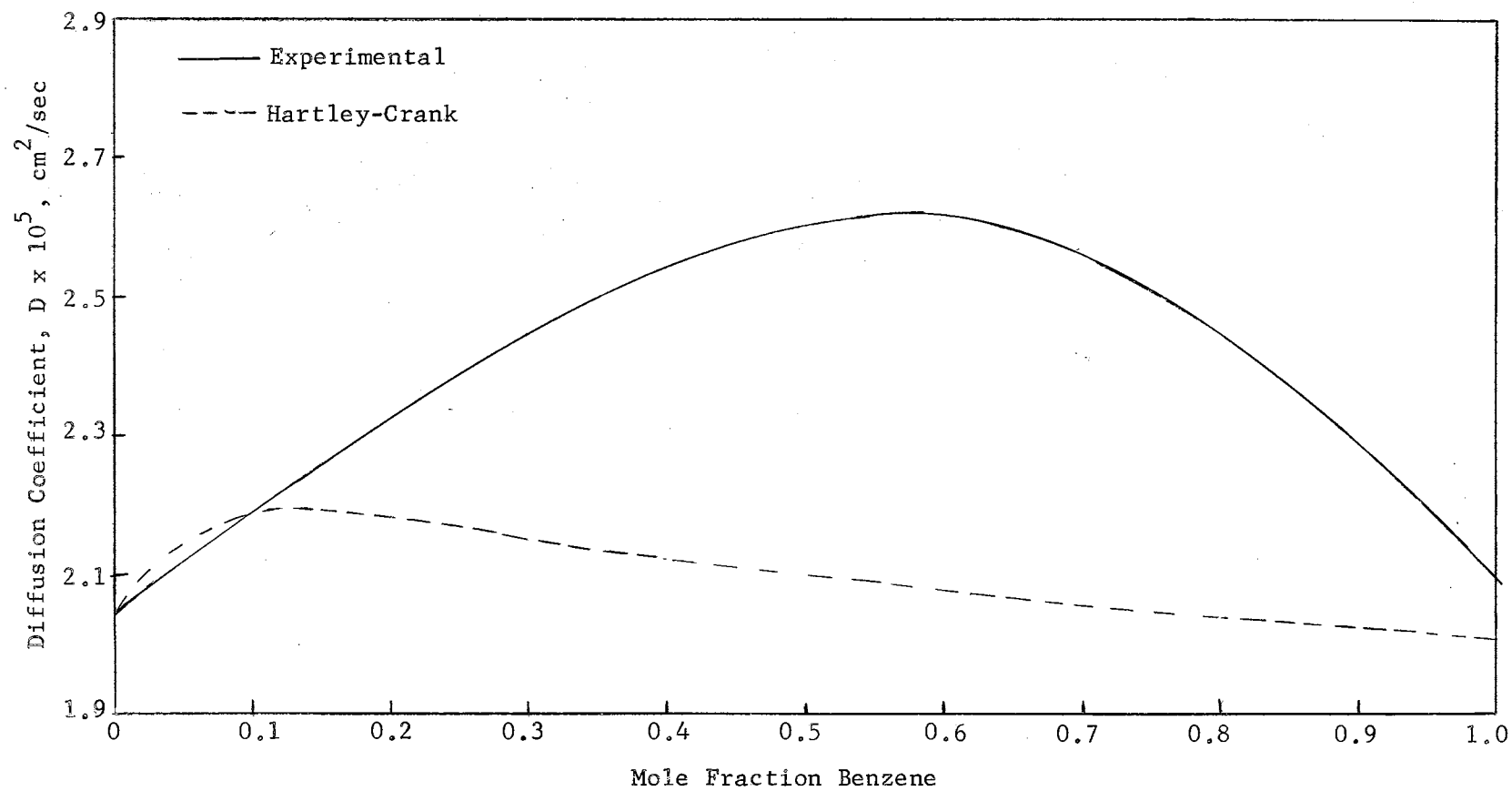


Figure 11. Comparison of Data with Hartley-Crank Theory at 30°C.

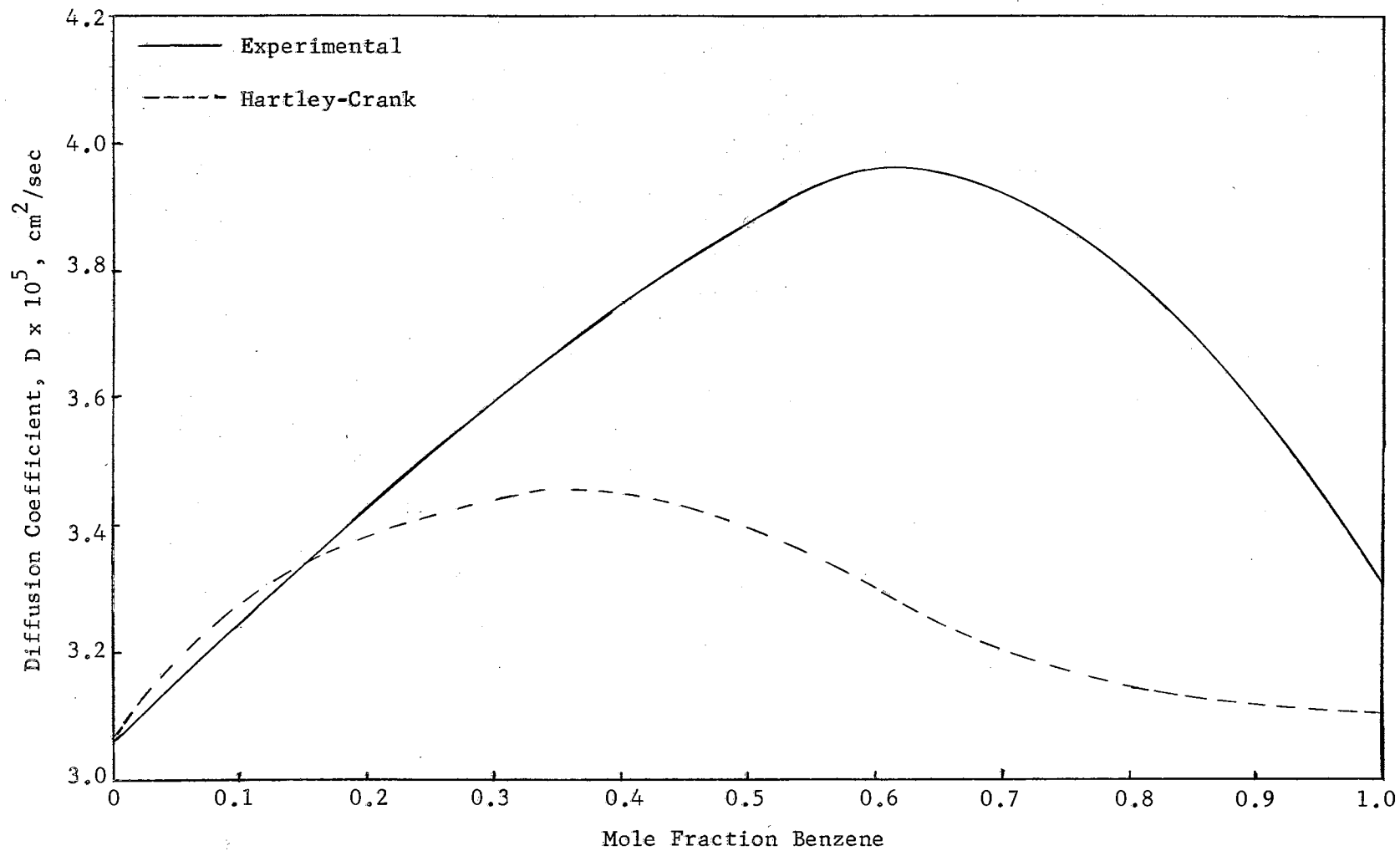


Figure 12. Comparison of Data with Hartley-Crank Theory at 55°C.

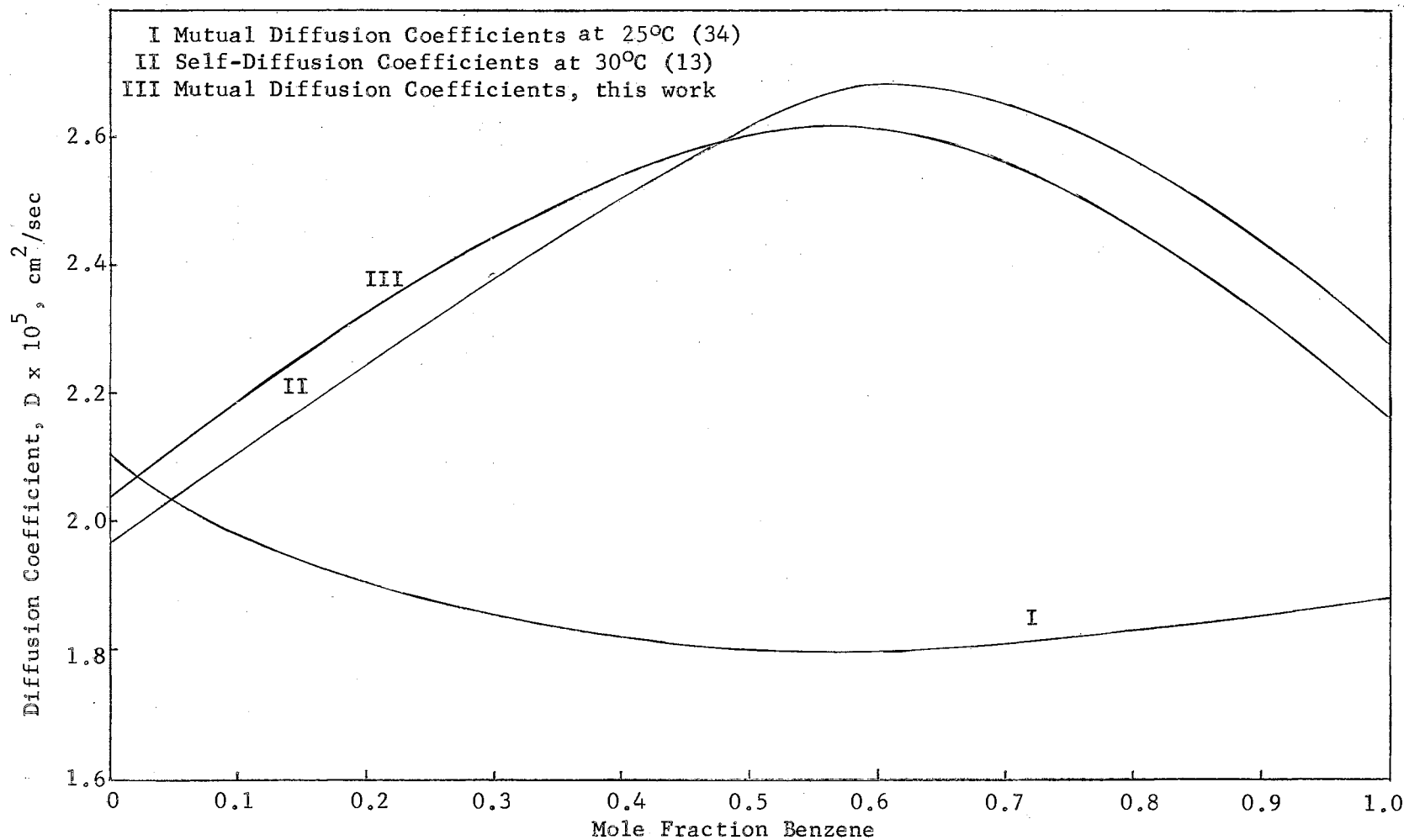


Figure 13. Comparison of Mutual Diffusion and Self-Diffusion Coefficients.

is small, yet from a look at the Figure 10, it becomes obvious that the correspondence over the concentration range is very poor. The observed data show consistently higher values at less than 0.5 mole fractions and lower values at mole fractions greater than 0.5. In the less than 0.5 mole fraction region, the correlation of Lamm comes nearer to the observed data as compared with the equation of Prager. At mole fractions greater than 0.5, the behavior of the two relations is similar as far as the deviation from the observed data is concerned. The results of this comparison seem to confirm the viewpoint of other workers, who have indicated that the relation of Prager is not applicable to non-ideal systems while the relation of Lamm, in the commonly applied form, Equation II-17, assumes the specific frictional properties of the system to be independent of concentration which is not true in the case of non-ideal solutions (35, 37). Comparison between the observed data of this work and that calculated by the relation of Lamm therefore, indicates that the simplified relation of Lamm, Equation II-17, may not be applicable to the Benzene-Cyclohexane mixtures.

Hartley and Crank have proposed a relation for describing the behavior of non-ideal systems, Equation II-11. The application of this equation followed the procedure outlined by Harned (34). The parameters, σ_A and σ_B were evaluated by using the extrapolated data of the present work to the two axis of concentration and the behavior of the system at the intermediate concentrations was calculated (35, 52). The results along with the observed data are plotted in Figures 11 and 12. The equation gives far smaller values of diffusion coefficients at the intermediate mole fractions. The average deviation

ranges from 10% at 30°C to 16% at 55°C. The only reason which can be thought of is that the parameters σ_A , σ_B are not independent of concentration. Also Bearman (6) has shown that the Hartley-Crank equation makes an indirect assumption of regular solution. As the system under study is not regular (58), this might be the reason for large discrepancy. The relation has also been shown to fail in other non-ideal systems where it has been tested (11, 28).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Mutual diffusion coefficients of Benzene-Cyclohexane solutions were determined in this study. The data were collected over the complete concentration range at 30° and 55°C. Viscosities of the system were also determined and are reported in the preceding chapter.

The Benzene-Cyclohexane system shows a maximum in mutual diffusion coefficients at a mole fraction of 0.6 while the viscosity goes through a minimum at a mole fraction of 0.76 at both 30°C and 55°C.

Agreement between the experimental diffusion data and the diffusion data calculated from self-diffusion coefficients using the relations of Lamm and Prager is poor over the complete concentration range, even though the average absolute value of diffusion coefficient deviates from the theoretical results only by 1%. This suggests that relations of Lamm and Prager may not be applicable to the system of this study.

Hartley and Crank theory fails to predict the behavior of this system. It shows as much as 16% deviation at 55°C and 10% deviation at 30°C. It seems, therefore, that Hartley and Crank theory does not apply to this system but applies only to regular solutions.

The concentration dependence of D_{μ} and $D_{\mu}/(d \ln a/d \ln x)$ is not linear. Although $D_{\mu}/(d \ln a/d \ln x)$ is more linear at higher temperature than at the lower temperature, yet the relation even at higher temperature

is not linear.

It is recommended in the light of above conclusions, that more studies on the systems of this type should be instigated. Such a study should include the measurements of self as well as mutual diffusion coefficients, viscosities, densities and activity coefficients. These data are necessary in modifying the existing relations or suggesting new uses for the behavior of this type of systems.

Serious thought should be given in future experiments to modify the technique of filling the diffusion cells. It is recommended that some kind of system be evolved to empty and fill the cell in the constant temperature bath itself. In this study, the solutions for the upper compartment were maintained at same temperature as that of the diffusion run in an auxiliary constant temperature bath. After the preliminary diffusion, the cells were removed from the bath, the upper compartment was emptied, rinsed and then filled with the solutions, kept in the auxiliary bath. It is the feeling of the author that this might introduce thermal gradients. In the case of volatile mixtures, there can also be a slight change in composition of the solution while filling the upper compartment of the diffusion cell.

It is suggested that the size of the constant temperature bath be increased to accommodate a wire cage so that the solutions to be filled in the upper compartment can be kept in it. It is also recommended that a technique be evolved to empty and fill the cells without having to remove them from the constant temperature bath.

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NOMENCLATURE

a = activity

A = component A

B = component B

C = concentration, gm/cc

d = differential operator

\bar{D} = integral diffusion coefficient, cm^2/sec .

D = differential diffusion coefficient, cm^2/sec .

F = free energy, calories

J = mass flux relative to mass average velocity, $\text{gm}/\text{cm}^2\text{-sec}$.

K = rate constant

\bar{K} = Boltzmann's constant

n = molar concentration

N = Avogadro's number

R = universal gas constant

T = temperature, $^{\circ}\text{C}$

V = specific volume, cc/gm

x = mole fraction

y = distance in the direction of molecular diffusion, cm

Z = volume fraction

ρ = density, gm/cc

σ = Hartley-Crank parameter

β = cell constant, cm^{-2}

γ = activity coefficient

μ = viscosity, cp

θ = time, sec.

ω = mass fraction

λ = frictional coefficients of Lamm's theory

Superscripts

' = lower compartment

" = upper compartment

''' = diaphragm

* = ideal property

o = pure component property

E = excess quantity

Subscripts

A = component A

B = component B

i = component i

j = component j

1 = component 1

2 = component 2

AB = mutual property of A and B

11 = self coefficient of 1

22 = self coefficient of 2

12 = mutual coefficient of 1 and 2

APPENDIX A

A REVIEW OF DIAPHRAGM CELL THEORY

A brief review of the diaphragm cell theory along with relations between the mutual diffusion coefficients is presented in the next few pages.

The diaphragm cell method was introduced by Northrop and Anson (47) in 1928. Since then the method has been continuously improved and has been well established theoretically as well as with regards to its limitations. Robinson (52) has made considerable improvements to theory and the experimental technique of the method. This review is an adaptation from his thesis.

Diffusion Equation

Fick defined the diffusion coefficient as

$$N_A = - D \nabla \rho_A \quad (\text{A-1})$$

where

N = mass flux of A relative to a fixed co-ordinate system,

gm of A/cm²-sec.

D = diffusion coefficient

ρ_A = mass concentration of A, gm of A/cc

Equation A-1 is the statement of Fick's First Law and states that mass flux of component A is directly proportional in magnitude and opposite in direction to the gradient of A. This equation has been extensively used for diaphragm cell experiments.

An alternate and more general definition is

$$J_i = \rho D \nabla \omega_i \quad (\text{A-2})$$

where

J_i = mass flux of component i, relative to mass average velocity, gm of component i/cm²-sec

ρ = total mass density, gm of solution/cc

D = diffusion coefficient, cm²/sec

ω_i = mass fraction of i, gm of i/gm of solution

D is called the "true" or "differential" diffusion coefficient.

In equation A-2, the same value of D applies irrespective of whether the concentrations are written in terms of i or j . The D defined by A-2 is not influenced by the geometry or convective flow conditions in the apparatus.

For a binary system, the following expression can be written

(52)

$$N_A = -D \nabla \rho_A + \rho_A [N_A V_A + N_B V_B] \quad (\text{A-3})$$

where

V_A = partial specific volume of A, cc of A/gm A in solution.

The term in parenthesis, in Equation A-3, is the total volume flux resulting from bulk flow. In the diaphragm cell experiments, one compartment is always closed, so that volume flux will be zero if system exhibits no volume changes on mixing. The quantity in the brackets drops out and Fick's Law will apply. The assumption of no volume changes on mixing has always been applied in the diaphragm cell work.

The Equation A-1 is usually integrated as follows:

Let y be measured orthogonally to the faces of the diaphragm,
and

let $y = 0$ and $y = L$ be the two faces of the diaphragm.

Then by a material balance on the two cell compartments,

$$(N_A)_{y=0} = -\frac{V^i}{A} \frac{d\rho_A^i}{dt} \quad (\text{A-4})$$

$$(N_A)_{y=L} = \frac{V^{ii}}{A} \frac{d\rho_A^{ii}}{dt} \quad (\text{A-5})$$

where

V = volume of solution, cc

A = effective cross sectional area for mass transfer, cm^2

t = time, sec

i, ii = refer to the lower and upper compartments, respectively

The assumption is made that quasi steady state conditions exist at any give time, i.e.

$$(N_A)_{y=0} = (N_A)_{0 < y < L} = (N_A)_{y=L} \quad (\text{A-6})$$

Replacing the right hand side of the Equation A-1 by $-\hat{D} \frac{\rho_A^{ii} - \rho_A^i}{L}$

and considering diffusion in the y -direction only, we get

$$N_A = -D \frac{d\rho_A}{dy} = -\hat{D} \frac{\rho_A^{ii} - \rho_A^i}{L} \quad (\text{A-7})$$

where D = diffusion coefficient defined by Equation A-7. Combining

Equations A-4, A-5 and A-7

$$d\Delta\rho_A = d\rho_A^{ii} - d\rho_A^i = -\frac{A}{L} \left[\frac{1}{V^{ii}} + \frac{1}{V^i} \right] \hat{D} d\rho_A dt \quad (\text{A-8})$$

or

$$d \ln \Delta\rho_A = -\beta \hat{D} dt \quad (\text{A-9})$$

where

$$\Delta\rho_A = \rho_A'' - \rho_A'$$

$$\beta = \frac{A}{L} \left[\frac{1}{V''} + \frac{1}{V'} \right]$$

where β is the cell constant, cm^{-2} . Integrating from $t = 0$ to $t = \theta$,

A-9 becomes

$$\ln \frac{(\Delta\rho_A)_o}{(\Delta\rho_A)_f} = \beta \bar{D} \theta \quad (\text{A-10})$$

\bar{D} = the "integral diffusion coefficient" or a time averaged value of \hat{D}

Subscripts o and f refer to initial and final conditions, respectively.

Equation A-10 is exclusively used for diaphragm cell experiments and is commonly called the "Simple Logarithmic Formula." This equation has the following limitations:

1. The assumption of quasi steady-state
2. The assumption of no volume changes

Using the afore-stated assumptions, Barnes (5) obtained formal solutions for two sets of initial conditions. These conditions were (1) pure solvent fills one compartment and the diaphragm, and (2) pure solvent fills one compartment and a linear concentration profile exists in the diaphragm. Barnes found that, in the first case, the quasi steady-state assumption may be significantly in error while, in the second case, the assumption introduces negligible error when the ratio of diaphragm pore volume to the compartment volume is less than 0.1. In the present study this ratio was 0.007.

Dullien (17) integrated the diffusion equation numerically for typical diaphragm cell conditions and found that even if D varied

with concentration, the quasi steady state conditions assumption should introduce error of less than 0.2%. Toor (62) investigated another aspect concerning the fluxes in the diaphragm. He reported that due to a tortuous path in the diaphragm, $\frac{d\rho_A}{dx}$ must be replaced by $\frac{\partial\rho_A}{\partial x}$, which may be a function of x and z co-ordinates. However, Toor proved mathematically that the solutions to the diffusion equation, with or without the unidirectional diffusion assumption, were similar.

Robinson (52), in his study analyzed the above mentioned work and reached the following conclusions:

- (1) The quasi steady state assumption appears to be valid in the diaphragm cell experiments.
- (2) A concentration profile should be established prior to starting a diffusion run.
- (3) Integration of the diffusion equation does not require the assumption of unidirectional diffusion.

Calculation of the Differential Diffusion Coefficient From the Integral Diffusion Coefficient

Although it is experimentally possible, in general, to measure only integral diffusion coefficients, it is desirable to convert the measured integral diffusion coefficients into differential diffusion coefficients. The latter are more useful in that they represent point conditions and can be readily used to compare data between the various investigators. Many early investigators failed to recognize the difference between the differential diffusion coefficients and the integral diffusion coefficients (35).

The basic relationship follows from Fick's Law (27) and is given as

$$\bar{D} = 1/(C'' - C') \int_{C'}^{C''} D dC \quad (\text{A-11})$$

This relation assumes that there are no volume changes on mixing. Gordon (27) has discussed in some considerable detail the relation between the two types of coefficients and has presented an iterative procedure to get differential coefficients from integral coefficients, Gordon's procedure is outlined below.

Assume that D is a function of concentration, in particular that

$$D/D^0 = 1 + f(\rho_A) \quad (\text{A-12})$$

where D^0 is the coefficient at infinite dilution.

It becomes apparent that if A-12 is true then Equation A-10 cannot be true. Nevertheless, it is convenient to define \bar{D} by means of Equation A-10, since it can easily be computed from the duration of the experiment, the known values of the cell constant and of

$$\frac{(\Delta\rho_A)_o}{(\Delta\rho_A)_f} .$$

A more general relation can then be developed considering the diaphragm cell as a steady-state problem. For a steady-state, $D \frac{\partial \rho_A}{\partial x}$ is constant for a particular instant of diffusion. If, at this time, ρ_A' and ρ_A'' are the concentrations of the lower and upper compartments, it is possible to define an effective diffusion coefficient, D^* , in terms of the flow:

$$-D^* (\rho_A' - \rho_A'')/L = D \frac{\partial \rho_A}{\partial x} \quad (\text{A-13})$$

Multiplication by dx and integration from $x = 0$ to $x = L$ gives

$$\frac{D^*}{D_0} = 1 + \frac{1}{\Delta\rho_A} \int_{\rho_A'}^{\rho_A''} f(\rho_A) d\rho_A \quad (\text{A-14})$$

where $\Delta\rho_A$ stands for $(\rho_A'' - \rho_A')$. Let us define another function $F(\rho_A', \rho_A'')$ by

$$\frac{D^0}{D^*} = 1 + F(\rho_A', \rho_A'') \quad (\text{A-15})$$

Then, substituting A-15 in A-10 and rearranging

$$\frac{\bar{D}}{D_0} = 1 + \frac{1}{(\beta D_0 \theta)} \int_{\Delta\rho_A}^{\Delta\rho_A^f} \frac{F(\rho_A', \rho_A'')}{\Delta\rho_A} d(\Delta\rho_A) \quad (\text{A-16})$$

Moreover, if ρ_A is defined as the concentration for which $\bar{D} = D$, it follows that $f(\rho_A)$ must be identical to the second term on the right side of Equation A-16, thus making it possible to solve for ρ_A^* . The actual mechanism of calculation is very simple. For given values of β and ρ_A , Equation A-14 can be integrated analytically (52), graphically (19), or numerically (27). Then evaluating the function $F(\rho_A', \rho_A'')$ Equation A-16 can be integrated numerically or graphically. Using A-16 and A-12, ρ_A^* can be calculated. The procedure is repeated each time with a different assumed value of ρ_A until the ρ_A^* calculated from A-16 differs insignificantly from ρ_A assumed arbitrarily.

As mentioned earlier, the above procedure assumes no volume changes on mixing.

Dullien and Schemilt (19) and Olander (48) have presented solutions to the basic diffusion equation assuming no volume changes. Robinson (52) reviewed the derivations of these authors and discovered some tacit assumptions in their works. He presented a set of equations of his own which involved no assumption other than that of quasi steady-state. A brief summary of his work is given below.

Define a function $f(\rho_A)$ such that

$$\frac{D}{D_o} = 1 + f(\rho_A)$$

where

$$D = D_o \text{ at } \rho_A = 0$$

and define another function,

$$G(\rho_A, \rho_A') = \rho_A V_B \left[\frac{V_A}{V_B} - \left(\frac{V_A}{V_B} \right)' \right] \quad (\text{A-17})$$

where V_A and V_B refer to partial specific volumes of A and B components, respectively. Then

$$\frac{D^*}{D_o} = \frac{1}{\Delta \rho_A} \int_{\rho_A}^{\rho_A''} \frac{1 + f(\rho_A)}{1 + G(\rho_A, \rho_A')} d\rho_A \quad (\text{A-18})$$

Let us define

$$\frac{D^o}{D^*} = 1 + F(\rho_A', \rho_A'')$$

Then

$$\frac{\bar{D}}{D_o} = \frac{\bar{\beta}}{\beta_o} \left[1 + \frac{1}{D^o \theta} \int_{(\Delta \rho_A)_o}^{(\Delta \rho_A)_f} \frac{F(\rho_A', \rho_A'')}{\beta \Delta \rho_A} d\Delta \rho_A + \frac{1}{D_o \theta} \int_{V_o''}^{V_f''} \frac{1 + f(\rho_A', \rho_A'')}{\beta \Delta \rho_A V''} dV'' \right] \quad (\text{A-19})$$

The equations can be applied in a manner similar to that used for Gordon's equations provided that the volume change data is available for the system.

Robinson (52) also indicated, that if the concentration differences employed are small the error involved in using the equations based on the assumption of no volume changes will be very small even for those systems in which the volume changes are known to occur.

APPENDIX B

ACTIVITY COEFFICIENTS AND ACTIVITY CORRECTION

The methods for calculating the activity coefficients and for calculating the activity correction for the system Benzene-Cyclohexane are illustrated in this appendix.

The activity coefficients were calculated from the excess free energy data of Scatchard (58). The data for excess free energy was given for the system in the following form.

$$F^E = (13.154 - 0.051158T + .0000577T^2)V_1^0 Z_1 Z_2 (1 + .084Z_2^2) \quad (B-1)$$

where:

F^E = excess free energy in calories

T = temperature, °C

V_1^0 = pure component volume of component 1, cc

Z_1, Z_2 = volume fractions of components 1 and 2, respectively

At constant temperature and pressure, the activity coefficient γ_i for any component, i , is given by the exact relation (41),

$$RT \ln \gamma_i = \left(\frac{\partial n_t F^E}{\partial n_i} \right)_{T, P, n_j} \quad (i \neq j) \quad (B-2)$$

where n_t is the total number of moles and n_j is the number moles of all j . For a binary mixture of components 1 and 2, the Equation B-2 reduces to

$$RT \ln \gamma_1 = \left(\frac{\partial F^E}{\partial x_1} \right)_{T, P, x_2} \quad (B-3)$$

Replacing the volume fractions, Z_1 and Z_2 , by equivalent mole fractions, x_1 and x_2 , and carrying out the differentiation after replacing F^E by its equivalent from B-1, the following relation for the activity coefficient is obtained.

$$RT \ln \gamma_1 = \emptyset(T) \left[\left\{ \frac{x_2}{d_2 x_1 + d_1 x_2} - \frac{d_2 x_1 x_2}{(d_2 x_1 + d_1 x_2)^2} \right\} + 0.084 \left\{ \frac{d_1^2 x_2^3}{(d_1 x_2 + d_2 x_1)^3} - \frac{3d_2 x_2^3 d_1 x_1}{(d_1 x_2 + d_2 x_1)^4} \right\} \right] \quad (\text{B-4})$$

where

d_1 = density of component 1, gm moles/cc

d_2 = density of component 2, gm moles/cc

x_1 = mole fraction of 1

x_2 = mole fraction of 2

$$\emptyset(T) = (13.154 - .051158T + .00005777T^2)$$

Using B-4, activity coefficients can be calculated.

Activity Correction.

The activity correction term as discussed in Chapter II, is given as (3, 35),

$$D^0 = D / \frac{\partial \ln a_1}{\partial \ln x_1} \quad (\text{B-5})$$

where

D = uncorrected diffusion coefficient

D^0 = corrected diffusion coefficient

a_1 = activity of component 1

x_1 = mole fraction of component 1

Now

$$\frac{\partial \ln a_1}{\partial \ln x_1} = \frac{\partial \ln a_2}{\partial \ln x_2} = 1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1} \quad (\text{B-6})$$

or

$$\frac{\partial \ln \gamma_1}{\partial \ln x_1} = x_1 \frac{\partial \ln \gamma_1}{\partial x_1} \quad (\text{B-7})$$

Substituting $\ln \gamma_1$ from B-4 into B-7 and carrying out the differentiation, the following relation is obtained.

$$\begin{aligned} \frac{d \ln \gamma_1}{d \ln x_1} = \frac{\phi(T)}{RT} x_1 \left\{ \frac{2d_2^2 x_1 x_2}{(d_1 x_2 + d_2 x_1)^3} - \frac{2d_2 x_2}{(d_1 x_2 + d_2 x_1)^2} \right\} + \\ 0.084 \left\{ \frac{12d_2^2 d_1^2 x_1 x_2^3}{(d_1 x_2 + d_2 x_1)^5} - \frac{6d_1^2 d_2 x_2^3}{(d_1 x_2 + d_2 x_1)^4} \right\} \quad (\text{B-8}) \end{aligned}$$

The activity coefficient and the correction term were calculated using B-4 and B-8 respectively. The calculations were performed on IBM 1410 Digital Computer. The results are listed in Tables B-I and B-II.

TABLE B-I

ACTIVITY COEFFICIENTS AND ACTIVITY CORRECTION FOR
BENZENE-CYCLOHEXANE MIXTURES AT 30°C

Mole Fraction Benzene	Activity Coefficient	$\frac{\partial \ln \gamma_1}{\partial \ln x_1}$	$\frac{\partial \ln a_1}{\partial \ln x_1}$
0.05	1.24581	-0.02081	0.97918
0.1	1.21948	-0.03746	0.96253
0.2	1.17230	-0.05967	0.94032
0.3	1.13180	-0.06936	0.93063
0.4	1.09734	-0.06915	0.93084
0.5	1.06841	-0.06145	0.93845
0.6	1.04464	-0.04888	0.95111
0.7	1.02581	-0.03354	0.96645
0.8	1.0119	-0.01803	0.98196
0.9	1.00311	-0.00544	0.99455
1.0	1.00000	0.0	1.0

TABLE B-II

ACTIVITY COEFFICIENTS AND ACTIVITY CORRECTION FOR
BENZENE-CYCLOHEXANE MIXTURES AT 55°C

Mole Fraction Benzene	Activity Coefficient	$\frac{\partial \ln \gamma_1}{\partial \ln x_1}$	$\frac{\partial \ln a_1}{\partial \ln x_1}$
0.05	1.1031	-0.0185	0.98149
0.1	1.09211	-0.02485	0.97514
0.2	1.0818	-0.02948	0.97051
0.3	1.06317	-0.03428	0.96571
0.4	1.04704	-0.03419	0.9658
0.5	1.03329	-0.03044	0.96955
0.6	1.02185	-0.02418	0.97581
0.7	1.0127	-0.0166	0.98339
0.8	1.00587	-0.00893	0.99107
0.9	1.00154	-0.00269	0.9973
1.0	1.0	0.0	1.0

APPENDIX C

TABULATED DATA

TABLE C-I

DATA FROM CELL CALIBRATIONS AT 25°C

The residue weights corrected for buoyancy and listed in this table. The volume of the pipet used was 19.767cc. Initially the compartment contained pure water.

Cell	Residue Weights, gm		Diffusion Time sec x 10 ⁻⁵
	W''	W'	
I	0.01709	0.04288	3.4878
	0.01786	0.04293	3.6940
II	0.01171	0.04493	3.1116
	0.01288	0.04586	3.1081
	0.01137	0.04425	3.1204
III	0.02321	0.05578	3.8232
	0.02253	0.05477	3.9635
IV	0.01125	0.04598	3.9038
	0.01192	0.04638	3.0544
V	0.01812	0.04348	3.8698
	0.02187	0.05359	3.7904
VI	0.01203	0.04319	3.2052
	0.01146	0.04362	3.436
	0.01355	0.04419	3.524

TABLE C-II

DATA FROM DIFFUSION OF BENZENE-CYCLOHEXANE MIXTURES AT 30°C

Data for the runs are listed in this table. Concentrations were calculated from the refractive indexes by the method illustrated in Appendix D. Each refractive index is a mean of three observations.

Identification	Refractive Indexes			Diffusion Time sec x 10 ⁻⁵
	Upper Initial	Upper Final	Lower Final	
1. VI	1.420778	1.42448	1.429117	4.775
2. IV	1.420778	1.430713	1.43645	4.822
3. V	1.43112	1.44305	1.45075	4.3396
4. V	1.436392	1.44912	1.456438	4.5674
5. IV	1.45219	1.45660	1.461551	4.0536
6. III	1.45498	1.461498	1.467392	4.60
7. I	1.462186	1.47553	1.48701	4.1472
8. III	1.45023	1.476267	1.48906	4.734
9. I	1.467392	1.483276	1.467539	4.88
10. VI	1.478992	1.48012	1.48337	3.79

TABLE C-III

DATA FROM DIFFUSION OF BENZENE-CYCLOHEXANE MIXTURES AT 55°C

Identification	Refractive Indexes			Diffusion Time sec x 10 ⁻⁵
	Upper Initial	Upper Final	Lower Final	
1. V	1.420778	1.425295	1.427872	3.442
2. III	1.420778	1.42563	1.429003	3.385
3. I	1.420778	1.42592	1.428718	3.35
4. II	1.420778	1.431739	1.445542	2.8512
5. II	1.420778	1.432024	1.447968	2.6214
6. III	1.420778	1.437178	1.451825	3.3818
7. IV	1.420778	1.437794	1.454710	3.1212
8. VI	1.446976	1.449294	1.451425	2.7978
9. IV	1.453895	1.45714	1.45957	3.2662
10. VI	1.428775	1.45210	1.46862	3.435
11. II	1.461922	1.471393	1.483335	2.58
12. III	1.469504	1.477814	1.485355	2.5796
13. III	1.471240	1.479978	1.485763	3.16
14. IV	1.481758	1.485712	1.489860	2.9568

TABLE C-IV
 VOLUMETRIC DATA FOR DIFFUSION CELLS*

Cell	Upper Volume, cc	Lower Volume, cc	Diaphragm Volume, cc
I	48.20	49.76	0.37
II	48.62	47.10	0.31
III	50.12	47.96	0.33
IV	49.52	49.08	0.27
V	47.62	50.38	0.34
VI	51.14	49.50	0.29

*Data from reference 52

TABLE C-V
 CELL CONSTANTS

Cell	Cell Constant, cm^{-2}			Average
	(i)	(ii)	(iii)	
I	0.1296	0.1287		0.12915
II	0.0902	0.0906		0.0904
III	0.1144	0.1149	0.1146	0.11463
IV	0.0911	0.0915		0.0913
V	0.1240	0.1232		0.1236
VI	0.0938	0.0942	0.0945	0.0942

TABLE C-VI

DENSITY DATA FOR BENZENE-CYCLOHEXANE MIXTURES AT 30°C

Mass Fraction Benzene	ρ , gm/cc	ρ_A , gm/cc
0.0	0.76916	0.0
0.1019	0.77622	0.07910
0.2199	0.78527	0.17269
0.3321	0.79473	0.26394
0.4713	0.80768	0.38066
0.5622	0.81678	0.45919
0.6679	0.82809	0.55310
0.7413	0.83634	0.61997
0.8799	0.85303	0.75058
1.0	0.86849	0.86849

TABLE C-VII

DENSITY DATA FOR BENZENE-CYCLOHEXANE MIXTURES AT 55°C

Mass Fraction Benzene	ρ , gm/cc	ρ_A , gm/cc
0.0	0.74486	0.0
0.1499	0.75342	0.11253
0.3296	0.76891	0.25350
0.4296	0.77923	0.33474
0.5330	0.79188	0.42235
0.6321	0.80758	0.51048
0.8193	0.82292	0.67423
1.0	0.84224	0.84424

TABLE C-VIII

REFRACTIVE INDEX DATA FOR BENZENE-CYCLOHEXANE MIXTURES AT 30°C

<u>Mass Fraction Benzene</u>	<u>Mole Fraction Benzene</u>	<u>Refractive Index</u>
0.0	0.0	1.42077
0.1728	0.1835	1.43037
0.2591	0.2653	1.43476
0.3264	0.3430	1.43992
0.4367	0.4557	1.44682
0.6124	0.6301	1.46053
0.7259	0.7405	1.46988
0.819	0.83	1.47807
1.0	1.0	1.49357

APPENDIX D

SAMPLE CALCULATIONS

Sample calculations for the various quantities derived from the experimental data are shown in this chapter.

Cell Constant Calculations.

The buoyancy corrected residue weights are listed in Table C-I.

The buoyancy correction was applied as follows:

Tare weight of sample bottle = 57.1005gms

Weight of standard bottle = 57.2249

Gross weight of bottle + residue = 57.1184gms

Weight of standard bottle = 57.2224

Volume of the sample delivered = 19.767cc

The residue weight was found from Equation IV-1.

$$\begin{aligned} \text{Residue weight} &= (57.1184 - 57.10053) - (57.1005/54.2249) \\ &\quad (54.2224 - 54.2249) \\ &= 0.01784 - (-0.0027)1.0613 \\ &= 0.018125\text{gms} \end{aligned}$$

This residue weight corresponds to an entry in Table C-I for first calibration of cell V.

The above residue weight is the weight of residue for the final upper sample. In a similar way the residue weight of the final lower sample was determined. The actual cell constant calculation is shown below.

$$W'' = 0.018125 \text{gms}$$

$$W' = 0.04348$$

KCL concentrations:

$$(\rho_{Af})'' = 0.018125/19.767 = 0.0009167 \text{gm/cc}$$

$$(\rho_{Af})' = 0.4348/19.767 = 0.002199 \text{gm/cc}$$

$$(\rho_{A_o})' = 0.0$$

Cell volumes:

$$V'' = 47.62 \text{cc}$$

$$V' = 50.38 \text{cc}$$

$$V''' = 0.34 \text{cc}$$

$$\begin{aligned} (\rho_{A_o})' &= \left[\rho_{Af}' (V' + \frac{1}{2}V''') + \rho_{Af}'' (V'' + \frac{1}{2}V''') - \rho_{A_o}''' (V'' + \frac{1}{2}V''') \right] / (V' + \frac{1}{2}V''') \\ &= 0.002199(47.79) + 0.0009167(50.55) - 0.0/47.79 \\ &= 0.003169 \text{gm/cc} \end{aligned}$$

$$\begin{aligned} (\rho_A)_{\text{Avg}} &= (0.003169 + 0.002199 + 0.0009167 + 0.0)/4.0 \\ &= 0.0016992 \text{gm/cc} \end{aligned}$$

From Stokes data (56), \bar{D} at this average concentration = $1.886 \times 10^{-5} \text{cm}^2/\text{sec}$.

The cell constant β is then given by A-10,

$$\beta = \frac{1}{\bar{D}\theta} \ln (\Delta\rho_A)_o / (\Delta\rho_A)_f$$

$$(\Delta\rho_A)_o = 0.0 - 0.003169 = -0.003169$$

$$(\Delta\rho_A)_f = 0.0009167 - 0.02199 = -0.0012823$$

$$\text{Time, } \theta = 3.8698 \times 10^5 \text{ sec}$$

$$\beta = \frac{\ln(-0.003169/-0.0012823)}{(3.8698)(1.886)}$$

$$= 0.90474/(3.8698)(1.886)$$

$$= 0.1240 \text{cm}^{-2}$$

This value of β corresponds to the entry in Table C-IV for the first calibration of Cell V.

Integral Diffusion Coefficient Calculations.

The refractive index was curve fitted as a function of mass fraction at 30°C. Concentration was then developed as a function of mass fraction. The relations are shown below:

At 30°C

$$\text{R.I.} = 1.4209 + 0.04614X_A + 0.03659X_A^2 + 0.009964X_A^3 \quad (\text{D-1})$$

$$\rho_A = 0.76925X_A + 0.06567X_A^2 + 0.03356X_A^3 \quad (\text{D-2})$$

At 55°C

$$\rho_A = 0.7281X_A + 0.12946X_A^2 + 0.01546X_A^3 \quad (\text{D-3})$$

where X_A = mass fraction benzene

Data for a typical run are as follows:

Refractive indexes:

$$\text{R.I.}_f'' = 1.425292$$

$$\text{R.I.}_f'' = 1.427872$$

$$\text{R.I.}_o'' = 1.420778$$

$$\text{Diffusion time} = 3.442 \times 10^5 \text{ secs.}$$

The data correspond to entry 1. V in Table C-III

Mass fractions using D-1:

$$X_f'' = 0.008867$$

$$X_f' = 0.136718$$

$$X_o'' = 0.0$$

The run is at 55°C. Therefore using D-3

Concentrations:

$$\rho_{Af}'' = 0.06642 \text{ gm/cc}$$

$$\rho_{Af}' = 0.10282 \text{ gm/cc}$$

$$\rho_{A_o}'' = 0.0$$

Volumetric data for Cell V:

$$V' = 47.62 \text{ cc}$$

$$V'' = 50.38 \text{ cc}$$

$$V''' = 0.34 \text{ cc}$$

$$\begin{aligned} (\rho_{A_o})' &= 0.10282(47.79) + 0.06642(50.55) - 0.0(50.55) / 47.79 \\ &= 0.14561 \text{ gm/cc} \end{aligned}$$

$$\begin{aligned} (\rho_A)_{\text{Avg}} &= (0.14561 + 0.06642 + 0.10282 + 0.0) / 4.0 \\ &= 0.07871 \text{ gm/cc} \end{aligned}$$

$$\beta = 0.1236$$

$$\theta = 3.442 \times 10^5 \text{ secs.}$$

\bar{D} can be determined from Equation A-10

$$(\Delta\rho_A)_o = 0.0 - 0.14561 = -0.14561$$

$$(\Delta\rho_A)_f = 0.06642 - 0.10282 = -.0364$$

$$\begin{aligned} \bar{D} &= 1.0 / (3.442 \times 10^5) (0.1236) [\ln(-0.14561 / -0.0364)] \\ &= 3.2611 \times 10^{-5} \text{ cm}^2/\text{sec} \end{aligned}$$

This corresponds to entry 1.V in Table II.

Density Calculations.

Typical data for density calculations are as follows:

Tare weights:

$$\text{Pycnometer + wire on caps + hook} = 37.8291 \text{ gms}$$

$$\text{Room temperature} = 25^\circ\text{C}$$

Gross weights:

$$\text{Pycnometer + wire + hook + sample} = 54.7171\text{gms}$$

$$\text{Room temperature} = 26.5^{\circ}\text{C}$$

$$\text{Weight of wire + hooks} = 1.6539$$

$$\text{Volume of pycnometer} = 19.4455\text{cc}$$

$$\text{Weight of empty pycnometer, } W_B = 37.8291 - 1.6539 = 36.1752\text{gms}$$

Density of air at 740mm of mercury and at the respective room temperatures,

$$\text{At } 25^{\circ}\text{C} = 1.1533 \times 10^{-3} \text{ gm/cc}$$

$$\text{At } 26.5^{\circ}\text{C} = 1.1433 \times 10^{-3} \text{ gm/cc}$$

Weight of the empty pycnometer corrected to vacuo is given as (52)

$$\begin{aligned} W_B^{\circ} &= W_B \left[1 + \rho_{\text{air}} \left(\frac{1}{\rho_{B+S}} - \frac{1}{\rho_{\text{wire}}} \right) \right] & (D-4) \\ &= 36.1752 \left[1 + (1.1533 \times 10^{-3}) \left(\frac{1.0}{2.23} - \frac{1.0}{8.4} \right) \right] \\ &= 36.181\text{gms} \end{aligned}$$

$$\begin{aligned} \text{Weight of filled pycnometer, } W_{B+S} &= 54.7171 - 1.6539 \\ &= 53.0632\text{gms} \end{aligned}$$

Assume $\rho_{B+S} = 1.4895\text{gm/cc}$. This is the density of the filled pycnometer, glass and sample.

Corrected weight of filled pycnometer via D-4,

$$\begin{aligned} W_{B+S}^{\circ} &= 53.0632 \left[1 + (1.1475) \left(\frac{1.0}{1.4895} - \frac{1.0}{8.4} \right) \right] \\ &= 53.0699\text{gms} \end{aligned}$$

ρ_{B+S} can be calculated using D-5 (52),

$$\rho_{B+S} = \frac{W_{B+S}^{\circ}}{\left(V + \frac{W_B}{P_B} \right)} \quad (D-5)$$

$$\rho_{B+S} = 53.0699 / \left[\left(\frac{36.181}{2.23} \right) + 19.4455 \right] = 1.48957 \text{ gm/cc}$$

The assumed and calculated values of ρ_{B+S} agree to within 0.00007 gm/cc. No additional iterations are required.

Finally using D-6 (52)

$$\begin{aligned} \rho_S &= (W_{B+S}^0 - W_B^0) / V & (D-6) \\ &= \frac{(53.0699 - 36.181)}{19.4455} \\ &= 0.83849 \text{ gm/cc} \end{aligned}$$

The value of density is that of pure Benzene at 30°C listed in Table C-VI.

Viscosity Calculations.

Viscosities were calculated from the following relation (14),

$$\frac{\mu}{\mu_W} = \frac{\rho \theta}{\rho_W \theta_W} \quad (D-7)$$

where

μ = viscosity

ρ = density

θ = flow time

W = refers to water, the calibration fluid.

Typical data are:

Temperature 30°C

$\rho = 0.86849 \text{ gm/cc}$

$\theta = 82.4 \text{ secs}$

$\rho_W = 0.99567 \text{ gm/cc}$

$\theta_W = 101.5 \text{ secs}$

$\mu_W = 0.8007 \text{ cp}$

Then

$$\begin{aligned}\mu &= (0.8007)(0.86849)(82.4)/(0.99567)(101.5) \\ &= 0.5673\text{cp}\end{aligned}$$

This value corresponds to the viscosity of pure Benzene listed in Table III.

Diffusion Coefficients from Prager's Equation.

Correlation of Prager is given in Chapter II, Equation II-15.

Typical values at 30°C are:

$$D_{11} = 2.475\text{cm}^2/\text{sec}$$

$$1 + \frac{\partial \ln \gamma_1}{\partial \ln X_1} = .99455$$

$$D_{12} = (2.475 \times 10^{-5}) \times 0.99455 = 2.4615 \times 10^{-5} \text{cm}^2/\text{sec}$$

This value of mutual diffusion coefficient corresponds to mole fraction of 0.9 and is listed in Table VII.

Diffusion Coefficient From Lamm's Correlation.

Equation II-17 is the correlation of Lamm. Typical data are:

$$D_{11} = 2.475 \times 10^{-5} \text{cm}^2/\text{sec}$$

$$D_{11}^0 = 1.98 \times 10^{-5} \text{cm}^2/\text{sec}$$

$$n_1 = 0.1$$

$$V_1^0 = 1.152$$

$$1 + \frac{\partial \ln \gamma_2}{\partial \ln N_2} = 0.99455$$

$$N_2 = 0.9$$

$$\left(\frac{1.0}{2.475 \times 10^{-5}}\right) - \left(\frac{0.1}{1.98}\right)(1.152) = \left(\frac{0.9}{D_{12}}\right)(.99475)$$

$$D_{12} = 2.45 \times 10^{-5} \text{cm}^2/\text{sec}$$

This corresponds to an entry in Table VII.

Diffusion Coefficient From Hartley-Crank Theory.

In dilute solutions a mole fraction, Harned (34) has shown that

$$D_A / \left(\frac{\partial \ln a_A}{\partial \ln X_A} \right) \left(\frac{\mu_A^\circ}{\mu} \right) = D_A^\circ + k_1 \left(\frac{\Delta\mu_A}{\mu_A^\circ} \right) \quad (D-8)$$

where

D_A = diffusivity at low concentration, cm^2/sec .

D_B = diffusivity at high concentration, cm^2/sec .

k_1 = constant

$$\Delta\mu_A = \mu - \mu_A^\circ$$

o = refers to infinite dilution

Similarly

$$D_B / \left(\frac{\partial \ln a_B}{\partial \ln X_B} \right) \left(\frac{\mu_B^\circ}{\mu} \right) = D_B^\circ + k_2 \frac{\Delta\mu_B}{\mu_B^\circ} \quad (D-9)$$

Now from Equation II-11, when N_B or X_B approaches zero, then

$$\frac{1}{\sigma_B} = \frac{N}{RT} \left[D_A^\circ + k_1 \frac{\Delta\mu_A}{\mu_A^\circ} \right] \mu_A^\circ \quad (D-10)$$

Similarly,

$$\frac{1}{\sigma_A} = \frac{N}{RT} \left[D_B^\circ + k_2 \frac{\Delta\mu_B}{\mu_B^\circ} \right] \mu_B^\circ \quad (D-11)$$

Substituting these values of σ_A and σ_B in Equation II-11, we obtain

$$D = \frac{\partial \ln v_A}{\partial \ln X_A} \frac{1}{\mu} \left[X_A \left(D_A^\circ + k_1 \frac{\Delta\mu_A}{\mu_A^\circ} \right) \mu_A^\circ + X_B \left(D_B^\circ + k_2 \frac{\Delta\mu_B}{\mu_B^\circ} \right) \mu_B^\circ \right] \quad (D-12)$$

Typical data are:

temperature = 55°C

$$D_A^o = 3.06 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$D_B^o = 3.244 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$\mu_A^o = 0.455 \text{ cp}$$

$$\mu_B^o = 0.5618 \text{ cp}$$

$$D_A = 3.6923 \times 10^{-5} \text{ cm}^2/\text{sec}$$

$$D_B = 3.8829 \times 10^{-5} \text{ cm}^2/\text{sec}$$

Activity correction = 0.97445 corresponding to D_A . Activity correction = 0.9991 corresponding to D_B . Using D-8,

$$\frac{(3.6923 \times 10^{-5})(0.5377)}{(0.97445)(0.455)} = 3.06 \times 10^{-5} + \frac{.0822}{.455} k_1$$

$$0.1805 k_1 = 4.48 \times 10^{-5} - 3.06 \times 10^{-5}$$

$$k_1 = \frac{1.42 \times 10^{-5}}{0.1805} = 7.863 \times 10^{-5}$$

Similarly using Equation D-9,

$$k_2 = 0.494 \times 10^{-5}$$

Now for a mole fraction of 0.7,

$$X_A = 0.7$$

$$X_B = 0.3$$

$$\mu = 0.4485 \text{ cp}$$

$$\Delta\mu_A = 0.4485 - 0.455 = -0.007$$

$$\Delta\mu_B = 0.4485 - 0.5618 = -0.1133$$

Activity correction = 0.98339.

Using Equation D-12,

$$\begin{aligned}
 D &= \left(\frac{0.98339}{0.4485} \right) \left[0.7 \left(3.06 \times 10^{-5} + (.00007863) \frac{(-.07)}{.455} \right) .455 + \right. \\
 &\quad \left. .03 \left(3.244 \times 10^{-5} + (.00000494) \frac{(-.1133)}{.5618} \right) .5618 \right] \\
 &= 3.215 \times 10^{-5}, \text{ cm}^2/\text{sec}
 \end{aligned}$$

Diffusivities D_A^0 , D_B^0 , are observed by extrapolating the experimental diffusion data to the two axis of concentration.

VITA

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