

SOLUBILITIES OF NOBLE GASES IN
ALCOHOLS AT 25°C AND
ONE ATMOSPHERE

By

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PREFACE

The solubilities of non-polar gases in polar liquids at 25°C and atmospheric pressure were studied. Data were taken for nine systems: three gases (helium, neon, and argon) in three alcohols (propanol, pentanol, and heptanol). The apparatus was designed such that the volume of gas was held constant and the solubility was measured by the pressure drop of the gas. The experimental results of this work were compared with the experimental results of other investigators and with calculated solubilities using four correlations for predicting solubilities of non-polar gases in polar liquids.

I am indebted to Dr. R. L. Robinson, my advisor, for his excellent counseling, encouragement, and constant interest during this study. I also wish to express my appreciation to those graduate students who gave helpful suggestions during this work, especially Mr. V. C. Smith and Mr. D. D. Dillard.

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CHAPTER I

INTRODUCTION

The purpose of this study was to (1) design and construct an apparatus which could be used to determine experimental solubilities of gases in liquids, (2) measure the solubilities of argon, helium, and neon in the alcohols n-propanol, n-pentanol, and n-heptanol, and (3) use the data obtained to test several theoretical correlations for calculating the solubilities of non-polar gases in polar solvents.

The literature on gas solubility contains both experimental solubility data and theoretical correlations for calculating solubilities. Particularly lacking were data on light gases in polar solvents. Thus nine systems were studied in this investigation: three inert gases in three alcohols. Data were available in the literature for the three argon systems, thus providing a comparison with the experimental data of this work. No data were available for the other six systems (helium and neon in the three alcohols).

Several techniques for measuring gas solubility are also presented in the literature. For the present work, an apparatus combining simplicity of operation and accuracy of results was designed to eliminate as many as possible of the inefficiencies of operation and corrections to results which were required by existing apparatus.

Four theoretical correlations for calculating solubilities in polar solvents were found in the literature. Each correlation was based on a

different theoretical approach. These correlations were applied to the systems studied in this work and the theoretical results were compared with the experimental results of this work.

CHAPTER II

SURVEY OF LITERATURE

The literature survey consisted of three distinct sections: 1) equipment which have been used to take experimental gas-liquid solubility data, 2) data presented on solubility of inert gases in alcohols, that is helium, neon, and argon in the alcohols methanol through octanol, and 3) theoretical correlations for calculating the solubility of non-polar gases in polar liquids.

Gas Solubility Equipment

Battino and Clever (1) have discussed in detail numerous methods for measuring the solubility of gases in liquids, including manometric-volumetric methods, mass spectrometric methods, gas chromatographic methods, and chemical methods.

Two of the better available apparatus, those of Cook and Hanson (8) and Dymond and Hildebrand (11), will be discussed in some detail as a valuable introduction to the design of the present system. Cook and Hanson spent much time studying the causes of error in solubility measurement. They described in detail these sources of error.

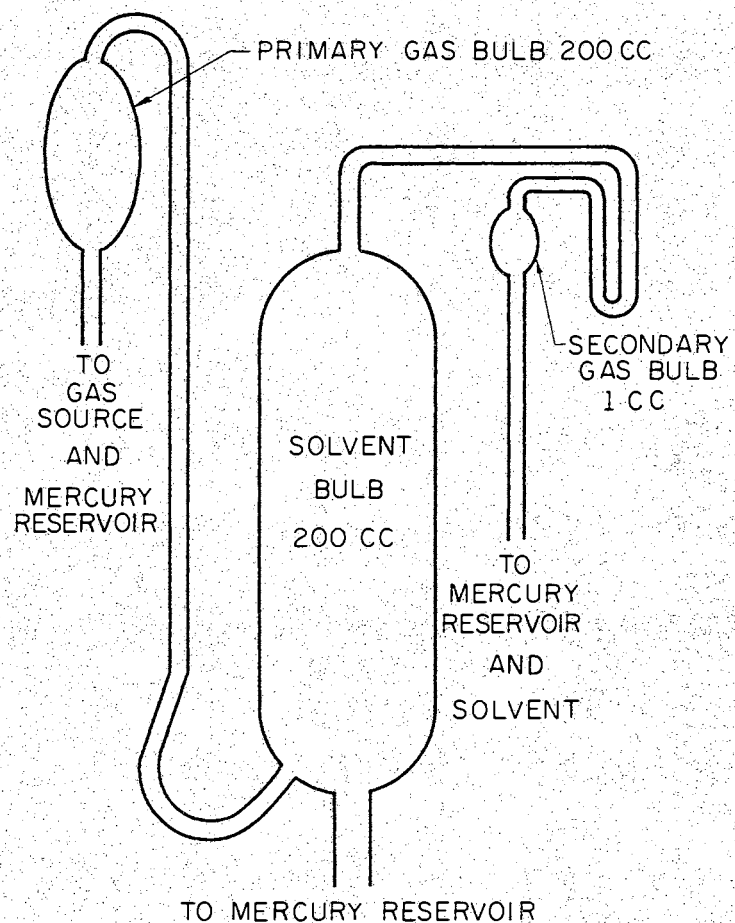
The Cook and Hanson apparatus is shown in Figure 1-a. The apparatus contained three main bulbs--a primary gas bulb, a secondary gas bulb, and a solvent bulb. The volumes of the bulbs were calibrated by weighing the mercury required to fill the volume.

The solvent bulb was filled with solvent and the solvent was degassed by boiling off 10-20% of the solvent over a two to three hour period. An infrared lamp was used to heat the solvent.

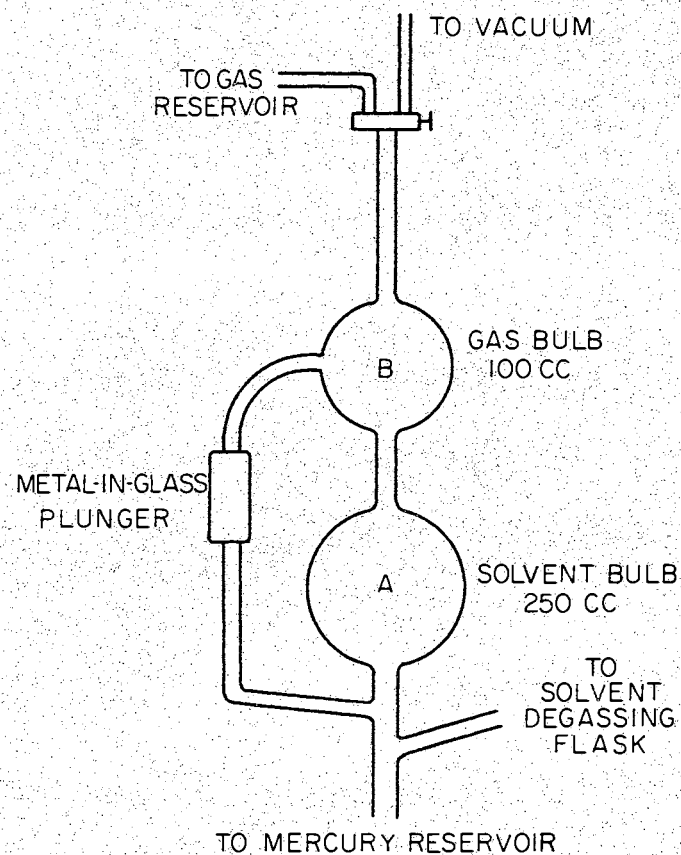
The solvent bulb was positioned so that the solvent could be compressed between mercury slugs. The solvent was considered to be degassed if no bubbles remained in the solvent bulb when the solvent was compressed. To double check for degassing, Cook and Hanson placed a vacuum thermocouple gage, which detected the presence of non-condensable components, after a liquid nitrogen trap.

The primary gas bulb was evacuated and then filled with the gas. The gas was compressed to a given volume and the pressure was read on a mercury manometer. At this time the gas was still dry and had come into contact with mercury only. The gas was transferred to the solvent bulb. The bulb was shaken vigorously until the gas volume was reduced to about one cc (the size of the secondary gas bulb), at which time the gas was transferred to the secondary gas bulb. The pressure was measured at the given volume and the gas was returned to the solvent bulb and shaken again. When the pressure reading agreed within one mm Hg with the previous reading, the pressure was recorded. The volume of solvent was measured from the known volume of the solvent bulb and by weighing the mercury which was required to finish filling the bulb. All transferring of solvent and gas was done with mercury. Since the final gas is saturated with solvent vapor the final number of moles of gas had to be corrected for this composition effect.

The Dymond and Hildebrand apparatus (shown in Figure 1-b) contained a solvent and a gas bulb which were calibrated by displacing mercury. The solvent was degassed by boiling and freezing. The gas pressure was



(a) COOK AND HANSEN



(b) DYMOND AND HILDEBRAND

Figure 1. Two Experimental Solubility Apparatus from the Literature

measured in a dry state and the gas was then transferred to the solvent bulb. In the above ways the Dymond and Hildebrand apparatus was similar to that of Cook and Hanson. The main difference in these apparatus was in the way the gas and liquid were mixed. Dymond and Hildebrand had their gas bulb mounted directly above the solvent bulb and connected by a glass tube. They also connected the two bulbs with a sidearm which enclosed a metal-in-glass plunger. The plunger was magnetically operated and pumped solvent from the solvent bulb to the gas bulb. As the solvent ran down the side of the gas bulb, a large surface area was exposed for the gas to go into solution. Also no large gas bubbles were carried from the gas bulb back into the solvent bulb.

As was the case with Cook and Hanson, Dymond and Hildebrand measured the final pressure with the gas partially saturated with solvent. Again the final number of moles of gas present in the gas reservoir had to be corrected for this composition effect.

Experimental Solubility Data

Solubility data in the literature are usually expressed in one of three ways, as a Bunsen Coefficient, Ostwald Coefficient, or Henry's Law Constant.

The Bunsen Coefficient, α , is defined as the volume of gas, reduced to 0°C and 760 mm Hg, which is absorbed by a unit volume of solvent (at the temperature of the measurement) under a gas pressure of 760 mm Hg. Thus it can be shown that

$$\alpha = \frac{V_g}{V_s} \frac{273.15}{T} \quad (\text{II-1})$$

where V_g = volume of gas absorbed at temperature and pressure of measurement

V_s = volume of solvent at temperature and pressure of measurement

T = temperature of the measurement ($^{\circ}\text{K}$).

In equation (II-1) the corrections to standard conditions assume ideal gas behavior. Other equations of state can be used, but the equation of state should be specified and equation (II-1) should be adjusted.

The Ostwald Coefficient, ℓ , is defined as the volume of gas, reduced to the temperature of the measurement and 760 mm Hg, which is absorbed by a unit volume of solvent (at the temperature of the measurement) under a gas pressure of 760 mm Hg. The Ostwald Coefficient is then

$$\ell = \frac{V_g}{V_s} \quad (\text{II-2})$$

where V_g and V_s are the same as for equation (II-1). Again ideal gas behavior is assumed in making corrections of V_g to standard conditions.

Henry's Law states that the amount of gas which dissolves is proportional to its partial pressure, or

$$p^* = H x_g$$

where p^* = partial pressure of the gas

x_g = mole fraction of the gas in the solvent

H = Henry's Law constant.

For this work, p^* = one atmosphere, and therefore,

$$H = 1.0/x_g \quad (\text{II-3})$$

Literature data on solubility of rare gases in alcohols is relatively scarce. The earliest data is that of Axel Lannung (22) in 1930,

in which he experimentally measured the solubilities of helium, neon, and argon in both methanol and ethanol. He presented his results as both Ostwald and Bunsen coefficients at six temperatures (15, 18, 20, 25, 30, and 37°C). His apparatus employed the same principle as that of Cook and Hanson (8) in which a known volume of dry gas was shaken above a known volume of degassed solvent at a given temperature. The gas pressure was measured before and after shaking and the number of moles absorbed was calculated.

In 1958, Gjaldbaek and Niemann (13) presented the solubilities of argon in n-propanol, n-butanol, and n-pentanol. The data were presented at 25°C and 35°C as Bunsen coefficients. Gjaldbaek and Niemann used the same apparatus as Lannung.

In 1960, Boyer and Bircher (4) presented the solubilities of argon in eight alcohols (methanol through octanol). The data were taken at 25°C and were presented as Ostwald coefficients. Boyer and Bircher compared their results with those of Lannung and of Gjaldbaek and Niemann. Boyer and Bircher used a modified E. H. Sargent Company manometric Van Slyke-Neill blood gas apparatus. With this apparatus the solvent is saturated with gas, then the gas was extracted from the solvent and measured. The procedures are described by Van Slyke and Peters (28).

Theoretical Methods

Four theoretical correlations for calculation of solubilities in polar liquids were found in the literature. The first, by Gjaldbaek and Niemann (13), used regular solution theory with corrections for Flory-Huggins mixing. Prausnitz and Shair (30) presented a new model for the dissolution process and used the model and the theorem of

corresponding states to develop their correlation. Loeffler and McKetta (24) presented a correlation based on the concept of "continued association." Lin and Chao (23) used the "group contribution theory" to find the solubilities in polar liquids.

The assumptions of each of these correlations and the working equations will be shown in this section. Complete derivation of the equations will be given in Appendix A.

Gjaldbaek and Niemann

The solubilities of non-polar gases in non-polar liquids can be calculated from the equation of Gjaldbaek and Hildebrand (12)

$$-\log x_2 = -\log x_2^i + 0.4343 \frac{\bar{v}_2}{RT} (\delta_1 - \delta_2)^2 + \log \frac{\bar{v}_2}{v_1} + 0.4343 \left(1 - \frac{\bar{v}_2}{v_1}\right) \quad (\text{II-4})$$

where x_2 - solubility of gas in mole fraction

x_2^i - "ideal" solubility of gas

\bar{v}_2 - partial molar volume of the dissolved gas

δ_1 - solubility parameter of the solvent

δ_2 - solubility parameter of the gas

v_1 - molar volume of the solvent

R - gas constant

T - absolute temperature.

This equation was developed from regular solution theory with corrections for Flory-Huggins mixing.

Gjaldbaek and Niemann (13) used their experimental solubility data for several non-polar gases in several polar liquids to back out values of δ_1^* , the δ_1 necessary to correctly predict the experimental solubility. From the results, they developed the following correlation

for δ_1^* ,

$$\delta_1^* = \delta_1 - (\epsilon - 1)(0.165 - 0.00143(\alpha \times 10^{25})) \quad (\text{II-5})$$

where α - polarizability of the gas

ϵ - dielectric constant of the liquid.

Prausnitz and Shair

Prausnitz and Shair (30) presented a new model for the dissolution process. The model was comprised of two steps: (1) The gas is isothermally condensed to a hypothetical liquid at one atmosphere pressure and (2) the hypothetical liquid is mixed with the solvent.

Using the fact that the solute in the liquid solution is in equilibrium with the gas at unit fugacity, they write the equation

$$\frac{1}{x_2} = \frac{f_2^L \gamma_2}{f_2^0} \quad (\text{II-6})$$

where f_2^L - fugacity of hypothetical liquid at one atmosphere

f_2^0 - fugacity of pure gas at initial conditions

γ_2 - activity coefficient of gas.

Using experimental solubility data, Prausnitz and Shair showed that the fugacity of a hypothetical liquid is a universal function of reduced temperature, that is, the fugacity follows corresponding states theory. Thus they made a plot of f_2^L/P_c , where P_c is the critical pressure of the gas, as a function of the reduced temperature of the gas, T_R . They also plotted $(\log \gamma_2)/v_2$ as a function of δ_2 , where v_2 is the molar volume of the gas and δ_2 is the solubility parameter of the gas, with each alcohol as a parameter.

Prausnitz and Shair used the two generalized plots and equation (II-6) to calculate the solubility of gases in polar solvents.

Loeffler and McKetta

Loeffler and McKetta (24) presented the following correlation for solubilities of non-polar gases in alcohols:

$$-\ln \phi_o = \ln f^{oL} + \left(1 - \frac{v_o}{v}\right) + \frac{bv_o\phi_a^2}{RT} \quad (\text{II-7})$$

where ϕ_o - volume fraction of the gas
 f^{oL} - fugacity of hypothetical liquid at pressure of 1 atm
 v - volume of one "true" mole of solution
 v_o - molar volume of hypothetical liquid
 b - semiempirical parameter
 ϕ_a - volume fraction of the alcohol
 R - gas constant
 T - absolute temperature.

This correlation is based on the concept of "continued association," that is, a substance consists of an equilibrium mixture of single molecules with linear polymers of all orders from two to infinity.

The total volume, v_T , of equation (II-7) is defined as

$$\frac{1}{v_T} = \frac{\phi_o}{v_o} + \frac{\phi_a (1 - K\phi_1)}{v_a} \quad (\text{II-8})$$

where

$$\phi_1 = \frac{[2K\phi_a + 1 - (4K\phi_a + 1)^{1/2}]}{2K^2\phi_a} \quad (\text{II-9})$$

and K - association equilibrium constant
 ϕ_1 - volume fraction of alcohol monomer
 v_a - molar volume of alcohol.

The quantity b in equation (II-7) cannot be calculated from pure component properties and therefore must be determined from experimental

data. Loeffler and McKetta, therefore, used 164 selected data points for fourteen gases in six alcohols to generate a plot of b as a function of the critical temperature (T_c) of the gas. This plot is given in their article (24).

The association equilibrium constant, K , was found by starting with the equilibrium constants for methanol and ethanol by Kretschmer and Wiebe (21) from solution data and estimating the relative values for the other alcohols from the work of Danhauser and Bahe (9). From this a consistent set of equilibrium constants was found. A plot of K as a function of the temperature of the system is given in their article.

A complete derivation of equations (II-7), (II-8), and (II-9) is given in Appendix A.

Lin and Chao

The correlation of Lin and Chao (23) for calculating solubilities of inert gases in alcohols is an extension of "group contribution theory" of solutions developed by Chao, Robinson, Smith and Kuo (6). In this theory the functional groups (for alcohols they are: CH_3- , CH_2- , and $\text{HO}-$) are considered to be basic identifiable structural units of molecules. If the manner of interaction among these groups is known, the interactions of mixtures of molecules of diverse species may be predicted as described.

Lin and Chao presented the following correlation:

$$kT \ln H = e_c + e_i + kT \ln \frac{RT}{v} \quad (\text{II-10})$$

where k - Boltzman constant

T - temperature of the system

H - Henry's Law constant

e_c - energy required to create a cavity in the solvent the size of the solute molecule

e_i - energy of interaction between the solute molecule and the solvent molecules which are close enough to influence it.

They assumed the entropy effect associated with the energy of interaction of the molecules to be negligible.

Lin and Chao calculated e_c with the following relation

$$e_c = \frac{1}{6} \pi \sigma^3 \rho_E \quad (\text{II-11})$$

where ρ_E - energy density

σ - gas molecule diameter.

The method used to find ρ_E is discussed in Appendix A.

The value of e_i was calculated using

$$e_i = \sum_u S \lambda_u \frac{A_u}{\sum_w A_w} \quad (\text{II-12})$$

where S - total surface area of the gas molecule

A_u - surface area of groups of type u

λ_u - surface energy density of u group and gas interaction

$\frac{A_u}{\sum_w A_w}$ - fraction of total surface of the solvent molecules taken up by u groups

$S \lambda_u$ - energy of interaction.

Lin and Chao present a plot of λ_u as a function of $\ln (\alpha+1)$ for the three groups of which normal alcohols are composed (CH_2 -, CH_3 -, and HO -). They used paraffin data to calculate λ_{CH_2} and λ_{CH_3} and used data of several gases in methanol to find λ_{OH} .

The derivation of equation (II-10) and a discussion of the procedure for using the equations are given in Appendix A.

CHAPTER III

EXPERIMENTAL APPARATUS

The apparatus used in this study was designed so that it would be simple to use and so that all known causes of error in solubility measurement could be minimized.

Cook and Hanson (8) did extensive work to determine why the solubility data in the literature do not agree within 1%. They concluded that if the chemicals are sufficiently pure and the temperature, pressure, and volume are measured accurately, the errors must be caused by one or more of the following:

- (1) failure to attain equilibrium in the system,
- (2) failure to degas solvent,
- (3) failure to accurately measure the amount of gas dissolved,
- (4) failure to keep the gas or solvent free of contamination while transferring.

The apparatus used in this work was designed on the following principles:

- (1) The solvent was degassed by continuous boiling under extremely low pressure.
- (2) The volume of the gas reservoir remained constant and the solubility was calculated from the pressure drop of the gas.
- (3) The initial gas pressure was read before the gas had come into contact with the solvent.

- (4) The attainment of equilibrium was accelerated by stirring.
- (5) Equilibrium was considered to be established when no further rate of solution (pressure drop in gas) was observed.
- (6) Bulk flow of gas from the gas reservoir into the solvent bulb through the fine capillary tubing prohibited diffusion of solvent vapor into the gas reservoir. Thus composition corrections were not made in the solubility calculations.

The apparatus is shown in Figure 2. The solvent was degassed in the degassing flask. The degassed solvent was transferred to the solvent bulb through the solvent transfer line. The syringes, connected to the solvent bulb, were used to raise and lower the level of the solvent in the solvent bulb. Bulb A, Bulb B, and the tubing between stopcocks 7 and 10 comprised the gas reservoir. Contact between the gas and solvent was made in the solvent bulb. With stopcocks 6 and 11 closed, the entire system could be evacuated to test for leaks. The stirring device, which was mounted in the solvent bulb, was driven by a magnet, which in turn was driven by the motor mounted on the outside of the constant temperature bath.

For purposes of discussion, the apparatus will be divided into six separate component systems.

- (1) the degassing system,
- (2) the gas measurement system,
- (3) the gas-liquid contact system,
- (4) the electrical system,
- (5) the vacuum system,
- (6) the temperature control system.

In the following discussions manufacturer's specifications of the

equipment will not be given. The equipment specifications and suppliers are listed in Appendix F.

The Degassing System

The degassing system was designed such that once the alcohol is put into the system, it can be degassed and transferred to the solvent bulb without breaking any connections in the system. This eliminates the chance of contamination of the degassed solvent.

The degassing flask had a volume of three liters. This large flask was used to minimize the total amount of time required for degassing. Since approximately 250 cc of solvent was needed per run, seven or eight runs could be made before the flask had to be refilled. The solvent was degassed for eighteen hours initially and two to three hours before each run, rather than twelve hours before each of the runs. The flask was heated with a heating mantle. The input voltage to the heating mantle was regulated with a powerstat. A condensor was mounted above the degassing flask to reflux the solvent during degassing.

Stopcocks 1 and 2 were greaseless, high vacuum stopcocks. These stopcocks prevented the possibility of condensing vapors washing grease into the solvent. Stopcocks 3 and 4 were identical to stopcocks 1 and 2. These were also used to prevent contamination of the solvent while it was being transferred. The solvent transfer line was 9 mm O.D. special wall glass tubing.

The Gas Measurement System

This system includes the gas reservoir, which is that volume initially occupied by the gas, the transducer for pressure measurement,

and the gas transfer line.

The Gas Reservoir

The gas reservoir of the system was comprised of Bulb A, Bulb B, and the tubing between these bulbs and stopcocks 7 and 10.

Bulb B was attached to the tubing by an "O" ring ball joint so the volume of the gas reservoir could be varied. This arrangement facilitates study of a wide range of gases and solvents. Problems, such as that of Cook and Hanson (8), in which 95% of the gas had to go into solution, were avoided.

Bulb A was used only with argon. Since approximately 550 cc were needed for argon, the presence of Bulb A made it necessary to have Bulb B for argon be only about 370 cc. A secondary use of Bulb A was for the calibration of the volume of the tubing portion of the gas reservoir. The purpose and procedure of this calibration are explained in detail in Appendix B. The tubing is 9 mm I.D. special wall, except for the capillary tubing, which is 1 mm I.D.

Bulb A and the separate Bulb B's were calibrated gravimetrically before they were mounted in the system.

Pressure Measurement

The pressure was measured with the transducer which was connected directly to the gas reservoir. The transducer was then connected to the potentiometer, on which the emf readings were taken. The transducer was calibrated after it was mounted into the system. The transducer was mounted inside a chamber adapter which was connected to the gas line with a Swagelock fitting and a Kovar to glass seal.

Gas Transfer Line

The gas transfer line was designed to minimize the danger of overpressuring the transducer. This danger exists since the gas was at a pressure of 1500 psia in the gas bomb and the maximum pressure that the transducer could withstand was 20 psia.

A pressure regulator which indicated both gas bomb and downstream pressures was positioned as shown in Figure 2. The regulator was connected to copper tubing with a Swagelock fitting. The 3/4 inch copper tubing was used to give a certain amount of flexibility in this line for the changing of gas bombs. The copper tubing was connected to the glass tubing with a Swagelock fitting and Kovar-to-glass seal.

Stopcocks 8, 9, 10, and 11 were high vacuum, greased stopcocks. Stopcock 7 was a high vacuum, greased stopcock with capillary sidearms and bore.

The Gas-Liquid Contact System

The gas-liquid contact system was composed of the solvent bulb and its auxiliary parts, the syringes and the motor-pulley system, which was used to drive the stirring device in the solvent bulb. A detailed sketch of the solvent bulb is shown in Figure 3.

This section was designed to meet the following specifications:

- (1) the stirring device had to break the liquid-gas interface continuously and also mix the solvent continuously,
- (2) the volume of gas above the solvent was to be kept as small as possible; thus no corrections would have to be made in the final gas pressure reading to account for the solvent vapor pressure,
- (3) the surface area of the gas-liquid interface should be as large as

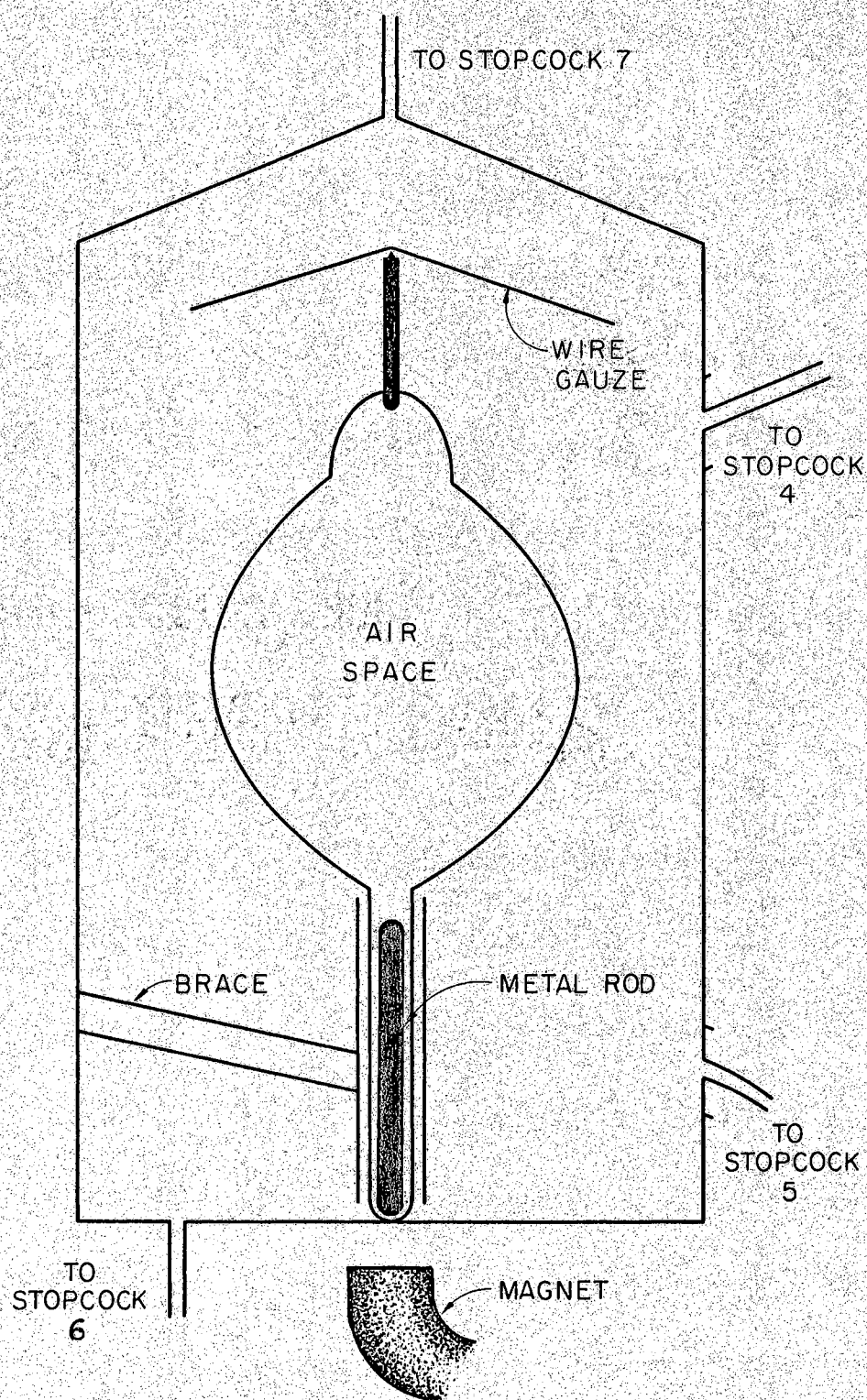


Figure 3. Solvent Bulb

possible,

- (4) the volume of solvent which actually absorbed gas must be known, and
- (5) no motor or electromagnet could be put in the temperature bath because of insufficient cooling capacity.

Testing revealed that a bobing type of stirring device would work best with the above specifications. The float (stirring device) had three main parts, the metal rod, the air space, and the wire gauze. The air space was sized large enough that the stirring device would float, but yet small enough that a powerful magnet would submerge it. Thus as the magnet rises near the cell the float is pulled down and as the magnet draws away from the cell, the float rises to the surface, causing the wire gauze to continuously break the surface.

The solvent bulb was calibrated gravimetrically before it was mounted into the system. The top of the solvent bulb was designed to be as flat as possible so that a large gas-liquid interface would exist for a small volume of gas. The wire gauze was shaped to fit squarely against the top of the solvent bulb. The syringes were mounted so that the level of the solvent could be adjusted by adjusting the syringes. Thus at the end of each run the syringes could be screwed in and the actual volume of solvent which absorbed gas could be calculated.

The stirring device was driven by the magnet. The magnet was driven in the following way. A small wheel was mounted on the drive shaft of a 90 rpm motor. A rod was mounted off center on the wheel and connected with a nylon line to the bar on which the magnet was mounted. As the wheel rotated, the magnet moved up and down.

All tubing connected to the cell was one mm I.D. capillary tubing. By using this tubing, the diffusion of gas up the sidearms was minimized and assumed to be negligible. Capillary tubing was used to connect the solvent bulb to the gas reservoir to prohibit alcohol vapors from diffusing into the gas reservoir.

Electrical System

The purpose of the electrical system was to make consistently accurate readings of the pressure with the transducer. A diagram of the electrical system is shown in Figure 4.

The power supply was used to supply a five volt input to the transducer. Because of drift in the power supply, its voltage had to be monitored. The power supply output could not be monitored directly on the potentiometer since the maximum allowable input to the potentiometer is 0.160 volts. Thus, a 2000 ohm and one ohm resistor were put in series with each other and in parallel with the transducer. The voltage drop across the one ohm resistor was about $1/2000$ the total drop of 5 volts, or 2.5 mv. The potentiometers were used to measure the pressure drop across the one ohm resistor, thus monitoring the power supply output, and to measure the output of the transducer.

Vacuum System

The vacuum system was used to degas the solvent, to evacuate the solvent bulb to a pressure below 0.005 mm Hg. before the solvent was transferred and to evacuate the gas reservoir before it was loaded with gas.

A two stage vacuum pump with a rating of 10^{-6} mm Hg was used during the investigation. The vacuum line ran from the pump to a glass "T." One branch of the "T" was connected to a McLeod Gage (lowest reading was 0.005 mm Hg). The other branch ran through a cold trap to a glass manifold. Two lines came off the manifold, each with a high vacuum greased stopcock. One of these lines was connected directly to Bulb A (above stopcock 8) and the other was connected to the degassing flask (above stopcock 1).

All vacuum lines were 3/8 inch copper tubing. These lines were connected to the glass units (cold trap, glass "T," manifold) with thick walled, high vacuum rubber tubing. All connections were greased with high vacuum stopcock grease.

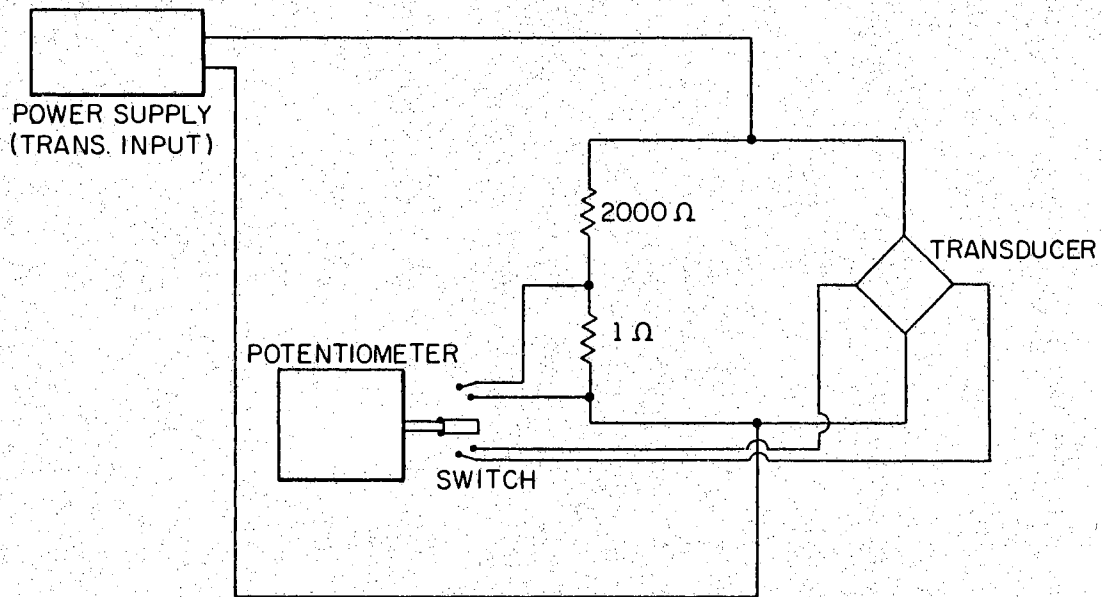
The cold trap, submerged in a dewar flask containing liquid nitrogen, was used to condense vapors during degassing and drying of the solvent bulb and thus prohibit the vapors from ruining the pump oil.

The McCleod gage was connected between the cold trap and the pump so that the pressure measured would not include the vapor pressure of the solvent.

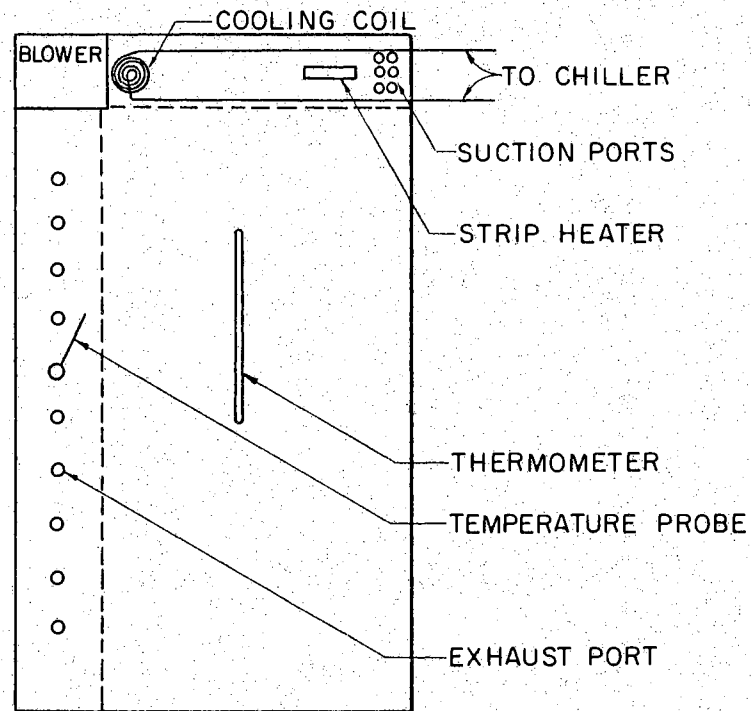
A temporary line was made which could be connected from the inlet of the cold trap to the drainage line of the solvent bulb (below stopcock 6). The temporary line permitted rapid drying of the solvent bulb while preventing solvent vapors from being drawn up through the gas reservoir.

Temperature Control System

The temperature control system was used to maintain the system at 25°C. A diagram of the system is shown in Figure 4.



(a) ELECTRICAL SYSTEM



(b) TEMPERATURE CONTROL SYSTEM

Figure 4. Electrical and Temperature Control Systems

The temperature in the air bath was controlled with a proportional temperature controller. The air was circulated with a "squirrel cage" blower. The blower, positioned in the top left corner of the bath, drew air into the circulation channel at the top right corner of the bath. The air passed across the heater, across the cooling coils, and finally was drawn into the blower. The air was exhausted downward from the blower and distributed throughout the bath through exhaust ports along a distribution channel. The temperature sensor for the controller was mounted in the exhaust channel with the top directly in one of the exhaust ports.

Bath temperature was measured with a thermometer which was mounted in the back of the bath. Two thermometers were used during the investigation. The first was a Fahrenheit thermometer with divisions of 0.05°F . The second was a Centigrade thermometer with divisions of 0.01°C . Both were calibrated at 25°C with a platinum resistance thermometer.

Heat was provided by a 250 watt strip heater which was connected to the temperature controller. Water at $34\text{--}40^{\circ}\text{F}$ was provided to the cooling coils of the air bath and the condenser of the degassing bulb by a commercial chiller. The cooling water was transported through tygon tubing. The cooling coil in the air bath consisted of approximately eight feet (six feet of transfer line and two feet of coil) of $1/4$ inch copper tubing.

Materials

All alcohols and gases were purchased from the Matheson Company, Inc. Chromatograms were supplied with each alcohol. The purity of the gases was stated in the catalog. All materials were used as received;

specifications were as follows:

<u>Chemical</u>	<u>Minimum Purity, Volume per cent</u>
Helium	99.995
Neon	99.995
Argon	99.995
Propanol	99.5
Pentanol	99.5
Heptanol	99.1

CHAPTER IV

OPERATING PROCEDURE

The experimental procedure for testing the equipment and for taking the solubility data will be discussed in this chapter. The following topics will be discussed: the calibration of the equipment (Bulb A, Bulb B, solvent bulb, transducer, and the tubing in the gas containing portion of the apparatus), leak testing, preparation for taking data and the procedure used in taking the solubility data.

Calibrations of Volumes

In order to calculate solubilities using a volumetric apparatus, the volume of solvent which absorbs gas and the number of moles of gas absorbed must be known. The initial and final volumes of gas must be known in order to calculate the number of moles of gas absorbed. Thus the solvent bulb, Bulb A, the three Bulb B's, and the volume of the tubing in the gas containing portion of the system had to be accurately calibrated. The five bulbs were calibrated gravimetrically, while the tubing was calibrated using a gas expansion method. These volume calibrations are discussed below.

Gravimetric Calibrations

The volumes of the five bulbs (three Bulb B's, Bulb A, and the solvent bulb) were calibrated by weighing the water required to fill

the bulbs and calculating the volume from the known density of water at the temperature of the measurement.

The balance used to weigh the water had a maximum capacity of 200 grams. Since the bulbs plus water weighed more than 200 grams, the bulbs could not be weighed dry and then weighed full of water, but rather, the water added to dry bulbs had to be weighed in portions. A plastic squeeze bottle was filled with about 130 grams of distilled water (squeeze bottle weight was about 70 grams). The bottle was weighed, then the water was transferred to the glass bulb. The plastic bottle was weighed again, and the difference in weights was equal to the weight of the water added. This procedure was repeated until the glass bulb was filled. Care was taken to assure that no water was spilled. After the bulb became full, the water was drained and the temperature of the water was recorded.

Each of the three Bulb B's was filled with water to the very top of the ball joint. The volume of Bulb A was calibrated such that the volume between stopcocks 8 and 9 and the bore of stopcock 9 were included. To calibrate the solvent bulb, three of the four capillary arms were plugged so that they were air tight. When the bulb was filled with distilled water, the water did not enter the arms.

Gas Expansion Calibration

The initial and final gas volumes had to be known. The volumes of Bulb B and Bulb A were found gravimetrically before being mounted into the system. However, the volume of the main gas line could not be measured conveniently by gravimetric methods. Thus, the following gas expansion technique was used. The system was brought to 25°C,

stopcocks 7 and 10 were closed and stopcocks 8 and 9 were opened. The system was evacuated to below 0.005 mm Hg. Stopcock 9 was closed and stopcocks 10 and 11 were opened. The system was filled with air to atmospheric pressure. Stopcock 10 was closed and the system was allowed to come to equilibrium (the transducer readings became constant). The following readings were then taken: (1) the output of the transducer, EMF, (2) the voltage drop across the one ohm resistor, EMF_0 , and (3) the temperature of the system, T.

Stopcock 8 was then closed and stopcock 9 was opened. The gas expanded into Bulb A. After the system came to equilibrium, EMF, EMF_0 , and T were recorded again. Stopcocks 8 and 9 were opened, and the system was reevacuated.

Each run was made with the above procedure. Then Bulb B was removed and one of the other two was mounted. The ball joint was again checked for leaks. Once the system was air tight, three runs were made with the second gas bulb. Finally, three runs were made with the last Bulb B.

The method used in calculating the gas volume from the above information is explained in detail in Appendix B.

The volumes between point C and point B (see Figure 2) and between point B and stopcock 7 (including the bore) were found by filling the solvent bulb with water. The water levels were set at C and the syringes were read. The level was then raised to B and the syringes were read again. The level was raised to the top of stopcock 7 and another reading was taken. The two volumes were then calculated.

Calibration of Transducer

The pressure was measured by means of a pressure transducer. The readings from the transducer were in terms of its output voltage. Thus the transducer had to be calibrated to find the actual pressure as a function of output voltage of the transducer.

The following procedure was used: A Texas Instrument (TI) pressure gage (description given in Appendix F) was joined to the system at the "0" ring ball joint connection for Bulb B. The TI gage could not be placed in the air bath. Thus it was set on top of the air bath and a 3/8 inch copper line joined the TI gage to the ball joint.

The temperature controller, cooling water, and blower were turned on and the transducer was given several hours to come to 25°C. With stopcocks 7 and 10 closed, stopcocks 8 and 9 were opened, thus drawing a vacuum on Bulb A, the transducer, and the TI gage. The system was allowed to set with the pump drawing on the system for five to six hours. This was done so that the TI gage could be accurately zeroed. After zeroing the TI gage and transducer, stopcock 9 was then closed and the system pressure was monitored for three to four hours to check for leaks around the ball joint.

When the system was leak tight, it was again evacuated. The following values were recorded: (1) the TI gage reading, TIG, (2) the output of the transducer, EMF, (3) the voltage drop across the one ohm resistor, EMF_0 , and (4) the temperature of the TI gage, T.

Stopcock 8 was then closed. With stopcock 11 open, a small amount of air was let in through stopcock 10. The system was allowed to set until both the TI gage readings and the transducer readings became constant. Again EMF, EMF_0 , TIG, and T were recorded. More air was then

put into the system. The pressure was allowed to rise at predetermined pressure intervals. The approximate pressure was read directly from the TI gage. If too much air entered the system, it could be drawn out by slightly opening stopcock 8.

The above procedure was followed up to a pressure of approximately 850 mm Hg. For pressures above atmospheric, air was blown into the system. While filling the system, approximately fifteen data points were taken, five from 0-600 mm Hg, and ten from 600-850 mm Hg. (The pressure readings during solubility experiments were generally in the range of 700-800 mm Hg.) After the reading was taken at the maximum pressure, readings were taken as the pressure was lowered from atmospheric pressure to a high vacuum. Stopcock 8 was slightly opened and air was removed from the system. The system was given time to reach equilibrium, and the data were recorded.

Four runs were made using the above procedure. Two from vacuum to 850 mm Hg and two from 850 mm Hg to vacuum. The average deviation between the calculated pressures from the transducer and the true pressure calculated from the TI gage was 0.2 mm Hg.

Leak Testing

One of the causes of error which Cook and Hanson (8) mentioned was that of contamination of solvent or gas. Since an air-tight system was imperative, the equipment had to be continuously checked for leaks.

The following method was used to check for leaks: Stopcocks 1, 4, 5, 6, and 11 were closed and stopcocks 7, 8, 9, and 10 were opened. The system was drawn down to 0.001 mm Hg. for half an hour. Any large leaks would be detected with the McCleod gage. If there were no large leaks, stopcocks 7, 9, and 10 were closed. The system was allowed to set for six to ten hours. A reading was made on the transducer,

indicating the pressure between stopcocks 7, 9, and 10. This reading was recorded. Stopcock 9 was opened. When the McCleod gage indicated that the pressure had dropped below 0.005 mm Hg (approximately five minutes) the transducer was read again. A change of 0.001 mv indicated a pressure change of 0.05 mm Hg. If the pressure did not rise over 0.05 mm Hg per hour, leaks were considered negligible. A 0.05 mm Hg rise per hour would be too large during an actual run, but the system did not leak this much during a normal run. During leak testing the pressure driving force is approximately 740 mm Hg. During a normal run the driving force was initially the maximum value of 70 mm Hg; within one hour the driving force would drop about 30 mm Hg, and after two hours, to 10 mm Hg. For the above reason, 0.05 mm Hg pressure rise per hour for a driving force of 740 mm Hg was considered satisfactory.

If the volume between stopcocks 7, 9, and 10 was vacuum tight, stopcock 9 was closed and stopcock 10 was opened. A transducer reading was taken. Stopcock 9 was then opened and the new reading taken. The above procedure was used for the entire system.

Eventually all leaks were entirely eliminated except two. One was in the gas transfer line; the other was in the syringes. Both were quite small and the danger of them causing contamination was eliminated through proper experimental procedure.

Preparation for Taking Data

This section describes the procedure which was used each time a new solvent was introduced to the system, including the filling of the degassing bulb, initial degassing, and filling of the syringes.

Filling the Degassing Flask

The degassing flask was evacuated to 0.005 mm Hg for several hours to insure that the cell was dry. Air was let into the bulb and stopcock 2 was removed. A funnel and a piece of 1/4 inch copper tubing were used to transfer the solvent from its storage bottle into the degassing bulb through stopcock 2. The solvent was put into the degassing bulb as quickly as possible to prevent contamination by water vapor in the air. As soon as the flask was full, stopcock 2 was replaced. The stopcock was greasless and could easily be removed and replaced. The degassing flask was a three liter flask. Generally 1750-2000 ml solvent would be put in the flask so that several runs could be made before refilling and yet the solvent did not blow out the top during boiling. Glass beads were used as boiling chips.

Degassing the Solvent

Stopcocks 3 and 8 were closed. The heating mantle was turned on with the variac set on 40. After giving the solvent time to warm, the cooling water was started through the condenser. Stopcock 1 was fully opened, and stopcock 2 was slightly opened, thus slowly evacuating the space above the solvent. When the pressure above the solvent dropped to the solvent vapor pressure at the temperature of the system, the solvent began to boil.

For the first hour, a great deal of air boiled off the solvent and went overhead to the vacuum pump. There were few vapors condensing. After most of the air had been drawn overhead, the vapors began to condense. The head was adjusted so that the condensate line was about half way up the condenser. The system was watched carefully during the

first two hours of boiling. When the reflux rate steadied, the system could be left unattended. The cold trap had to be checked every five to six hours when the propanol was being degassed. The trap did not need to be cleaned for pentanol or heptanol, since, due to their low vapor pressures, very little boiled over. To clean the cold trap, stopcocks 1 and 2 were closed. The trap was removed, rinsed with acetone, dried, and placed back in the system. The system was then evacuated to below 0.005 mm Hg before stopcocks 1 and 2 were reopened.

Each of the solvents were degassed a minimum of eighteen hours during the initial degassing.

Filling Syringes

Before a run could be made, the volume between the syringes and stopcock 5 had to be filled with solvent. Since the solvent in the syringes did not need to be degassed, solvent saturated with air or inert gas was put in the syringes. Thus they only needed to be filled from the degassing bulb before the first run of a new solvent.

The following procedure was used to fill the syringes: The solvent bulb, syringes, and transfer line between stopcocks 3 and 4 were evacuated below 0.005 mm Hg. Then stopcock 5 was closed and the solvent bulb was drawn on a short time longer. Since the syringes had a small leak, stopcock 5 was kept closed. While evacuating the solvent bulb, the cooling water was turned off and the heating mantle variac was turned up to 80. When the transfer line to stopcock 3 filled with solvent, stopcock 7 was closed and stopcock 3 was opened. The pressure differential between the bulbs forced the solvent into the solvent bulb. When the solvent bulb was half full, stopcock 3 and 4 were closed. Stopcock 9

was closed and stopcocks 7, 10, and 11 were opened. Stopcock 5 was then opened and solvent filled the syringes, which had been evacuated. Any air which was in the syringes would have been pushed into the solvent bulb by screwing the syringes in. Stopcock 6 was then opened and the solvent was drained. The capillary tubing and small bulb between stopcock 5 and the solvent bulb were drained by unscrewing one of the syringes. The solvent was drained slowly and carefully. Just the right amount of solvent was drained so that when the syringes were set on 2.0 (all the way up) and 1.0, respectively, the solvent level was just above stopcock 5. If too much was drained, more had to be transferred from the degassing flask.

When enough solvent was drained the syringe was tightened and stopcocks 5 and 7 were closed and stopcock 4 was opened. The auxiliary line was then connected directly from the cold trap to the drainline (stopcock 6). The solvent bulb was then evacuated and all solvent was dried from the volume between stopcocks 3, 5, and 7.

The cell dried in approximately thirty minutes with the propanol, and in two hours with the pentanol. The vapor pressure of the heptanol was so low that twelve hours or more was required to dry the cell. Therefore the cell was heated with a heating tape. Though the solvent was not driven off, it was degassed as it vaporized. With the syringes full, the apparatus was ready for an experimental run.

Taking Solubility Data

Before each run the solvent was degassed for an additional two to three hours. After degassing, the solvent bulb was drawn down to 0.002 mm Hg while the solvent was being heated. The solvent was transferred

with the same procedure used in filling the syringes, except that the solvent bulb was filled up to mark C. Stopcock 4 was closed and the volume between stopcocks 3 and 4 was half filled with solvent. Then stopcock 3 was closed. A small amount of solvent was held between stopcocks 3 and 4 because as the solvent in the solvent bulb cools, the solvent contracts by as much as two per cent, or 4.0 cc. The excess solvent in the transfer line was used to make up for this shrinkage.

While transferring the solvent, stopcocks 8, 9, and 10 were open; stopcocks 7 and 11 were closed. Stopcock 10 was then closed and gas was put into the transfer line. The transfer line was charged in the following way: The control valve on the pressure regulator was turned counterclockwise until it seemed to be coming loose. Valve E was closed, then valve D was opened. The control valve was turned clockwise until the downstream pressure gage began to indicate a pressure above atmospheric. The control valve was then set at the desired downstream pressure. Valve E was then opened and the transfer line was charged.

The following procedure was used to purge the main gas line and gas bulb: The gas transfer line was charged to 4.0 psig. The main gas line was evacuated to 0.005 mm Hg. Stopcock 9 was closed. With valve D open and valve E closed, stopcock 10 was opened, then closed. Valve E was then opened. Stopcock 10 was then opened and closed. Then valve E was opened. This procedure was repeated until the system pressure rose to at least 300 mm Hg. The pressure was monitored on the transducer. Stopcock 9 was then opened and the system evacuated to less than 0.005 mm Hg. The gas transfer line was kept at 4.0 psig at all times except when the gas was expanded into the system. The system was purged twice.

The system was then filled to a pressure of approximately 800 mm Hg using the above procedure. For helium and neon, the volume charged was that volume between stopcocks 7, 9, and 10. Their respective gas bulbs were used. For argon, the volume charged was between stopcocks 7, 8, and 10.

The system was then allowed to come to thermal equilibrium (approximately two hours). This was again determined when the transducer readings did not vary with time. When the gas reached thermal equilibrium, the following readings were taken: (1) the output voltage of the transducer, EMF, (2) the voltage drop across the one ohm resistor, EMF_0 , and (3) the temperature of the system, T.

The syringes had been set on approximately 1.0 and 2.0. Since each syringe had a capacity of 2.0 cc, the solvent level could be raised 1.0 cc or lowered 3.0 cc. Thus the solvent level had to be within 1.0 cc of mark B. If the level had dropped since filling the solvent, some of the solvent was transferred through stopcock 4. The line between stopcocks 3 and 4 had to be heated to get the solvent to flow into the solvent bulb. Once the solvent level was set, stopcock 4 was closed. The system was now ready for the actual absorption of gas.

Stopcock 7 was opened. The pressure on the solvent was now approximately 800 mm Hg. Stopcock 5 was opened, and the solvent level was dropped enough that the screen on top of the float would break the gas-liquid interface. Stopcock 5 was then closed. The motor was turned on and stirring began.

The pressure in the system was monitored with the transducer. When the pressure did not drop during a one hour period, the run was considered to be complete. The following readings were made: EMF, EMF_0 , and T.

Stopcock 7 was then closed and stopcocks 8 and 9 were opened. The system was evacuated for ten minutes. The above readings (EMF , EMF_0 , and T) were again taken. This was done to find the zero point of the transducer.

Stopcock 9 was closed and stopcocks 11, 10, and 7 were opened, in that order. Stopcock 5 was then opened. The readings of the two syringes were recorded. The solvent level was raised to mark B with the syringes, and their readings were taken again. These readings were the final data taken for the run. The cell was then drained and dried as explained in the section on filling the syringes. After drying the cell, a new run was made.

The methods used to calculate the solubility are shown in Appendix B.

Results

The results of the calibrations of the three Bulb B's, Bulb A, the volume of the tubing in the gas reservoir, and the transducer are given in Appendix E in the section on experimental data.

Table I lists the experimental results according to systems studied. The "average absolute percent deviation" is the sum of the absolute value of the differences between the individual Ostwald coefficients and the average Ostwald coefficient for the given system. Both H (average) and Ostwald (average) are arithmetic averages.

TABLE I
EXPERIMENTAL RESULTS

Solvent	Gas	Run Number	Ostwald Coefficient			Henry's Law Constant	
			ℓ	Average	Avg Abs % Dev	H, atm	Average H, atm
Propanol	Helium	26	.02598	.02603	.34	12540	12520
		27	.02594			12560	
		28	.02616			12450	
	Neon	24	.03666	.03675	.24	8886.	8865.
		25	.03684			8844.	
	Argon	21	.2454	.2458	.12	1328.	1326.
		22	.2463			1324.	
		23	.2458			1326.	
Pentanol	Helium	19	.02295	.02297	.05	9817.	9812.
		20	.02298			9807.	
	Neon	15	.03119	.03150	.74	7225.	7155.
		16	.03146			7205.	
		17	.03185			7076.	
	Argon	12	.2276	.2260	.60	991.	998.
		13	.2271			993.	
		14	.2238			1008.	
		18	.2254			1001.	
Heptanol	Helium	29	.02050	.02065	.68	8429.	8372.
		31	.02080			8314.	
	Neon	34	.02868	.02884	.54	6028.	5995.
		35	.02900			5963.	
	Argon	32	.2103	.2107	.15	823.	822.
		33	.2110			820.	
Water	Argon	36	.03160	.03095	1.50	42820	43700
		37	.03025			44730	
		38	.03099			43670	

CHAPTER V

DISCUSSION OF RESULTS

The purposes of this chapter are the following:

- (1) to compare the experimental results of this work with data from the literature,
- (2) to discuss the results of controlled experiments with regard to possible sources of error in experimental data, and
- (3) to discuss the results of four theoretical correlations in comparison to the present experimental data.

Experimental Results

The experimental results are shown in Table I. For the alcohol systems, the greatest average deviation from the mean for any of the systems was 0.74% for the pentanol-neon system. Five of the nine systems had average deviations from the mean of less than 0.5%. Thus the data were satisfactorily reproducible. Error analysis (which is discussed in Appendix D) shows the expected error to be 0.55%.

Table II shows the data of this work and the experimental data from the literature which are plotted in Figures 5, 6, and 7.

Figure 5 shows the experimental data for Boyer and Bircher (4), Gjaldbaek and Niemann (13), and this work for argon in various alcohols. Several points should be noted from this figure.

First, the data of Boyer and Bircher seem to fall into two groups,

the alcohols methanol through butanol comprising one group and the alcohols pentanol through octanol comprising the other group. There appears to be a transition zone between the two groups of alcohols. Second, a smooth curve through the data of Gjaldbaek and Niemann would be concave downward, while smooth curves through the data of Boyer and Bircher and the data of this work would be concave upward. Third, for propanol, the data of this work fall below the data of the other two sources, while in the case of pentanol, the present data fall between the other two sources. Fourth, for both propanol and heptanol the present data are approximately 3.4% lower than the data of Boyer and Bircher, while the present data is only 1.34% lower in the case of pentanol.

Figures 6 and 7 show the data of Lannung (22) and of this work for helium and neon, respectively. The apparent inconsistency of the data between the two sources should be noted.

Of the literature data available for the systems studied in this work, no two literature sources were found which agreed within the combined experimental uncertainty claimed by the authors. In view of the disagreement among the alcohol data for this work and the literature sources, the decision was made to run argon in water, for which five different literature sources had an average deviation from the mean of 0.64%. A comparison of the data shows that the data of this work is 10.1% lower than the mean of the five literature sources. The author can only make the same comment about this discrepancy that Brasted and coworkers (5) made when their data differed from the literature. Brasted said, "The authors are unable to explain this discrepancy since it is felt that the present work was carried out under very rigorous conditions." The rigorous conditions used in this work will be

TABLE II
EXPERIMENTAL SOLUBILITY DATA FROM THE LITERATURE
AT 25°C AND ONE ATMOSPHERE
(OSTWALD COEFFICIENTS)

Solvent	Helium	Neon	Argon
Methanol	0.0358 (22)	0.0485 (22)	0.267 (4,22)
Ethanol	0.0321 (22)	0.0455 (22)	0.258 (4,22)
Propanol	0.0260*	0.0367*	0.246* 0.254 (4) 0.251 (13)
Butanol			0.246 (4) 0.240 (13)
Pentanol	0.0230*	0.0315*	0.226* 0.229 (4) 0.224 (13)
Hexanol			0.224 (4)
Heptanol	0.0207*	0.0288*	0.211* 0.218 (4)
Octanol			0.213 (4)
Water			0.0309* 0.0344 (18) 0.0335 (26) 0.0341 (10) 0.0341 (3) 0.0342 (19)

*Data of this work.

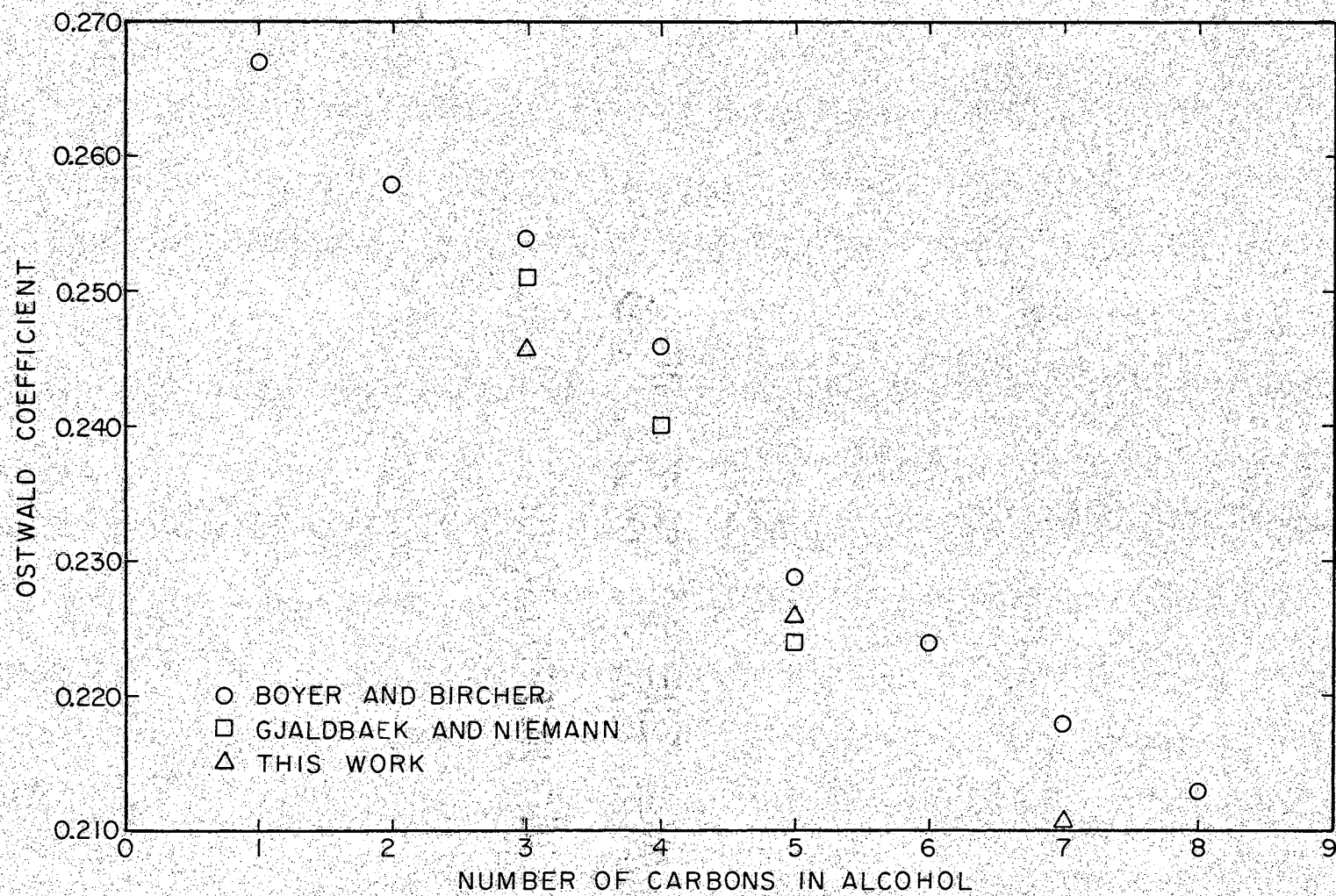


Figure 5. Ostwald Coefficients for Argon

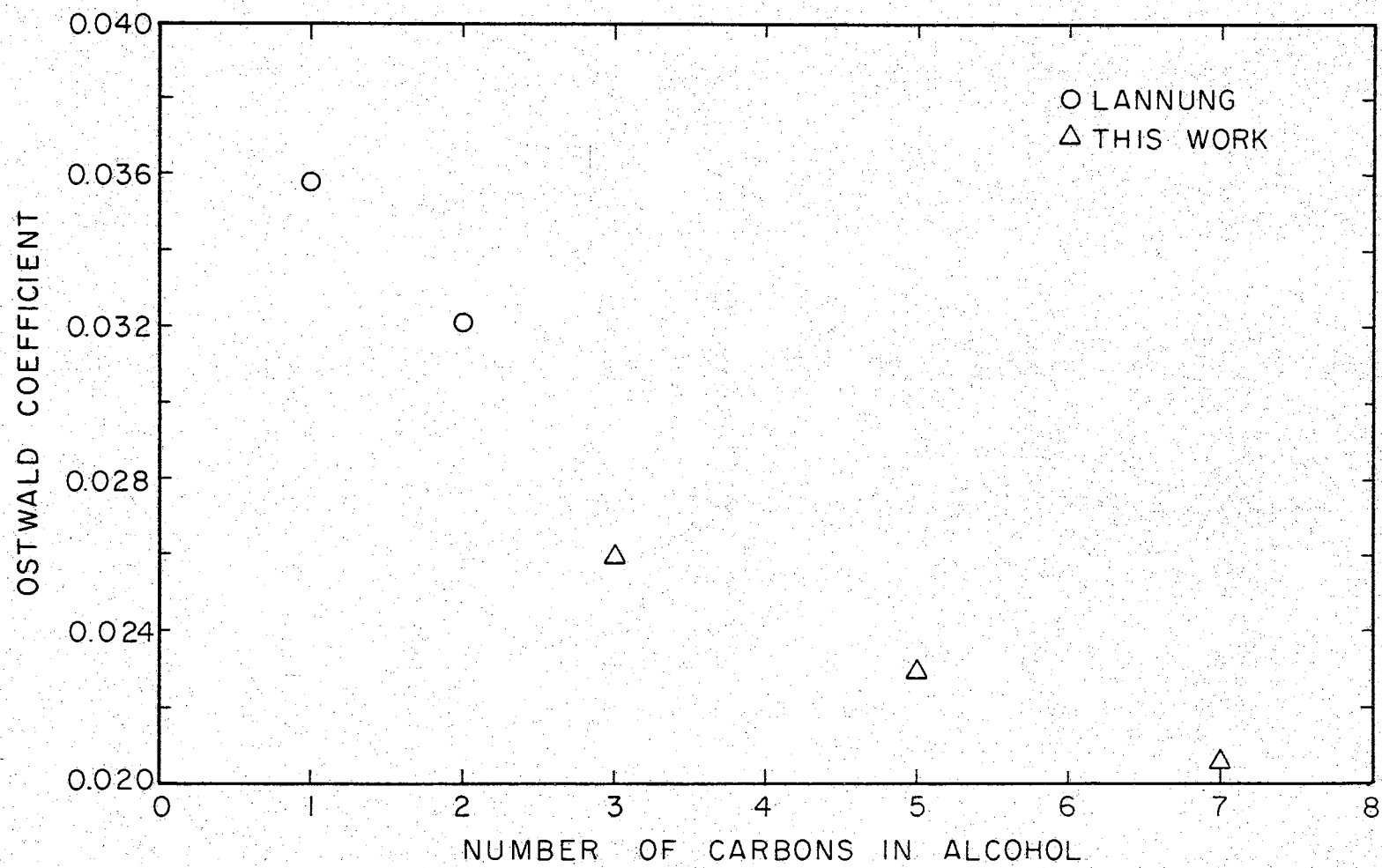
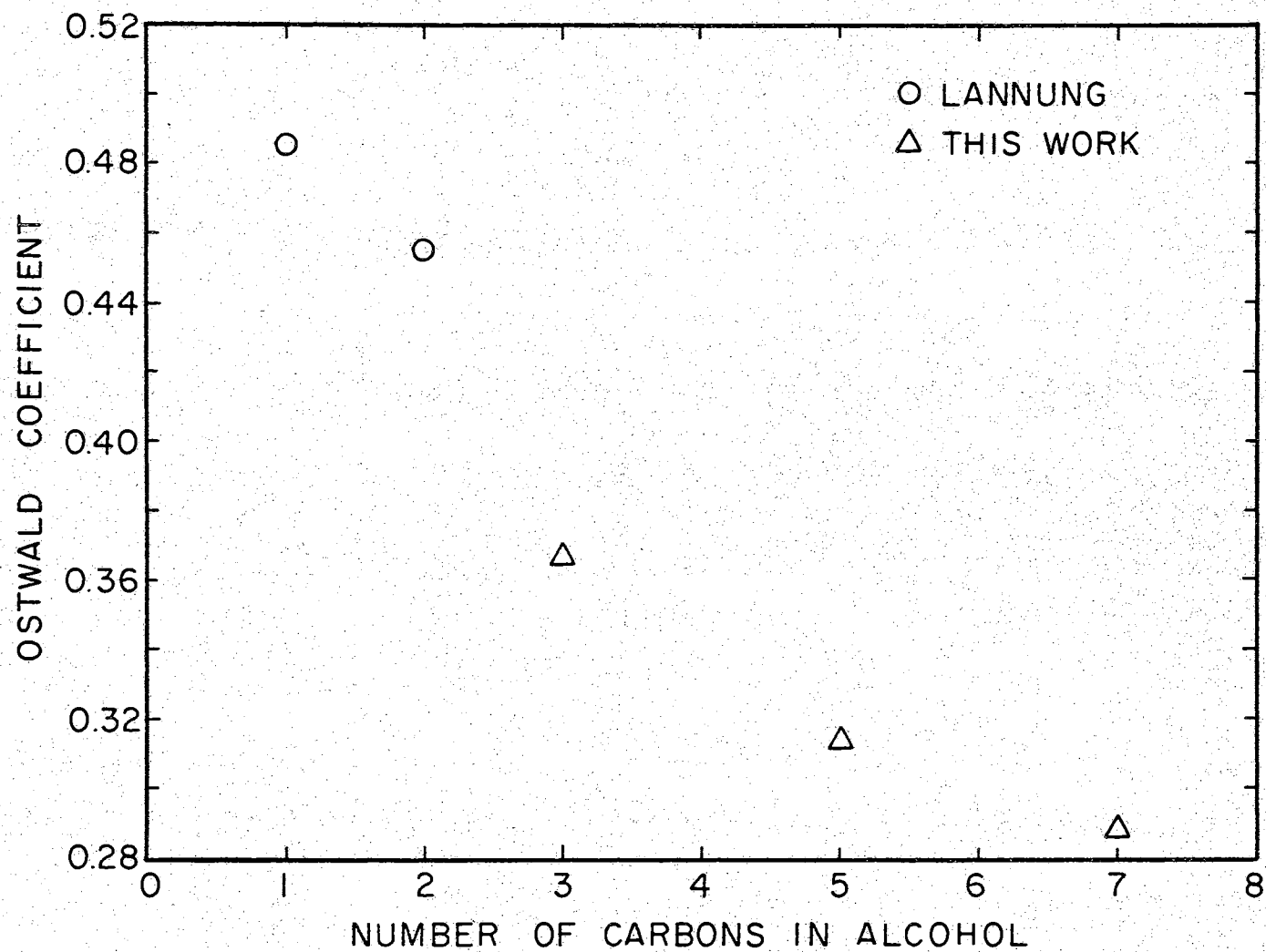


Figure 6. Ostwald Coefficients for Helium



discussed later in this chapter.

Various suggestions which have been made in the literature concerning plots of solubility data which might give a linear relationship include the following:

- (1) $RT \ln x_2$ vs. energy of vaporization of gas at the normal boiling point, for gases in a given solvent (25),
- (2) $\ln x_2$ vs. \ln (number of carbons of alcohol) for a given gas in various alcohols (23),
- (3) \ln (Ostwald coefficient) vs. critical temperature of gas for a given solvent (20),
- (4) \ln (Ostwald coefficient) vs. surface tension of solvent for a given gas (7), and
- (5) \ln (Henry's Law Constant) vs. polarizability of the gas for a given solvent (29).

Each of the suggested plots has been made for both the data of this work and the experimental data of the literature. The first four plots did not approach a straight line. The fifth plot did turn out favorably and is shown in Figure 8. It should also be noted that this is the plot which is used in the correlation of Lin and Chao to find the hard sphere Henry's Law Constant. The data of this work were plotted to determine hard sphere values for propanol, pentanol, and heptanol. The data of Boyer and Bircher and of Gjaldbaek and Niemann were combined to give parameters for methanol and ethanol. The data of this work gave very nearly a straight line for each alcohol. The combined literature data did not give straight lines.

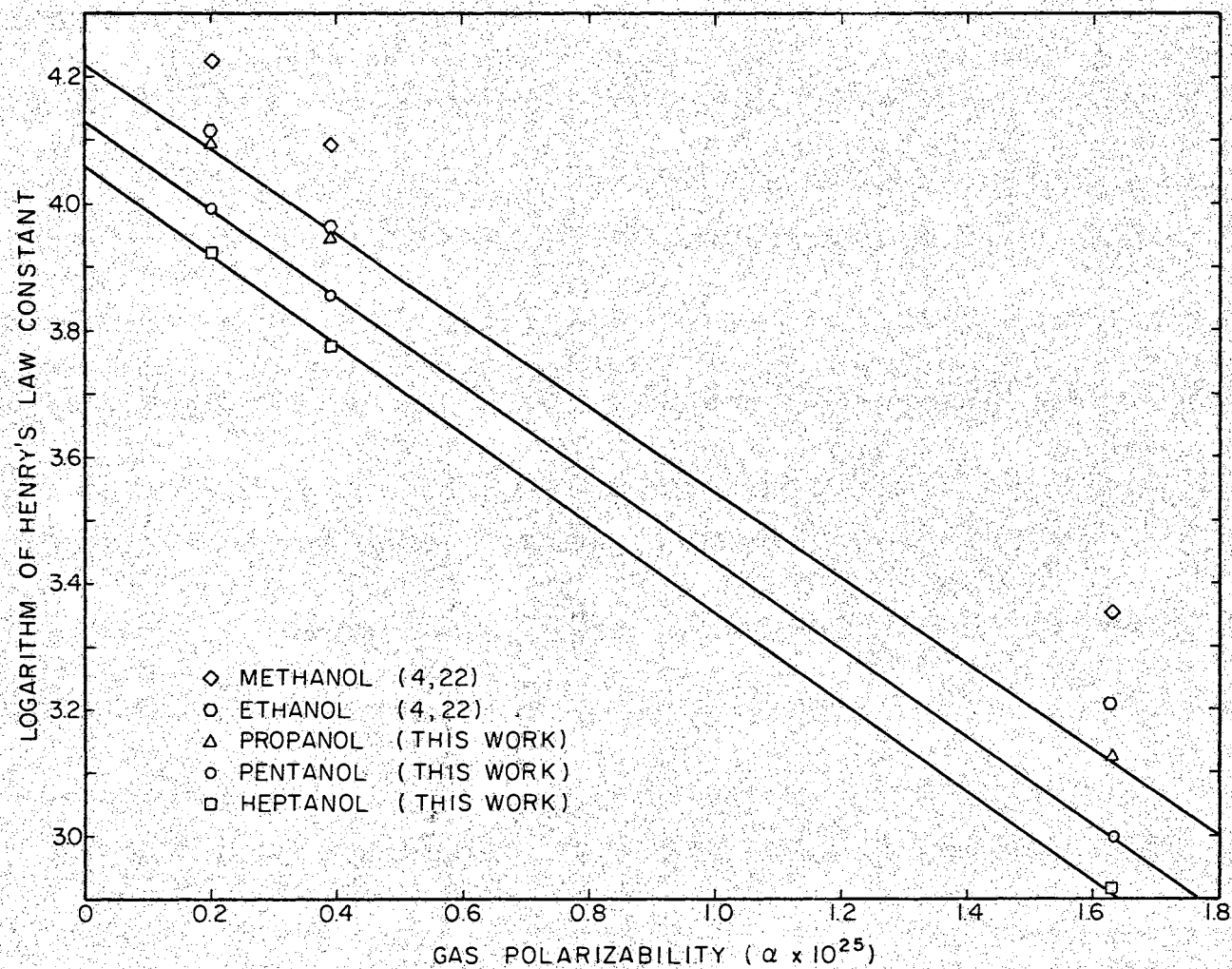


Figure 8. Henry's Law Constants of Experimental Data

Analysis of Experimental Error

In view of the disagreement between the data of this work on solubility of argon in water with the literature values, all sources of possible error in measurement of solubility data, as cited by Cook and Hanson (8), were carefully considered and are discussed below. The items suggested by Cook and Hanson will be discussed in order.

First Cook and Hanson suggested that there may be failure to attain equilibrium. Equilibrium must be attained twice during a run. First, thermal equilibrium must be reached in the gas reservoir before the initial pressure reading can be made. Second, chemical equilibrium must be reached in the solvent bulb before the final pressure reading can be made. In both cases transducer readings were taken continuously while the system was coming to equilibrium. When the readings did not vary for over an hour, the system was regarded as being at equilibrium.

This method of checking for the attainment of equilibrium seems reasonable since in a typical case a plot of $(p-p_0)$, where p is the system pressure and p_0 is the final system pressure, as a function of time (Figure 9) shows that the pressure of the system drops very quickly. In the plot shown, the pressure has dropped over 99% of the total drop after 410 minutes. The pressure drop from 468 minutes to 658 minutes (the final reading) was 0.4 mm Hg. A reading was taken after 720 minutes but there had been no change since the previous reading. It is interesting to note that a plot of $\ln (p-p_0)$ as a function of time is linear, illustrating that the dissolution process follows simple mass transfer laws.

Second, Cook and Hanson cited failure to degas the solvent as a possible source of error. Cook and Hanson said, "In the degassing

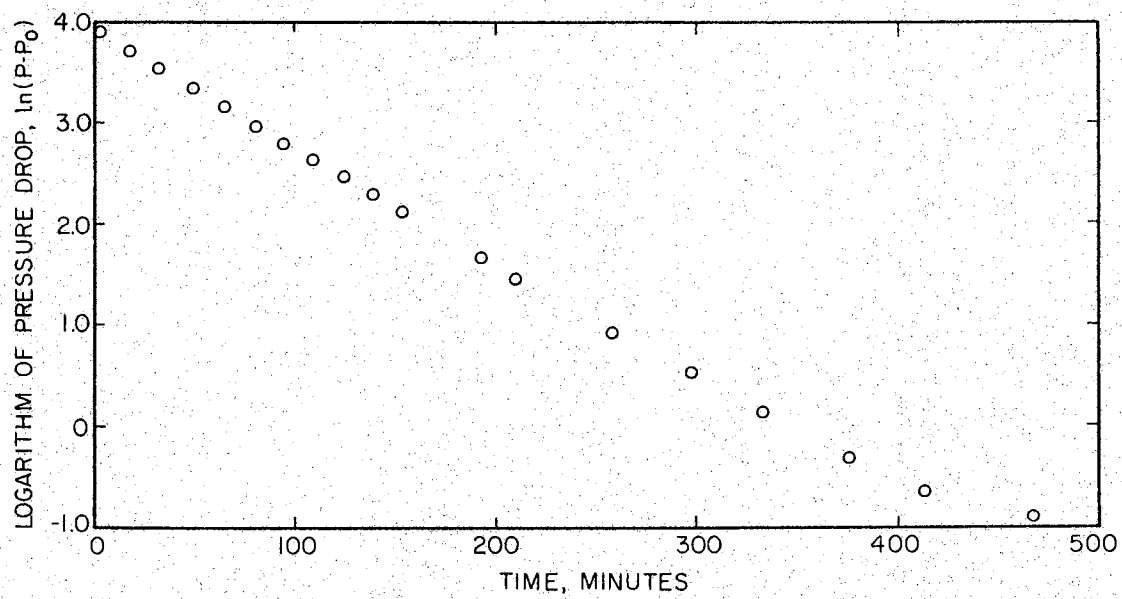
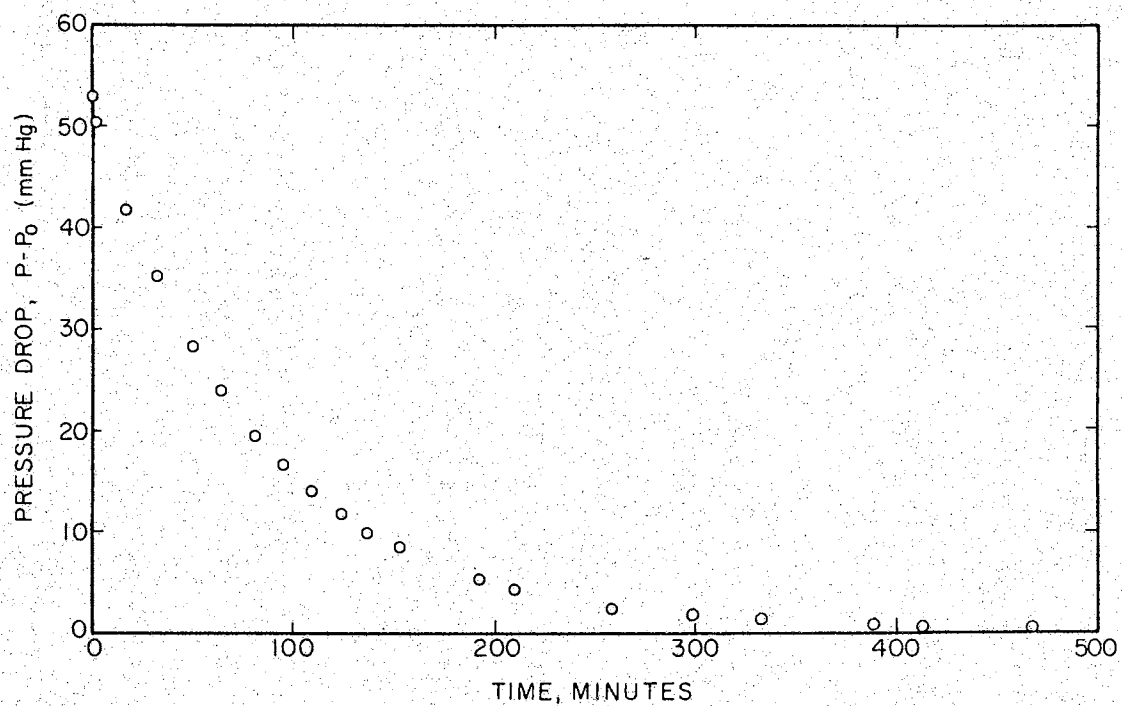


Figure 9. Typical Pressure Drop-Time Relationship for Solubility Experiment

process it was found that from 10 to 20% of the solvent should be evaporated, that the amount of solvent required to be evaporated is increased as the rate of boiling increases, and that the time required for degassing is about one to two hours." Cook and Hanson were degassing 200 cc of solvent in their work.

In this work up to 1750 cc of solvent were being degassed at one time. The solvent was initially degassed at least 12 hours for propanol and 18-24 hours for pentanol and heptanol. Possibly 5% of the propanol was boiled off. A negligible amount of the other two alcohols were boiled off during boiling. This was due mainly to the low vapor pressure of the latter two alcohols.

Although very little pentanol and heptanol were boiled off, it should be noted that the solvents were boiled under extremely low pressure for long periods of time. For pentanol, the vapor pressure is about 4.5 mm Hg at the temperature at which it was boiled. If the alcohol is saturated with the gas there should only be 4.5 mm Hg out of 760 mm Hg or 0.7% of the one atmosphere solubility left in the alcohol.

A third factor which Cook and Hanson cited was the failure to accurately measure the amount of gas dissolved. This could be caused by inaccurate calibration of the gas volume or by inaccurate pressure readings. Bulb A and Bulb B were calibrated gravimetrically and the average deviation from the mean was never more than 0.05% for any of the bulbs. The gas line was calibrated by expanding gas from the gas line and Bulb B into Bulb A. The average deviation from the mean for these runs was less than 0.33%, which would be less than 0.1% for the total gas volume of any given run.

If the pressure transducer had been giving inaccurate readings due to drift, then the data should have varied somewhat. Since the data agreed to within 0.7% for all systems, the author feels that drift in the transducer was adequately accounted for by subtracting the zero point for the readings.

The contamination of the gas by the alcohol vapors during the experiment would require calculations to account for the composition change in determining the final volume. In this work the equipment was designed with capillary tubing between the solvent bulb and gas reservoir of the system so that the gas would not be contaminated.

Finally, Cook and Hanson stated that the gas and solvent must be kept free of contamination during transfer. The entire system was vacuum tight. It was checked several times during the course of taking data. Each time Bulb B was changed, its ball joint was checked for a leak. The system was pulled down to 0.001 mm Hg before the solvent was transferred. The gas volume was purged at least twice before it was filled with gas.

During most runs the initial pressure was about 800 mm Hg and the final pressure was about 730-740 mm Hg, just below atmospheric. Thus if the ball joint leaked, during the last four to five hours of a run a small amount of air would leak into the system, thus causing the Ostwald coefficient to be low. In run 38 the initial pressure was raised so that the final pressure was 770 mm Hg. If the joint leaked, the solubility should have been too high. The Ostwald coefficient came out between the other two runs for argon in water. Thus the conclusion was made that the joints were not leaking.

The following test was made to evaluate the efficiency of the stirring device. The cell was filled with water. Plastic capillary tubing was inserted through the drainage line so that the tubing was flush with the bottom of the cell. Food coloring was then put into the bottom of the cell with a syringe through the tubing. The food coloring was slightly more dense than the water and would lie on the bottom of the cell. The stirring device was then turned on. Within ten minutes the food coloring had been well mixed. The coloring was then put in the bottom of a beaker with no mixing. The same amount of color change which took ten minutes with the stirring device took approximately ninety minutes by diffusion only. Thus the author concluded that the stirring device should have worked well in the taking of the data, since most runs took a minimum of seven hours.

In conclusion, the author believes that all sources of error which Cook and Hanson cited were eliminated in this work.

Testing of Solubility Correlations

The results of the theoretical calculations are given in Table III. The table also shows the percent deviation of each of the correlations from the data of this work. For two of the correlations (Gjaldbaek and Niemann (13); Prausnitz and Shair(30)), all the data needed to make the calculations were not available (specifically, the solubility parameters, δ , for helium and neon). Thus the data were used to back calculate the solubility parameters for helium and neon. The mean value of the backed out δ was then used to recalculate the solubility. These correlations can be evaluated only in as much as for the three different solvents the solubility parameter of a given gas should remain

TABLE III
RESULTS OF THEORETICAL CORRELATIONS (HENRY'S LAW CONSTANT $\times 10^{-3}$)

Gas	Alcohol	This Work	Lin and Chao	Gjaldbaek and Niemann		Prausnitz and Shair		Loeffler and McKetta		
				Backed Out ¹	δ (Ar) = 5.43 ²	Backed Out ¹	δ (Ar) = 5.43 ²	High	Low	Line
Helium	Propanol	12.52	11.31 (-10.6)*	12.04 (-3.76)		13.32 (6.41)		10.11 (-19.2)	8.95 (-28.5)	8.95 (-28.5)
	Pentanol	9.812	9.739 (-.745)	9.389 (-4.13)		9.864 (0.53)		6.931 (-29.4)	6.132 (-37.5)	6.132 (-37.5)
	Heptanol	8.372	8.424 (0.62)	7.328 (-12.4)		8.441 (0.83)		5.1255 (-37.2)	4.649 (-44.5)	4.649 (-44.5)
Neon	Propanol	8.865	7.460 (-18.8)	8.677 (-2.12)		10.48 (18.2)		6.858 (-22.6)	6.631 (-25.2)	14.99 (69.1)
	Pentanol	7.155	6.010 (-19.0)	7.202 (0.66)		7.300 (2.02)		4.679 (-34.6)	4.524 (-36.7)	10.23 (43.5)
	Heptanol	5.995	5.140 (-16.6)	5.727 (-4.46)		5.837 (-2.64)		3.526 (-41.2)	3.409 (-41.3)	7.707 (28.5)
Argon	Propanol	1.326	1.233 (-7.54)	1.347 (1.59)	1.306 (1.47)	1.494 (12.7)	1.062 (-19.9)	1.473 (11.1)	1.201 (-9.44)	1.647 (24.2)
	Pentanol	0.988	0.924 (-8.01)	1.137 (13.9)	1.103 (10.55)	0.996 (-.15)	0.699 (-29.9)	1.004 (0.59)	0.819 (-18.0)	1.122 (12.4)
	Heptanol	0.821	0.790 (-3.92)	0.919 (11.9)	0.893 (8.71)	0.824 (0.32)	0.608 (-25.9)	0.755 (-8.04)	0.616 (-25.0)	0.845 (2.79)

*Per cent deviation from this work.

¹Results for when backed out δ_2 was used in correlation.

² $\delta = 5.43$ from Gjaldbaek and Niemann (13) was used.

constant. Each of the four theoretical correlations will be discussed separately.

Gjaldbaek and Niemann

Since the solubility parameters (δ) of neon and helium were not available, the solubilities could only be calculated for argon.

Using $\delta = 5.43$ for argon, which was given in the article of Gjaldbaek and Niemann (13), the deviations of the calculated values from the experimental data of this work were 10.55%, 8.71%, and 1.47%. These results are considerably better than those of Loeffler and McKetta.

For helium and neon the experimental solubilities were used to back out solubility parameters. If the theoretical method is consistent with the experimental data, the solubility parameters should remain invariant from solvent to solvent. For helium the average value of the backed out δ was 3.58. The average deviation was 4.35%. For neon the values were 4.49 and 1.50%, respectively. A value of 5.53 was backed out for the solubility of argon as compared to the value of 5.43 given by Gjaldbaek and Niemann.

This correlation, although it cannot be effectively evaluated due to lack of input data, does not appear to be consistent with this work.

Prausnitz and Shair

Again the lack of solubility parameters prohibits the a priori calculation of solubility values. The solubilities which are presented in Table III were backed out from the experimental data of this work.

Using $\delta = 5.43$ for argon, the deviations of the calculated values from the experimental data of the present work were 19.9%, 25.9%, and 29.9%. These are definitely not within an acceptable range.

Using the experimental data of this work, the following gas solubility parameters were backed out:

	<u>Helium</u>	<u>Neon</u>	<u>Argon</u>
Propanol	1.55	3.675	5.05
Pentanol	1.475	3.450	4.875
Heptanol	1.470	3.425	4.875
Average	1.50	3.52	4.93

The back calculated solubility parameters for the gases agreed very well for the solvents pentanol and heptanol but not for propanol.

Loeffler and McKetta

Of the four theoretical methods used, this is the only one which had all the necessary data available.

In Table III three columns are presented, each one representing a different value for the parameter b , which Loeffler and McKetta determined empirically. For each gas they plotted a "range" for the value b , rather than a single point, in a plot of b as a function of critical temperature of the gas. They then constructed the "best curve" through the "ranges" of several gases. The plot is shown in their article (24). It should be noted that the value of the "best curve" b did not always fall in the "range." For neon and argon the entire "range" fell below the "best curve," while for helium the "best curve" intersected the minimum value of the "range," Table III presents a theoretical

solubility for each of the following values of b for a given gas:

- (1) the lowest value of b in the "range,"
- (2) the highest value of b in the "range," and
- (3) the value of b from the "best curve."

The following should be noted from the results.

- (1) Of all the results using the "best curve" b only one theoretical result, argon in heptanol, is within 10% of the experimental value. Only three values (all for argon) are within 25% of the experimental values.
- (2) For the "best curve" b the calculated theoretical values for neon and argon are all higher than the experimental values (the value of b is higher than the "range") and the theoretical values for helium are lower than the experimental values (the value of b is in the "range").
- (3) For argon in propanol and argon in pentanol, the calculated theoretical solubilities for the "low b " are too low and for the "high b " they are too high. Thus the value of b which would correspond to the experimental data is somewhere in the "range."
- (4) For all neon data the value of b which would correspond to the experimental data falls somewhere between the "best curve" b and the "range."
- (5) Only one of the values (neon in propanol--best line b) deviates by more than 50%.

In general, since the correlation only predicts solubilities within 50% of the experimental data, the correlation would not be very useful.

Lin and Chao

The values of solubilities calculated by the group contribution theory were presented in the paper of Lin and Chao. Lin and Chao used the plot of the interaction energy density as a function of polarizability of the gas to calculate e_1 for each system. They used the experimental data of Boyer and Bircher (4) and Lannung (22) and equations A-30 and A-33 to calculate $\ln H^0$ for several gases in the alcohols. They then plotted $\ln H^0$ as a function of the number of carbons in the alcohol with the gas molecule diameter as a parameter. Thus the theoretical values of Lin and Chao for argon are backed out directly from the data of Boyer and Bircher and will not be discussed.

All of the theoretical values of neon and helium agree within 20% of the experimental data of this work, while two of the values agree within 1.0%. This agreement is much better than that of Loeffler and McKetta, but is still not very good.

It should be noted that scarcity of the data on alcohols required Lin and Chao to modify the procedure for determining interaction energies for alcohols relative to that used for the paraffin.

Summary of Theoretical Calculations

Of the four theoretical correlations presented, none were very consistent with the experimental data of the author. It is difficult to draw firm conclusions concerning the correlations without enough data to properly use the correlations, that is, the lack of solubility parameters for helium and neon.

Literature data needed in order to use these correlations, such as hypothetical liquid volumes for the gases, are even in disagreement.

For example, apparent molar volumes of argon from various sources are as follows: 40.0 (7), 46.0 (22), 55.0 (34), and 57.1 (30). This inconsistency carries over to the molar volumes of helium and neon and the solubility parameter of argon.

The methods of Prausnitz and Shair and of Gjaldbaek and Niemann cannot be evaluated effectively until some firm values are established for the input data required in these correlations. The method of Loeffler and McKetta seems to be completely inadequate for predicting solubilities of inert gases in alcohols. The method of Lin and Chao also depends upon the experimental data in the literature. Thus the correlation is limited by the lack of reliable solubility data.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This study consists of an investigation of the solubility of non-polar gases in polar liquids--specifically, inert gases in alcohols. An apparatus was designed and constructed by the author specifically to minimize sources of error which are inherent in solubility work. The experimental data taken in this study were compared to the data from the literature and the results of four correlations for prediction of solubilities of polar gases in non-polar liquids.

The following conclusions were made from this study:

- (1) The design of the apparatus was sound, as illustrated by the reproducibility of the data. The apparatus was simple to use and was carefully designed to minimize all possible sources of error cited by Cook and Hanson (8). If error exists in the data, then the error is a systematic error caused by factors unknown to the author.
- (2) The solubility data for the alcohol systems from the literature are not consistent among the different sources or with this work. The data of Boyer and Bircher (4) does not appear to be consistent within itself.
- (3) The experimental solubility data for argon in water was very consistent among five investigators in the literature. The data of this work was 10.1% lower than the mean of this

literature data. However, the data of this work were taken under the most rigorous conditions; the author has no sound explanation for the disagreement.

- (4) The correlations of Prausnitz and Shair (30) and of Gjaldbaek and Niemann (13) could not be adequately evaluated due to insufficient and inconsistent data in the literature.
- (5) The correlation of Loeffler and McKetta (24) was inadequate for prediction of solubilities of inert gases in alcohols.
- (6) Presently, the correlation of Lin and Chao for alcohols is based on the data of Boyer and Bircher and other literature sources. The solubilities which were predicted by the correlation are not consistent with the data of this work.

The following recommendations are made from the results of this study for future work in this area of research:

- (1) The degassing cell should be designed to degas smaller amounts of solvent. A good way to check for adequate degassing is by freezing the solvent and checking for bubbles while thawing. A cell can easily be designed to make this possible.
- (2) The degassing cell should be designed so that it can be shaken during freezing. If the flask is rigid, the solvent supercools during freezing and crystalizes almost instantly, ruining the effect of freezing.
- (3) When solubility equipment is designed, care must be taken to ensure that the entire system can easily be tested for leaks.
- (4) Work needs to be done to develop correlations that do not rely on hypothetical data.

- (5) An investigator should build two apparatus which work on entirely different principles. Consistent data taken on these apparatus for the same systems would permit maximum confidence in results.

BIBLIOGRAPHY

1. Battino, R., and H. Lawrence Clever, Chem. Rev., **66**, 395 (1966).
2. Beers, Y., "Introduction to the Theory of Error," Addison-Wesley, Reading, Mass., 2nd. ed. (1957).
3. Ben-Naim, A., and S. Baer, Trans. Faraday Soc., **59**, 2735 (1963).
4. Boyer, F. L., and L. J. Bircher, J. Phys. Chem., **64**, 1330(1960).
5. Brasted, R. C., and C. Hirayama, J. Phys. Chem., **62**, 125(1958).
6. Chao, D. C., R. L. Robinson, Jr., M. L. Smith, and C. M. Kuo, Chemical Engineering Progress Symposium Series, **63**, 121(1967).
7. Clever, H. L., R. Battino, J. H. Saylor, and P. M. Gross, J. Phys. Chem., **61**, 1078(1957).
8. Cook M. W., and D. N. Hanson, Rev. Sci. Instr., **28**, 370(1957).
9. Dannhauser, W., and L. W. Bahe, J. Chem. Phys., **40**, 3058(1964).
10. Douglas, E., J. Phys. Chem., **68**, 169(1964).
11. Dymond, J., and J. H. Hildebrand, I&EC Fund., **6**, 130(1967).
12. Gjaldbaek, J. Chr., and J. H. Hildebrand, J. Am. Chem. Soc., **71**, 3147(1949); **22**, 609(1950).
13. Gjaldbaek, J. Chr., and H. Niemann, Acta. Chem. Scan., **12**, 1015 (1958).
14. Hall, N. A., and W. E. Ibele, Trans. Am. Soc. Mechan. Eng., **76**, 1039(1954).
15. Hildebrand, J. H., and R. L. Scott, "The Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 3rd ed., (1950).
16. Hodgeman, C. D., R. C. Weast, and S. M. Selby, "Handbook of Chemistry and Physics," Chem. Rubber Publishing Co., 37th ed., (1955).
17. Holborn, L., and J. Otto, Z. Physik., **23**, 77(1924).
18. Holland, C. J., N. L. Marable, E. R. Baker, and H. L. Clever, unpublished results (as cited in reference 1).

19. Klots, C. E., and B. B. Benson, J. Chem. Phys., 38, 89(1963).
20. Korosy, F., Trans. Faraday Soc., 33, 416(1937).
21. Kretchmer, C. B., and R. Wiebe, J. Chem. Phys., 22, 1697(1954).
22. Lannung, A., J. Am. Chem. Soc., 52, 68(1930).
23. Lin, H. M., and K. C. Chao, Unpublished Manuscript.
24. Loeffler, C. E. and J. J. McKetta, Jr., AIChE J., 12, 813(1966).
25. Miller, K. W., and J. H. Hildebrand, J. Am. Chem. Soc., 90, 3001 (1968).
26. Morrison, T. J., and N. B. Johnstone, J. Chem. Soc., 3441(1954).
27. Perry, J. H., "Chemical Engineers' Handbook," McGraw-Hill Book Co., New York, N. Y., 4th ed., (1963).
28. Peters, J. P., and D. D. Van Slyke, "Quantitative Clinical Chemistry," Vol. II, Williams and Wilkins Co., Baltimore, Md., (1932).
29. Pierotti, R. A., J. Phys. Chem., 67, 1840(1963).
30. Prausnitz, J. M., and F. H. Shair, AIChE J., 7, 682(1961).
31. Redlich, O., and A. T. Kister, J. Chem. Phys., 15, 849(1947).
32. Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., (1950).
33. Whalley, E., Y. Lupien, and W. G. Schneider, Can. J. Chem., 31, 722(1953).
34. Yen, L. C. and J. J. McKetta, Jr., AIChE J., 8, 501(1962).
35. Yntena, J. L., and Schneider, J. Chem. Phys., 18, 646(1950).

APPENDIX A

APPENDIX A

DERIVATION AND USE OF THEORETICAL CORRELATIONS

The working equations for the four theoretical correlations will be derived in this section. Due to lack of proper data, the method of use of the equations had to be altered. Thus the manner in which the equations are used in this work will also be explained in this section.

Gjaldbaek and Niemann

Gjaldbaek and Hildebrand (12) presented the following equation for the calculation of solubilities of non-polar gases in polar liquids:

$$-\log x_2 = -\log x_2^i + 0.4343 \frac{\bar{v}_2}{RT} (\delta_1 - \delta_2)^2 + \log \frac{\bar{v}_2}{v_1} + 0.4343 \left(1 - \frac{\bar{v}_2}{v_1}\right) \quad (A-1)$$

where x_2 - solubility of gas in mole fraction

x_2^i - "ideal" solubility of gas

v_2 - partial molal volume of the dissolved gas

δ_1 - solubility parameter of the solvent

δ_2 - solubility parameter of the gas

v_1 - molar volume of the solvent

R - gas constant

T - absolute temperature.

This equation was developed from regular solution theory with corrections for Flory-Huggins mixing.

Gjaldbaek and Niemann (13) used their solubility data for several gases in several alcohols and calculated values of δ_1 which would give the known solubility. This empirical value was called δ_1^* . From a plot of $(\delta_1 - \delta_1^*)$ as a function of $(\epsilon - 1)$, where ϵ is the dielectric constant of the solvent, Gjaldbaek and Niemann saw that a linear relationship existed. The above plot was made for several gases, and the slopes of the above plots were plotted as a function of the polarizability (α) of the gas. This plot resulted in a straight line with a slope of (-0.00143) and an intercept at $\alpha = 0.0$ of 0.165.

Gjaldbaek and Niemann correlated δ_1 with δ_1^* by the following equation.

$$(\delta_1 - \delta_1^*) = (\epsilon - 1)(-0.00143 (\alpha \times 10^{25}) + 0.165) \quad (\text{A-2})$$

$$\text{or} \quad \delta_1^* = \delta_1 - (\epsilon - 1)(-0.00143 (\alpha \times 10^{25}) + 0.165) \quad (\text{A-3})$$

Thus Gjaldbaek and Niemann corrected the solubility parameter of polar solvents with the dielectric constant of the solvent and the polarizability of the gas.

The solubility parameters for neon and helium were not available for this work. Thus the solubility parameter of the solvent was calculated using equation A-3. The solubility parameter of the gas was then backed out using the solubility data of this work and the following equation.

$$\delta_2 = \delta_1^* - \left[\frac{RT}{0.4343 \bar{v}_2} (-\log x_2 + \log x_2^1 - \log \frac{\bar{v}_2}{\bar{v}_1} - 0.4343 (1 - \frac{\bar{v}_2}{\bar{v}_1})) \right]^{\frac{1}{2}} \quad (\text{A-4})$$

The above equation is derived from equation A-1.

Prausnitz and Shair

Prausnitz and Shair presented a new model for the dissolution process. The model was comprised of two steps: (1) The gas is isothermally condensed to a hypothetical liquid at one atmosphere pressure and then (2) the hypothetical liquid is dissolved in the solvent.

Since the solute in the liquid solution is in equilibrium with the gas at unit fugacity, the equation of equilibrium is

$$\Delta G = \Delta G_{\text{condensation}} + \Delta G_{\text{mixing}} = 0$$

where

$$\Delta G_{\text{condensation}} = RT \ln \left(\frac{f_2^L}{f_2^0} \right)$$

$$\Delta G_{\text{mixing}} = RT \ln \gamma_2 x_2$$

Thus

$$\frac{f_2^L \gamma_2 x_2}{f_2^0} = 1.0$$

or

$$\frac{1}{x_2} = \frac{f_2^L \gamma_2}{f_2^0} \quad (A-5)$$

The fugacity of the hypothetical liquid at one atmosphere depends only on the temperature and the properties of the solute, not on any properties of the solvent. Prausnitz and Shair used this fact and the theorem of corresponding states to show that the fugacity of a hypothetical liquid is a universal function of reduced temperatures. They then constructed the plot of f_2^L/P_c as a function of the reduced temperature, which permitted calculation of f_2^L for equation A-5.

In dealing with polar solvents, the regular solution theory cannot be used to find the activity coefficient of the gas. The activity coefficient of the gas may be expected to depend on its molar volume,

its solubility parameter, the temperature, and the properties of the solvent in the following way:

$$\ln \gamma_2 = v_2^L F(\delta_2, T, \text{properties of solvents})$$

where γ_2 - activity coefficient of the gas

v_2^L - molar volume of the solvent

δ_2 - solubility parameter of the gas

T - absolute temperature

Since v_2^L and δ_2 depend only on the solute, the above equation should apply to polar solvents. Prausnitz and Shair plotted $(\log \gamma_2)/v_2^L$ as a function of δ_2 with each alcohol as a parameter and found a consistent correlation. Prausnitz and Shair then used the two generalized plots and equation A-5 to find the solubility of gases in polar solvents.

The lack of solubility parameters for neon and helium prohibited the use of equation A-5 as Prausnitz and Shair prescribed. Thus these solubility parameters were backed out in the following way:

- (1) Since the plot of δ_2 vs. $(\log \gamma_2)/v_2^L$ given by Prausnitz and Shair contained only parameters for methanol, butanol, and octanol, a plot of number of carbons in the alcohol vs. $(\log \gamma_2)/v_2^L$ with δ_2 as parameters was made from the first plot. Smooth curves were drawn. From this plot the parameters for propanol, heptanol, and pentanol were drawn on the original plot of δ_2 vs. $(\log \gamma_2)/v_2^L$.
- (2) Values of f_2^L/P_c were read from the appropriate graph, and f_2^L was calculated.
- (3) Values of the Henry's Law Constant from the experimental data of this work were used to calculate x_2 .
- (4) Equation A-5 was used to calculate γ_2 .

- (5) The value of $(\log \gamma_2)/v_2^L$ was calculated.
- (6) A value of δ_2 was read from the appropriate plot for each gas in each alcohol.
- (7) The three values of δ_2 for each gas were averaged and the average was recorded.
- (8) The value of δ_2 of step 7 was used to calculate a new $(\log \gamma_2)/v_2^L$.
- (9) A value of the x_2 was then calculated with the value of f_2^L from step 2.

Loeffler and McKetta

Before showing the derivation of the equations used by Loeffler and McKetta (24) to calculate the solubility of gases in alcohols, the difference between one true mole of solution and one stoichiometric mole of solution should be explained. The author feels that this difference can best be explained in the following way. One true mole of a trimer of methanol would contain 6.03×10^{23} molecules of $(\text{CH}_3\text{OH})_3$ and would be three stoichiometric moles of the methanol. One true mole of "six-mer" would contain six stoichiometric moles of methanol.

The following definitions should be noted:

$$n_a = \sum n_i \qquad N^* = \sum i x_i \qquad N = \sum x_i = n_a/n_T$$

where n_i - number of moles of species i

n_T - total number of moles

x_i - mole fraction of species i

\sum - refers to only the alcohol molecules and does not include the gas.

The Helmholtz free energy for one stoichiometric mole of solution at constant volume is defined by Flory-Huggins theory to be

$$A_v = x_o A_o^o + x_o RT \ln \phi_o + \sum_{i=1}^{\infty} x_i (A_i^o + RT \ln \phi_i) + b v_x \phi_o \phi_a \quad (A-6)$$

where $b v_x \phi_o \phi_a$ includes both an entropy component and an energy of mixing.

The partial molal free energy for the gas is

$$\frac{\partial A_v}{\partial n_o} = \bar{A}_o \quad (A-7)$$

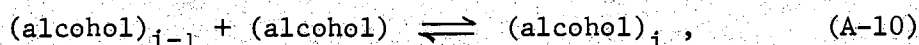
From equation A-6, the partial molal free energy of the gas is

$$\bar{A}_o = A_o^o + RT(\ln \phi_o + 1 - \frac{v_o}{v_T}) + b v_o \phi_a^2 \quad (A-8)$$

The volume of one true mole of solution is

$$\frac{1}{v_T} = \frac{\phi_o}{v_o} + \sum_{i=1}^{\infty} \frac{\phi_i}{v_i} \quad (A-9)$$

For equilibrium in the reaction,



the following must be true:

$$\bar{A}_i - \bar{A}_{i-1} = \bar{A}_1 \quad (A-11)$$

The volume of the solution is assumed not to change during the reaction of equation A-10, or $v_i = i v_1$. Thus when equations A-8 and A-11 are combined, the result is

$$RT \ln \frac{\phi_i}{\phi_{i-1} \phi_1} - RT + A_i^o - A_{i-1}^o - A_1^o = 0 \quad (A-12)$$

An additional entropy change of $R \ln (v_i / v_{i-1} v_1)$ must be added due to the differences in molal volumes of the polymers.

Since

$$\Delta A = \Delta E - TS$$

$$RT \ln \frac{\phi_i}{\phi_{i-1}\phi_1} - RT = -\Delta A + T (R \ln \frac{v_i}{v_{i-1}v_1})$$

$$RT \ln \frac{c_i}{c_{i-1}c_1} = -\Delta A + RT$$

or
$$-\Delta A + RT = RT \ln K'$$

where
$$K' = \frac{c_i}{c_{i-1}c_1} \quad . \quad (A-13)$$

From the above equation

$$\frac{c_i}{c_{i-1}} = K'c$$

or
$$\left(\frac{c_2}{c_1}\right)\left(\frac{c_3}{c_2}\right) \dots \left(\frac{c_i}{c_{i-1}}\right) = (K'c_1)^{i-1} = \frac{c_i}{c_1}$$

$$c_i = \frac{(K'c_1)^i}{K'} \quad . \quad (A-14)$$

Since
$$c_i = \left(\frac{\phi_i}{v_1}\right) = \left(\frac{v_i}{v_T}\right)\left(\frac{n_i}{v_1}\right) = \left(\frac{n_i}{v_T}\right) ,$$

the number of moles of each polymer can be expressed as

$$n_i = v_T c_i \quad . \quad (A-15)$$

From equations A-14 and A-15, the following can be written.

$$N^* = \sum i x_i = \frac{1}{n_T} \sum i n_i = \frac{v_T}{n_T K'} \sum_{i=1}^{\infty} i (K'c_1)^i \quad . \quad (A-16)$$

Using the approximation

$$\sum i (x)^i = \frac{x}{(1-x)^2}$$

one gets

$$N^* = \frac{v_T}{n_T K'} \frac{K'c_1}{(1-K'c_1)^2} \quad . \quad (A-17)$$

If $K = K'/v_1$, the result is

$$N^* = \frac{V_T}{n_T v_1} \frac{\phi_1}{(1-K\phi_1)^2} \quad (\text{A-17})$$

The molal volume of the alcohol can be defined in the following way:

$$\begin{aligned} v_a &= \frac{\sum x_i v_i}{\sum x_i} = \frac{\sum x_i (i v_1)}{\sum x_i} \\ v_a &= v_1 \frac{\sum i x_i}{\sum x_i} = v_1 \frac{N^*}{N} \\ N^* &= \frac{v_a}{v_1} N \end{aligned} \quad (\text{A-18})$$

Since $v_a = \frac{V_a}{n_a}$, $N = \frac{n_a}{n_T}$, $\phi_a = \frac{V_a}{V_T}$.

Equation A-18 can be written

$$N^* = \frac{V_T}{v_1 n_T} \phi_a \quad (\text{A-19})$$

From equations A-17 and A-19, one gets

$$\phi_a = \frac{\phi_1}{(1-K\phi_1)^2} \quad (\text{A-20})$$

Finally ϕ_1 can be expressed in the following way.

$$\phi_1 = \frac{(2K\phi_a + 1 - (4K\phi_a + 1)^{1/2})}{2K^2\phi_a} \quad (\text{A-21})$$

Since equation A-9 is not in a usable form, a usable expression for the true volume must be found. Since

$$\sum \frac{\phi_i}{v_i} = \sum c_i = \sum \frac{(K'c_1)^i}{K'} = \frac{c_1}{1-K'c_1}, \quad (\text{A-22})$$

the following can be written from equations A-20 and A-22

$$\sum c_i = \frac{c_1}{(1-K'c_1)} \left(\frac{\phi_a}{\phi_1} \right) (1-K\phi_1)^2$$

or

$$\sum c_i = \frac{\phi_a}{v_1} (1 - K\phi_1)$$

Thus

$$\frac{1}{v_T} = \frac{\phi_o}{v_o} + \frac{\phi_a}{v_1} (1 - K\phi_1) \quad (\text{A-23})$$

Equation A-8 is derived on the assumption that there is no volume change on mixing. However, for the dissolution of gases in alcohols there is a very large change in volume for the gas. For the partial pressure of the gas equal to one atmosphere,

$$a_o = f^{oL} \quad (\text{A-24})$$

where a_o - activity of the gas

f^{oL} - fugacity of hypothetical liquid at one atmosphere

Since

$$\Delta G = RT \ln a_o, \quad (\text{A-25})$$

equations A-8, A-24, and A-25 can be combined to give

$$-\log \phi_o = +\log f^{oL} + \frac{1}{2.3} \left(1 - \frac{v_o}{v_T}\right) + \frac{bv_o\phi_a}{2.3 RT}. \quad (\text{A-26})$$

Equations A-21, A-23, and A-26 are the basic equations of the Loeffler and McKetta correlation.

The following procedure was used in applying the equations of Loeffler and McKetta.

- (1) Knowing v_o , v_a , K , b , R , T , f^{oL} , assume a value for x_o .
- (2) Calculate ϕ_a and ϕ_o , where $\phi_a = \frac{x_a v_a}{x_o v_o + x_a v_a}$, $\phi_o = 1 - \phi_a$.
- (3) Calculate ϕ_1 , using equation A-21.
- (4) Calculate v_T , using equation A-23.
- (5) Calculate a new ϕ_o , using equation A-26.
- (6) Calculate a new x_o , and compare with the x_o which was assumed in step 1.
- (7) If they differ, return to step 1 using the new x_o .

Lin and Chao

The correlation of Lin and Chao (23) for calculating solubilities of inert gases in alcohols is based on the "group contribution theory" of solutions developed by Chao, Robinson, Smith and Kuo (6). In this theory the functional groups (for alcohols they are CH_3- , CH_2- , and $\text{HO}-$) are considered to be basic identifiable structural units of molecules. If the manner of interaction of each of these groups is known, the interactions of mixtures of molecules of diverse species may be predicted or described.

Lin and Chao show that

$$kT \ln H = -\chi + kT \ln \frac{RT}{v} \quad (\text{A-27})$$

where H - Henry's Law Constant

k - Boltzman Constant

T - absolute temperature

χ - energy of a dissolved molecule of gas

v - molar volume of the solvent.

The value χ in equation A-27 represents the energy of a dissolved solute molecule relative to that of the same molecule while in the gas phase. The energy χ is considered the sum of two parts:

- (1) e_c , the energy required to create a cavity in the solvent the size of the solute molecule. This energy is equivalent to that required to put a hard sphere which has the same volume as the cavity into the solvent.
- (2) e_i , the energy of interaction between the solute molecule and the solvent molecules which are close enough to influence it.

Lin and Chao assumed the entropy effect associated with the energy of interaction of the molecules to be negligible. Thus equation A-27 can be rewritten as

$$kT \ln H = e_c + e_i + kT \ln \frac{RT}{v} \quad (\text{A-28})$$

For a hard sphere molecule, the interaction energy of the solute molecules and solvent molecules can be neglected, giving

$$kT \ln H^0 = e_c + kT \ln \frac{RT}{v} \quad (\text{A-29})$$

Thus the two Henry's Law Constants can be related through equations A-28 and A-29 giving

$$kT \ln H = kT \ln H^0 + e_i \quad (\text{A-30})$$

The hard sphere Henry's Law Constant, H^0 , is dependent only on the properties of the solvent, and thus depends only on the cavity size to be generated and the temperature. Pierotti (29) plotted σ , the diameter of the gas molecule, as a function of α , the polarizability of the gas, for the inert gases and extrapolated to $\alpha = 0$ to get σ for the hard sphere. Pierotti then plotted $\ln H$ as a function of α and extrapolated to $\alpha = 0$ to get $\ln H^0$.

The energy required to create a cavity of a given size, e_c , can be calculated as the product of the energy density (ρ_E) and the cavity volume $\left(\frac{4}{3} \pi (\sigma/2)^3\right)$, or

$$e_c = \frac{1}{6} \pi \sigma^3 \rho_E \quad (\text{A-31})$$

Thus a plot of ρ_E as a function of σ must be made for each alcohol. The energy density of a hard sphere molecule ($\sigma=2.58\text{\AA}$) was calculated

using equations A-29 and A-31.

$$\rho_E = \frac{6kT}{\pi(2.58)^3} \ln \frac{H^0}{RT} \quad (A-32)$$

The energy density for infinite dilution was determined as the quotient of the energy of vaporization (ΔE) at 25°C and the molal volume of the solvent. The energy density was then assumed to be linear with respect to $1/\sigma$. Thus knowing ρ_E at both $\sigma = 2.58$ and $\sigma = \infty$ for each alcohol, the appropriate plot was made.

The energy of solute-solvent interaction, e_1 , can be expressed in the following manner:

$$e_1 = \sum_u S \lambda_u \frac{A_u}{\sum_w A_w} \quad (A-33)$$

where λ_u - surface energy density of u-group and gas interaction

S - total surface area of the gas molecule

A_u - surface area of type u

$\frac{A_u}{\sum_w A_w}$ - fraction of the total surface of the solvent molecules taken up by u-groups

$S \lambda_u$ - energy of interaction.

Lin and Chao used the above correlation and experimental data for the paraffins from the literature to find λ_u for the CH_3 group and the CH_2 group for each gas. The following is the procedure that they used:

- (1) They plotted $\log H$ (experimental data) as a function of polarizability for a given solvent. The intersection at $\alpha = 0$ gives $\log H^0$ for a given solvent.
- (2) They calculated ρ_E at $\sigma = 2.58$ for each solvent using equation A-34.
- (3) Using $\Delta E/v$, they calculated ρ_E at $\sigma = \infty$ for each solvent.

- (4) They plotted ρ_E vs. $1/\sigma$ for each solvent.
- (5) They calculated H^0 for the real gas in a given solvent using equation A-29.
- (6) They used equation A-30 to calculate e_i for a given gas in a given alcohol.
- (7) They calculated $\Sigma \lambda A$ from equation A-33, where λ_{CH_2} and λ_{CH_3} are unknown, A_{CH_2} and A_{CH_3} are known. If data for four gases in the paraffins were available, the best solution of the four equations and two unknowns was found.

Lin and Chao then plotted λ vs. $\ln (\alpha+1)$ for each group in each gas. They found the data to be very nearly linear and established the best straight line through the points.

Since very little data were available for the gases in alcohols, Lin and Chao could not solve directly for λ_{OH} . They assumed the following:

- (1) λ is linear with respect to $\ln (\alpha+1)$ and $\lambda = 0$ at $\alpha = 0$, or

$$\lambda = K_1 \ln (\alpha+1) \quad (A-35)$$

and (2) ρ_E is inversely proportional to σ , or

$$\rho_E = K_2 + \frac{K_3}{\sigma} \quad (A-36)$$

Lin and Chao then used all the data available for methanol and solved for K_1 , K_2 , and K_3 using the least squares method. From the solution they plotted λ vs. $\ln (\alpha+1)$. Knowing λ_{OH} , λ_{CH_2} , and λ_{CH_3} for any gas, Lin and Chao used all the experimental data available for alcohols and equation A-30 to calculate $\ln H^0$. They plotted $\ln H^0$ as a function of the number of carbons in the alcohol with σ as a parameter.

APPENDIX B

APPENDIX B

DERIVATION AND USE OF EQUATIONS FOR EXPERIMENTAL CALCULATIONS

Experimental calculations included (1) the calibration of the volume of the tubing in the gas reservoir and (2) the calculation of the solubilities from the PVT data taken with the apparatus.

Calibration of Tubing

The experimental procedure used to calibrate the gas line volume is described in Chapter III. The equations used in the calculations were derived in the following way:

Air was expanded from an unknown volume V_1 (Bulb B and tubing of gas reservoir) into a known volume V_a (Bulb A). Thus

$$\frac{V_1}{V_f} = \frac{V_1}{V_1 + V_a} \quad (B-1)$$

where V_f = total volume after expansion. Let

$$v = \frac{V}{n} \quad (B-2)$$

Since the system is closed, n = constant, or

$$\frac{V_1}{V_1 + V_a} = \frac{v_1}{v_f} = K \quad (B-3)$$

From equation B-3 one can get

$$V_1 = \left(\frac{K}{1-K} \right) V_a \quad (B-4)$$

Using the virial equation of state and dropping terms higher than the second virial coefficient, one can write

$$\frac{Pv}{RT} = 1 + \frac{B}{v} \quad (\text{B-5})$$

or
$$\frac{Pv^2}{RT} - v - B = 0 \quad (\text{B-6})$$

Solving for v , one gets

$$v = \frac{+1 \pm \sqrt{1 + \frac{4PB}{RT}}}{\left(-\frac{2P}{RT}\right)} \quad (\text{B-7})$$

Substituting equation B-7 into equation B-3, K can be calculated in the following way:

$$K = \frac{v_1}{v_f} = \frac{1 \pm \sqrt{1 + \frac{4BP_1}{RT_1}} (P_f) (T_1)}{1 \pm \sqrt{1 + \frac{4BP_f}{RT_f}} (P_1) (T_f)} \quad (\text{B-8})$$

Thus V_1 can be calculated from equation B-4 and B-8, where T_1 and P_1 are the initial temperature and pressure and T_f and P_f are the final temperature and pressure.

Since each of the gas bulbs had been calibrated gravimetrically, the volume of the gas line alone could be calculated with each of the three gas bulbs. These values did not turn out exactly the same for each gas bulb, so the best values for V_ℓ (volume of gas line) and V_a were found using a least squares method. The following equations were used. From equation B-4, V_r will be defined in the following way:

$$V_r = \frac{V_1}{V_a} = \frac{K}{K-1} \quad (\text{B-9})$$

Since $V_1 = V_\ell + V_B$, one can write

$$V_B = (V_r \times V_a) - V_\ell \quad (\text{B-10})$$

Three runs were made for each of the three bulbs, nine in all. The least squares fit gave the best value to be the following: $V_\ell = 17.74$ cc and $V_a = 180.51$ cc. This value of V_a corresponds within 0.1% of the value found gravimetrically (180.35 cc). For the nine values of V_ℓ which were calculated, the maximum deviation from the mean was 0.22%. This 0.22% deviation in the line volume would be less than 0.1% of the volume of the gas reservoir.

Calculation of Solubility

The experimental procedure used to take the solubility data is described in Chapter III. The equations used in the calculations were derived in the following way:

Using the virial equation of state and considering no terms higher than the second virial coefficient, one has

$$\frac{PV}{nRT} = 1 + \frac{Bn}{V}$$

or
$$\frac{B}{V} n^2 + n - \frac{PV}{RT} = 0$$

Using the quadratic formula, the number of moles can be expressed as

$$n = \frac{-1 \pm \sqrt{1 + \frac{4BP}{RT}}}{2\left(\frac{B}{V}\right)} \quad (B-11)$$

Thus knowing the pressure, temperature, and volume of the gas before and after a run, and the second virial coefficient of the gas, the number of moles of gas absorbed can be calculated.

From the number of moles of gas absorbed the volume of gas at one atmosphere and 25.0°C was calculated using the ideal gas law. From this the Ostwald coefficient is

$$\ell = \frac{760}{P_f} \frac{V_{\text{gas}}}{V_{\text{solvent}}} \left(\frac{P_f}{25^\circ\text{C}} \right) \quad (\text{B-12})$$

The Bunsen coefficient can be expressed as

$$\alpha = \ell \left(\frac{276.16}{T_f} \right) \quad (\text{B-13})$$

The Henry's Law Constant can be calculated using

$$H = \frac{P_f}{760 x_g} \quad (\text{B-14})$$

where x_g - mole fraction of gas in liquid.

The computer program used to calculate the solubility coefficients from the experimental results of this work is given in Appendix C.

APPENDIX C

Computer Program for Calculation of Solubility From Experimental Data

CALCULATION OF EXPERIMENTAL SOLUBILITIES

THIS PROGRAM CALCULATES BUNSEN COEFFICIENT, OSTWALD COEFFICIENT,
AND THE HENRY'S LAW CONSTANT FROM RAW EXPERIMENTAL DATA.

WTSV = MOLECULAR WEIGHT OF SOLVENT (GM/MOLE)
RHOSV = DENSITY OF SOLVENT AT 25 C (GM/CC)
A,B,C = COEFFICIENTS TO CONVERT TRANSDUCER OUTPUT TO PRESSURE
R = GAS CONSTANT (CC*ATM/MOLE*DEG)
EMF1 = INITIAL TRANSDUCER OUTPUT (MV)
EMF2 = FINAL TRANSDUCER OUTPUT (MV)
TF1 = INITIAL TEMPERATURE (F)
TF2 = FINAL TEMPERATURE (F)
BT = SECOND VIRIAL COEFFICIENT OF GAS (CC/MOLE)
VGS1 = INITIAL VOLUME OF GAS RESERVOIR (CC)
VGS2 = FINAL VOLUME OF GAS RESERVOIR (CC)
VSV = VOLUME OF SOLVENT WHICH ABSORBS GAS (CC)
P1 = INITIAL GAS PRESSURE (MM HG)
P2 = FINAL GAS PRESSURE (MM HG)
GMOL1 = INITIAL NUMBER OF MOLES OF GAS
GMOL2 = FINAL NUMBER OF MOLES OF GAS
ABMOL = MOLES OF GAS ABSORBED
VGSABS = VOLUME OF GAS ABSORBED AT STANDARD CONDITIONS (CC)
OSTWD = OSTWALD COEFFICIENT
BUNSEN = BUNSEN COEFFICIENT
XSV = NUMBER OF MOLES OF SOLVENT IN SOLVENT BULB
H = HENRY'S LAW CONSTANT

READ 11, N
11 FORMAT (I3)
READ 30, WTSV, RHOSV
30 FORMAT (2F12.7)
DO 110, I=1,N
READ 10, A,B,C,R
10 FORMAT (3F10.5, F10.2)
READ 20, EMF1, EMF2, TF1, TF2, K, J
20 FORMAT (4F10.5, 2I5)
READ 40, BT, VGS1, VGS2, VSV
40 FORMAT (4F12.6)
P1 = A + B*EMF1 + C*EMF1**2.0
P2 = A + B*EMF2 + C*EMF2**2.0
TK1 = ((TF1 - 32.0) * (5.0/9.0)) + 273.16
TK2 = ((TF2 - 32.0) * (5.0/9.0)) + 273.16
DP = P1 - P2
DEMF = EMF1 - EMF2
ROCF1 = (1.0 + (4.0*BT*P1)/(R*TK1))**0.5
ROCF2 = (1.0 + (4.0*BT*P2)/(R*TK2))**0.5
GMOL1 = (-1.0 + ROCF1) * VGS1 / (2.0*BT)
GMOL2 = (-1.0 + ROCF2) * VGS2 / (2.0*BT)
ABMOL = GMOL1 - GMOL2
VGSABS = ABMOL * 52.06 * 298.16
OSTWD = VGSABS * 760.0 / (P2*VSV)
BUNSEN = OSTWD * 273.16 / TK2

XGS = ABMOL
XSV = VSV * RHOSV / WTSV
TOTML = XGS + XSV
H = TOTML * P2 / (760.0*XGS)
39 IF (J-13) 41,51,41
41 IF (J-15) 42,52,42
42 IF (J-17) 43,53,43
43 IF (J-23) 44,54,44
44 IF (J-25) 45,55,45
45 IF (J-27) 46,56,46
46 IF (J-33) 47,57,47
47 IF (J-35) 48,58,48
48 IF (J-37) 49,59,49
49 CONTINUE
51 PUNCH 61, K
61 FORMAT (5X, 9HRUN NO. = ,I3,10X,17HHELIUM - PROPANOL //)
GO TO 70
52 PUNCH 62, K
62 FORMAT (5X, 9HRUN NO. = ,I3,10X,17HHELIUM - PENTANOL //)
GO TO 70
53 PUNCH 63, K
63 FORMAT (5X, 9HRUN NO. = ,I3,10X,17HHELIUM - HEPTANOL //)
GO TO 70
54 PUNCH 64, K
64 FORMAT (5X, 9HRUN NO. = ,I3,10X,15HNEON - PROPANOL //)
GO TO 70
55 PUNCH 65, K
65 FORMAT (5X, 9HRUN NO. = ,I3,10X,15HNEON - PENTANOL //)
GO TO 70
56 PUNCH 66, K
66 FORMAT (5X, 9HRUN NO. = ,I3,10X,15HNEON - HEPTANOL //)
GO TO 70
57 PUNCH 67, K
67 FORMAT (5X, 9HRUN NO. = ,I3,10X,16HARGON - PROPANOL //)
GO TO 70
58 PUNCH 68, K
68 FORMAT (5X, 9HRUN NO. = ,I3,10X,16HARGON - PENTANOL //)
GO TO 70
59 PUNCH 69, K
69 FORMAT (5X, 9HRUN NO. = ,I3,10X,16HARGON - HEPTANOL //)
GO TO 70
70 TYPE 75, P1, P2, DP, EMF1, EMF2, DEMF
75 FORMAT (3X, 4HP1 = ,F12.5, 5X, 4HP2 = ,F12.5, 5X, 4HDP = ,F12.5, /3X,
16HEMF1 = ,F10.5, 5X, 6HEMF2 = ,F10.5, 5X, 6HDEMF = ,F10.5)
TYPE 120, VGS1, VGS2, VSV
120 FORMAT (3X, 6HVGS1 = ,F10.5, 5X, 6HVGS2 = ,F10.5, 5X, 6HVSV = ,F10.5)
TYPE 130, XGS, XSV, H
130 FORMAT (3X, 5HXGS = ,F11.7, 5X, 5HXSV = ,F11.7, 5X, 3XH = ,F10.2)
TYPE 80, ABMOL, VGSABS
80 FORMAT (5X, 7HABMOL = ,F12.6, 5X, 8HVGSABS = ,F12.6 /)
89 TYPE 90, OSTWD, BUNSEN
90 FORMAT (5X, 16HOSTWALD = ,F10.6, 7X, 10HBUNSEN = ,F10.6 / //)
110 CONTINUE
END

APPENDIX D

APPENDIX D

ERROR ANALYSIS

Error analysis was used to establish limits of accuracy for the calculation of solubilities and to point out major sources of error present in the experiment. Beers (2) presents a detailed discussion of error analysis. His method for calculation of errors was used in this work.

The author assumed that the experimental measurement errors were independent and uncorrelated, i.e., the accuracy with which the pressure could be measured was independent of the temperature, etc. Beers describes the effects of independent and uncorrelated errors on the dependent variable with the following equation

$$\epsilon_y^2 = \sum_{i=1}^n \left(\frac{\partial y}{\partial x_i} \epsilon_{x_i} \right)^2 \quad (D-1)$$

where the equation relating dependent and independent variables is given by

$$y = y(x_1, x_2, \dots, x_n) \quad (D-2)$$

For this work, error analysis was used in the following two cases:

- (1) For the analysis of the error in measuring the number of moles absorbed.
- (2) For designing the gas bulbs to minimize the error when calculating the unknown line volume by expansion.

The ideal gas law was used in the calculation of the moles absorbed (for error analysis purposes only). For the isochoric equipment employed,

$$\Delta n = \frac{V}{RT} \Delta P. \quad (D-3)$$

Since errors arise in the calculation of V, T, and P, the equation of Beers gives

$$\epsilon_{\Delta n}^2 = \left(\frac{\partial \Delta n}{\partial T}\right)^2 \epsilon_T^2 + \left(\frac{\partial \Delta n}{\partial V}\right)^2 \epsilon_V^2 + \left(\frac{\partial \Delta n}{\partial \Delta P}\right)^2 \epsilon_{\Delta P}^2$$

or

$$\epsilon_{\Delta n}^2 = \frac{V^2 \Delta P^2}{R^2 T^4} \epsilon_T^2 + \frac{\Delta P^2}{R^2 T^2} \epsilon_V^2 + \frac{V^2}{R^2 T^2} \epsilon_{\Delta P}^2. \quad (D-4)$$

But the volume V was measured by expanding air from a known volume into an unknown volume. Thus

$$V_1 = \frac{P_2}{P_1 - P_2} V_A$$

where P_1 = initial pressure

P_2 = final pressure

V_A = known volume

V_1 = unknown volume.

Thus the error in measuring V_1 is dependent upon errors in measuring P_1 , P_2 , and V_A , or

$$\epsilon_{V_1}^2 = \left(\frac{\partial V_1}{\partial V_A}\right)^2 \epsilon_{V_A}^2 + \left(\frac{\partial V_1}{\partial P_1}\right)^2 \epsilon_{P_1}^2 + \left(\frac{\partial V_1}{\partial P_2}\right)^2 \epsilon_{P_2}^2$$

or

$$\epsilon_{V_1}^2 = \frac{P_2^2}{(P_1 - P_2)^2} \epsilon_{V_A}^2 + \frac{(P_2^2 + P_1^2) V_A^2}{(P_1 - P_2)^4} \epsilon_P^2 \quad (D-5)$$

For simplification, let $P_1 - P_2 = \Delta P_x$. Thus ΔP_x is the pressure change during expansion of air and ΔP is the pressure change during absorption of inert gas in alcohol. Substituting equation D-5 into equation D-4, the result is

$$\epsilon_{\Delta n}^2 = \frac{V^2 \Delta P^2}{R^2 T^4} \epsilon_T^2 + \frac{\Delta P^2 P_2^2}{\Delta P_x^2 R^2 T^2} \epsilon_{V_A}^2 + \frac{\Delta P^2 (P_2^2 + P_1^2) V_A^2}{R^2 T^2 (\Delta P_x)^4} \epsilon_P^2 + \frac{V^2}{R^2 T^2} \epsilon_{\Delta P}^2 \quad (D-6)$$

Since $\Delta P = P_3 - P_4$ and $\epsilon_{P_3} = \epsilon_{P_4}$

$$\begin{aligned} \epsilon_{\Delta P}^2 &= \left(\frac{\partial \Delta P}{\partial P_3} \right)^2 \epsilon_{P_3}^2 + \left(\frac{\partial \Delta P}{\partial P_4} \right)^2 \epsilon_{P_4}^2 \\ \epsilon_{\Delta P}^2 &= 1^2 \epsilon_{P_3}^2 + (-1)^2 \epsilon_{P_4}^2 = 2 \epsilon_P^2 \end{aligned} \quad (D-7)$$

Since the percent error in Δn is the quantity of interest, rearrangement gives

$$\frac{\epsilon_{\Delta n}^2}{\Delta n^2} = \frac{R^2 T^2}{V_1^2 \Delta P^2} \epsilon_{\Delta n}^2 \quad (D-8)$$

Substituting equations D-6 and D-7 into D-8 the percent error in the change in moles can be expressed as

$$\frac{\epsilon_{\Delta n}^2}{\Delta n^2} = \frac{\epsilon_T^2}{T^2} + \frac{P_2^2}{\Delta P_x^2 V_1^2} \epsilon_{V_A}^2 + \left[\frac{(P_2^2 + P_1^2) V_A^2}{\Delta P_x^4 V_1^2} + \frac{2}{\Delta P^2} \right] \epsilon_P^2 \quad (D-9)$$

As can be seen from equation D-9, minimizing ϵ_V will decrease the error in the measurement of Δn . Since

$$\frac{\epsilon_{V_1}^2}{V_1^2} = \frac{\epsilon_{V_A}^2}{V_A^2} + \frac{(P_1^2 + P_2^2)}{P_2^2 \Delta P_x^2} \epsilon_P^2 \quad (D-10)$$

and since P_1 and V_A are constant, the error can be minimized by taking the partial of equation D-10 with respect to P_2 . Thus

$$\frac{\partial \left(\frac{\epsilon_{V_1}^2}{V_1^2} \right)}{\partial P_2} = 0$$

Equation will reduce to $P_2^3 + 2P_1^2 P_2 - P_1^3 = 0$.

The real solution of this is $P_2 = 0.453 P_1$. (D-11)

Thus the gas bulbs and Bulb A were designed so that during the calibration of the unknown gas line volume, $P_2 \approx 0.45 P_1$.

Thus the error in the measurement of P, V, and T must be evaluated.

(1) Temperature--the temperature of the bath was measured with two different thermometers. During the first runs a Fahrenheit thermometer with divisions of 0.05° was used. The thermometer did not vary over 0.025°F during the runs. The second thermometer was a Centigrade thermometer with divisions of 0.01° . It did not vary over 0.02°C . Thus ϵ_p was equal to 0.02°K . (2) Pressure--In calibrating the transducer, the emf readings from the transducer were curve fit against the true pressure (from the Texas Instrument gage). The standard deviation of the true pressures from the curve was 0.2 mm Hg. Thus ϵ_p was equal to $0.2 \text{ mm Hg} = 2.365 \times 10^{-4} \text{ atm}$. (3) The standard deviation in the calibration of Bulb A was $\epsilon_{V_A} = 0.057 \text{ cc}$.

For a normal run with argon the expected percent error was calculated to be 0.550. The last term of equation D-9 ($\frac{2}{\Delta P^2} \epsilon_p^2$) is the dominating term. In fact, the other terms can be neglected in the calculation of the expected percent error.

A similar error analysis for a constant pressure, variable volume apparatus was made. The expected error was less, but due to difficulties in design the constant volume apparatus was used.

APPENDIX E

APPENDIX E

SAMPLE CALCULATIONS

Examples of all calculations made in this work are shown in this section. Since the solubilities which Lin and Chao calculated were presented, sample calculations of the correlation will not be given. The three theoretical methods, the calculation of the solubilities from the experimental data of this work, and the error analysis will be discussed.

Gjaldbaek and Niemann

The equation which Gjaldbaek and Neimann use to calculate solubility of gases in alcohols is

$$\begin{aligned}
 -\log x_2 &= -\log x_2^i + 0.4343 \frac{\bar{v}_2}{RT} (\delta_1^* - \delta_2)^2 + \log \frac{\bar{v}_2}{v_1} + -0.4343 \left(1 - \frac{\bar{v}_2}{v_1}\right) \\
 \text{or} \\
 -\ln x_2 &= -\ln x_2^i + \frac{\bar{v}_2}{RT} (\delta_1^* - \delta_2)^2 + \ln \frac{\bar{v}_2}{v_1} + \left(1 - \frac{\bar{v}_2}{v_1}\right) \quad (E-1)
 \end{aligned}$$

The data used in the calculation of the solubility of argon in propanol with the correlation of Gjaldbaek and Niemann were the following.

$$\begin{array}{lll}
 R = 1.987 \frac{\text{cal}}{^\circ\text{K gmol}} & \alpha = 1.63 \times 10^{24} \frac{\text{cc}}{\text{molecule}} & \epsilon = 20.1 \\
 T = 298.16 \text{ } ^\circ\text{K} & \delta_1 = 11.95 \left(\frac{\text{cal}}{\text{cc}}\right)^{1/2} & v_1 = 75.108 \frac{\text{cc}}{\text{gmol}} \\
 x = 0.00172 & \text{M.W.} = 60.064 \frac{\text{gm}}{\text{gmol}} & \delta_2 = 5.43 \left(\frac{\text{cal}}{\text{cc}}\right)^{1/2} \\
 \bar{v}_2 = 55.0 \frac{\text{cc}}{\text{gmol}} & \rho = 0.7997 \frac{\text{gm}}{\text{cc}} &
 \end{array}$$

First δ_1 is corrected to δ_1^* using

$$\delta_1^* = \delta_1 - (\epsilon - 1) (0.165 - 0.00143 (\alpha \times 10^{25}))$$

$$\delta_1^* = 11.95 - (20.1 - 1.0) (0.165 - 0.00143 (1.63))$$

$$\delta_1^* = 8.84$$

Thus x_2 is calculated using equation E-1,

$$-\ln x_2 = -\ln 0.00172 + \frac{(55.0)(8.84-5.43)^2}{(1.987)(298.16)} + \ln \frac{55.0}{75.108} + (1 - \frac{55.0}{75.108})$$

$$-\ln x_2 = -7.40$$

$$x_2 = 0.000609$$

$$x_1 = 1.0 - x_2 = 0.9994$$

The volume of gas absorbed per mole of solution at the temperature of the measurement and one atmosphere pressure (assuming ideal gas law holds) is

$$V_o = \frac{X_o RT}{P} = \frac{(0.000609)(298.16)(82.06)}{1.0}$$

$$V_o = 14.91 \text{ cc}$$

The volume of solvent per each mole of solution is

$$V_a = X_1 \rho (\text{M.W.}) = (0.9994)(0.7997)(60.064)$$

$$V_a = 75.06 \text{ cc}$$

Thus the Ostwald coefficient is

$$\ell = \frac{V_o}{V_a} = \frac{14.91}{75.06} = 0.1986$$

The Bunsen coefficient is

$$\alpha = \ell \left(\frac{273.16}{298.16} \right) = 0.1820$$

The Henry's Law Constant is

$$H = \frac{1}{X_o} = \frac{1}{0.000609} = 1641$$

Prausnitz and Shair

The calculations for the Prausnitz and Shair correlation are presented for argon in propanol using the value of 5.43 for the solubility parameter of argon.

At 298.16°K the reduced temperature of argon is 1.975. From Figure 2 of the article of Yen and McKetta (34), the value of f^{OL}/P_c is 4.9. From Figure 5 of the article of Prausnitz and Shair (30) the value of $(\log \gamma_2)/v_2$ for $\delta = 5.43$ is found to be 0.012 gmol/cc.

The other constants used in the calculations are given below:

$$\begin{array}{ll} P_c &= 48.0 \text{ atm} & \text{M.W.} &= 60.064 \frac{\text{gm}}{\text{gmol}} \\ v_2 &= 55.0 \frac{\text{cc}}{\text{gmol}} & \rho &= 0.7997 \frac{\text{gm}}{\text{cc}} \end{array}$$

The fugacity was equal to

$$f^{\text{OL}} = \frac{f^{\text{OL}}}{P_c} \times P_c = (4.9)(48.0) = 235.0$$

The activity coefficient is

$$\begin{aligned} \gamma_2 &= \exp \left(\frac{(\log \gamma_2)}{v_2} \times v_2 \times 2.303 \right) \\ \gamma_2 &= \exp (0.012 \times 55.0 \times 2.303) \\ \gamma_2 &= 4.53 \end{aligned}$$

Thus the Henry's Law Constant is

$$H = \frac{1}{X} = f^{\text{OL}} \times \gamma = 235.0 \times 4.53 = 1,062. \text{ atm}$$

From the above, the mole fractions of the gas and solvent can be calculated using

$$\begin{aligned} X_g &= \frac{1}{H} = \frac{1}{1062.} = 0.000940 \\ \text{and} \quad X_s &= 1.0 - X_g = 0.99906 \end{aligned}$$

The volumes of gas and solvent present for one mole of solution can be calculated by

$$V_g = \frac{X_g RT}{1.0} = \frac{(0.000940)(82.06)(298.16)}{1.0} = 23.0 \text{ cc}$$

and

$$V_s = \frac{X_s (\text{M.W.})}{\rho} = \frac{(0.999)(60.064)}{(0.7997)} = 80.3 \text{ cc}$$

The Ostwald and Bunsen coefficients can be calculated in the following way:

$$\ell = \frac{V_g}{V_s} = \frac{23.0}{80.3} = 0.287$$

$$\alpha = \ell \left(\frac{273.16}{298.16} \right) = 0.263$$

Loeffler and McKetta

Loeffler and McKetta used the following equation to calculate solubilities:

$$-\ln \phi_o = \ln f^{oL} + \left(1 - \frac{v}{v_o}\right) + \frac{bv_o \phi_a^2}{RT}$$

The following calculations are for argon in propanol using the value of b which was on the "best curve" or "best line." The value b was read from Figure 4 of the article of Loeffler and McKetta. The fugacity was calculated in the same manner as for the correlation of Prausnitz and Shair. The following constants were used:

$$R = 1.987 \frac{\text{cal}}{\text{gmol } ^\circ\text{K}} = 82.06 \frac{\text{atm cc}}{\text{gmol } ^\circ\text{K}}$$

$$T = 298.16 \text{ } ^\circ\text{K} \quad v_a = 75.108$$

$$b = 14.2 \frac{\text{cal}}{\text{cc}} \quad \text{M.W.} = 60.064 \frac{\text{gm}}{\text{gmol}}$$

$$v_o = 55.0 \frac{\text{cc}}{\text{gmol}} \quad \rho = 0.7997 \frac{\text{gm}}{\text{cc}}$$

$$K = 142.0 \quad f^{oL} = 235.0 \text{ atm}$$

Let x_o = mole fraction of the gas

x_a = mole fraction of the solvent

Assume $x_o = 0.5$

Then $x_a = 1.0 - x_o = 0.5$

The volume fractions of gas and liquid can be written as

$$\begin{aligned}\phi_o &= \frac{x_o v_o}{x_o v_o + x_a v_a} = \frac{(0.5)(55.0)}{(0.5)(55.0) + (0.5)(75.108)} \\ &= 0.4227\end{aligned}$$

$$\text{and } \phi = 1.0 - \phi_o = 0.5773$$

Thus ϕ_1 can be calculated using equation A-30, or

$$\begin{aligned}\phi_1 &= \frac{[2K\phi_a + 1 - (4K\phi_a + 1)^{1/2}]}{2K^2\phi_a} \\ \phi_1 &= \frac{[2(142.0)(0.5773) + 1.0 - (4(142.0)(0.5773) + 1)^{1/2}]}{2(142.0)^2(0.5773)}\end{aligned}$$

$$\phi_1 = 0.006306$$

The true molar volume of the solution can be calculated using equation A-33, or

$$\begin{aligned}\frac{1}{v_T} &= \frac{\phi_o}{v_o} + \frac{\phi_a(1 - K\phi_1)}{v_a} \\ \frac{1}{v_T} &= \frac{0.4227}{55.0} + \frac{(0.5773)(1.0 - (142.0)(0.006306))}{75.108} \\ v_T &= 117.8 \frac{\text{cc}}{\text{gmol}}\end{aligned}$$

The new volume fraction for the gas can now be calculated using the following equation:

$$\begin{aligned}-\ln \phi_o &= \ln f^{oL} + \left(1 - \frac{v_o}{v_T}\right) + \frac{bv_o\phi_a^2}{RT} \\ -\ln \phi_o &= \ln(235.2) + \left(1 - \frac{55.0}{75.108}\right) + \frac{(14.2)(55.0)(0.5773)^2}{(1.987)(298.16)} \\ -\ln \phi_o &= 6.432 \\ \phi_o &= 0.001608\end{aligned}$$

A new mole fraction for the gas can be calculated in the following manner:

$$x_{oc} = \frac{\phi_o v_a}{v_o + \phi_o (v_a - v_o)} = \frac{(0.001608)(75.108)}{55.0 + (0.001608)(75.108 - 55.0)}$$

$$x_{oc} = 0.002194$$

The new x_o can be checked with the assumed x_o . If they agree within 0.01% the solubility coefficients can be calculated. If not, the calculated x_o (x_{oc}) can be substituted into step one for x_o . The trial and error is continued until the two values of x_o do agree within 0.01%.

For this system the calculations converge on $x_o = 0.000607$.

Thus $x_a = 0.9994$.

Thus the volume of gas absorbed per one mole of solution at the temperature of the measurement and one atmosphere pressure (assuming ideal gas law holds) is

$$V_o = \frac{x_o RT}{P} = \frac{(0.000607)(82.06)(298.16)}{1.0}$$

$$V_o = 14.85 \text{ cc}$$

The volume of solvent per each mole of solution would be

$$V_a = \frac{x_a (\text{M.W.})}{\rho} = \frac{(0.9994)(60.064)}{(0.7997)}$$

$$V_a = 75.06 \text{ cc}$$

Thus the Ostwald coefficient is

$$\ell = \frac{V_o}{V_a} = \frac{14.85}{75.06} = 0.1979$$

The Bunsen coefficient is

$$\alpha = \ell \left(\frac{273.16}{298.16} \right) = 0.1813$$

The Henry's Law Constant is

$$H = \frac{1}{x_o} = \frac{1}{0.000607} = 1647. \text{ atm}$$

Experimental Data

The three Bulb B's, Bulb A, the gas tubing of the gas reservoir, the solvent bulb, and the transducer were calibrated before the solubility data were taken. Due to breakage, the line volume and Bulb A were calibrated a second time after Run 28. The potentiometer was recalibrated after Run 14. The results of these calibrations were the following:

	Bulb A	Line Volume
Run 12-28	179.937 cc	17.424 cc
Run 29-39	180.513 cc	17.738 cc

Bulb B--Helium, 76.543 cc; Neon, 97.900 cc; Argon, 368.83 cc.

Solvent Bulb--198.944 cc

Volume (Level B--Level C) -- 0.020 cc

Volume (Level B--Stopcock 7) -- 0.308 cc

The results of the transducer calibrations were

	A	B	C
Runs 12-14	-0.0140	49.905	-0.02153
Runs 15-39	-0.0809	49.888	-0.01903

where true pressure = $A + B(\text{emf}) + C(\text{emf})^2$

emf = output voltage of transducer

The following data were taken on Run 21

	EMF	EMF ⁰	EMFC
Initial zero point	1.5020	2.49884	1.5027
Initial pressure reading	17.6098	2.49900	17.6168
Final pressure reading	16.2612	2.4990	16.2677
Final zero point	1.50534	2.49906	1.5059

	EMF	EMF ^o
Syringe readings--Initial	1.297 cc	2.000 cc
Final	0.000 cc	0.000 cc

The value EMFC is the corrected output voltage of the transducer (EMF) after the EMF had been corrected for the drift in the output voltage of the power supply. The following equation was used:

$$\text{EMFC} = \frac{2.5}{\text{EMF}^o} \times \text{EMF}$$

Thus

$$\text{EMF1} = 17.6168 - 1.5927 = 16.1141, \text{ and}$$

$$\text{EMF2} = 16.2677 - 1.5059 = 14.7618.$$

The initial volume of gas was the contents of the gas reservoir, or $\text{VGS1} = V_A + V_B + V_L = 179.94 + 368.83 + 17.42 = 566.19\text{cc}$. It should be noted that VGS1 does not include V_A for helium and neon runs. The final gas volume differed from the initial gas volume by the volume between stopcock 7 and level B and the volume that the stopcocks were lowered, or $\text{VGS2} = 566.19 + 0.308 + (1.297 - 0.000) + (2.000 - 0.000) = 569.80 \text{ cc}$.

The volume of solvent absorbing gas was equal to the volume of the solvent bulb and the capillary tubing between levels B and C less the volume change of the syringes, or $\text{VSV} = 198.94 + 0.020 - (1.297 - 0.000) - (2.000 - 0.000) = 195.66 \text{ cc}$. The initial and final temperatures TFI and TFf , were 77.0°F .

The following are the constants which were used to calculate the experimental solubilities:

$$R = 62365 \frac{\text{cc mm Hg}}{\text{gmol } ^\circ\text{K}}$$

$$\text{WTSV} = 60.064 \frac{\text{cc}}{\text{gmol}}$$

$$\text{BT} = -16.1 \frac{\text{cc}}{\text{gmol}}$$

$$\text{RHOSV} = 0.7997 \frac{\text{cc}}{\text{gm}}$$

The above values were the data that were put into the computer program of Appendix C. The results were the following:

$$P_1 = 798.878 \text{ mm Hg}$$

$$P_2 = 732.209 \text{ mm Hg}$$

$$\text{Ostwald Coefficient} = 0.2454$$

$$\text{Bunsen Coefficient} = 0.2248$$

$$\text{Henry's Law Constant} = 1328.5 \text{ atm}$$

Error Analysis

The following equation was used to calculate the expected percent error in measuring the number of moles absorbed. This calculation is typical for argon in propnaol.

$$\frac{\epsilon_{\Delta n}^2}{\Delta n^2} = \frac{\epsilon_T^2}{T^2} + \frac{P_2^2}{\Delta P_X^2 V_1^2} \epsilon_{V_A}^2 + \left[\frac{(P_2^2 + P_1^2) V_A^2}{\Delta P_X^4 V_1^2} + \frac{2}{\Delta P^2} \right] \epsilon_P^2$$

$$\text{where } T = 298.16 \text{ } ^\circ\text{K}$$

$$V_1 = 100 \text{ cc}$$

$$P_1 \approx 800 \text{ mm Hg}$$

$$V_A = 180 \text{ cc}$$

$$P_2 \approx 740 \text{ mm Hg}$$

$$\epsilon_T = 0.02 \text{ } ^\circ\text{K}$$

$$\Delta P \approx 60 \text{ mm Hg}$$

$$\epsilon_P \approx 0.2 \text{ mm Hg}$$

$$\Delta P_X \approx 380 \text{ mm Hg}$$

$$\epsilon_{V_A} \approx 0.057 \text{ cc}$$

The solution will be given term by term.

$$\frac{\epsilon_T^2}{T^2} = \frac{(0.02)^2}{(298.16)^2} = 4.49 \times 10^{-9}$$

$$\frac{P_2^2}{\Delta P_X^2 V_1^2} \epsilon_{V_A}^2 = \left[\frac{740 \times 0.057}{380 \times 100} \right]^2 = 1.23 \times 10^{-6}$$

$$\frac{(P_2^2 + P_1^2) V_A^2}{\Delta P_X^4 V_1^2} \epsilon_P^2 = \frac{(800^2 + 740^2) \times (180)^2 (0.2)^2}{(380)^4 (100)^2} = 7.4 \times 10^{-6}$$

$$\frac{2}{\Delta p^2} \epsilon_p^2 = \frac{2(.2)^2}{60^2} = 0.222 \times 10^{-4}$$

$$\begin{aligned} \frac{\epsilon \Delta n^2}{\Delta n^2} &= (0.00449 + 1.23 + 7.4 + 22.2) \times 10^{-6} \\ &= 30.83 \times 10^{-6} \\ &= 0.55\% \end{aligned}$$

TABLE IV
GAS PROPERTIES FROM LITERATURE

	Helium	Neon	Argon
Ideal Solubility $\times 10^4$	2.51 (7)	5.13 (7)	21.6 (22)
Molar Volume, V, cc/mole (24)	33.0	49.8	55.0
Solubility Parameter, (cal/cc) ^{1/2} (13)			5.43
Critical Temperature, °K (16)	5.3	44.5	151.0
Critical Pressure, atm (16)	2.26	25.9	48.0
Critical Density, cc/gm (16)	0.0693	0.0484	0.531
Polarizability $\times 10^{24}$, cc/molecule (23)	0.204	0.393	1.63
Diameter, °A (23)	2.63	2.78	3.40
f^0_L/p_c (30)	212.0	23.0	4.9
High	52.5	22.7	13.0
b (24) cal/cm ³ Low	50.0	22.3	10.8
Line	50.0	32.0	14.2
Virial Coefficient, cc/g mole	11.7 (35)	16.2 (17)	-16.1 (33)
Virial Coefficient of Air, cc/g mole	6.19 (14)		

TABLE V
ALCOHOL PROPERTIES FROM LITERATURE AT 25°C

	Methanol	Ethanol	Propanol	Butanol	Pentanol	Heptanol
Density, gm/cc (32)	0.7873	0.7850	0.7997	0.8057	0.8113	0.8205
Molecular Weight, gm/gm mole (27)	32.032	46.048	60.064	74.080	88.096	116.128
Molar Volume, cc/mole	40.686	58.660	75.108	91.945	108.59	141.53
Solubility Parameter, (cal/cm ³) ^{1/2} (24)	14.35	12.80	11.95	11.20	10.90	10.34
Dielectric Constant (16)	32.63	24.30	20.10	17.1	13.9	11.1
K, mole/cc (24)	365.0	220.0	142.0	68.0	40.0	13.0

TABLE VI

RAW EXPERIMENTAL DATA

Run Number	Gas	Solvent	Pressure		Gas Reservoir Volume		Solvent Volume	Moles of Gas Absorbed	Ostwald*	Bunsen*	Henry's Law Constant
			Initial	Final	Initial	Final					
12	Argon	Pentanol	796.56	734.36	566.19	569.68	195.79	.001759	.2276	.2085	991.
13	Argon	Pentanol	803.14	741.23	566.19	568.93	196.53	.001779	.2271	.2081	993.
14	Argon	Pentanol	800.67	738.83	566.19	569.84	195.62	.001740	.2238	.2051	1007.
15	Neon	Pentanol	805.26	746.11	115.32	118.34	196.25	.0002456	.03119	.02857	7225.
16	Neon	Pentanol	791.54	728.65	115.32	119.12	195.47	.0002409	.03128	.02865	7204.
17	Neon	Pentanol	802.69	737.89	115.32	119.22	195.37	.0002469	.03185	.02918	7075.
18	Argon	Pentanol	808.66	745.88	566.19	569.78	195.68	.001769	.2254	.2065	1000.
19	Helium	Pentanol	800.54	737.61	93.97	97.48	195.76	.0001782	.02295	.02103	9816.
20	Helium	Pentanol	790.54	727.18	93.97	97.66	195.58	.0001757	.02298	.02105	9807.
21	Argon	Propanol	798.88	732.21	566.19	569.79	195.67	.001891	.2454	.2248	1328.
22	Argon	Propanol	797.19	730.67	566.19	569.59	195.87	.001896	.2462	.2256	1323.
23	Argon	Propanol	800.78	733.90	566.19	569.77	195.69	.001898	.2458	.2251	1326.
24	Neon	Propanol	802.06	734.87	115.32	118.67	195.92	.0002838	.03666	.03359	8886.
25	Neon	Propanol	796.28	727.91	115.32	118.93	195.66	.0002821	.03683	.03375	8843.

TABLE VI (Continued)

Run Number	Gas	Solvent	Pressure		Gas Reservoir Volume		Solvent Volume	Moles of Gas Absorbed	Ostwald*	Bunsen*	Henry's Law Constant
			Initial	Final	Initial	Final					
26	Helium	Propanol	809.70	744.41	93.97	97.09	196.14	.0002040	.02598	.02380	12540
27	Helium	Propanol	793.12	724.93	93.97	97.73	195.50	.0001977	.02594	.02377	12560
28	Helium	Propanol	803.14	737.36	93.97	97.21	196.02	.0002033	.02616	.02367	12450
29	Helium	Heptanol	792.31	732.67	94.28	97.94	195.61	.0001580	.02051	.01879	8429
30	Helium	Heptanol	811.81	752.13	94.28	97.86	195.69	.0001573	.01988	.01821	8696.
31	Helium	Heptanol	806.10	745.56	94.28	97.86	195.69	.0001631	.02079	.01905	8314.
32	Argon	Heptanol	799.80	742.04	567.08	570.15	195.62	.001642	.2103	.1927	822.8
33	Argon	Heptanol	794.35	737.22	567.08	569.68	196.09	.001640	.2109	.1933	820.3
34	Neon	Heptanol	798.84	737.43	115.64	119.66	195.25	.0002221	.02868	.02628	6028.
35	Neon	Heptanol	798.23	729.86	115.64	118.88	196.02	.0002230	.02899	.02656	5963.
36	Argon	Water	802.63	743.60	115.64	118.62	196.28	.0002482	.03160	.02895	42820
37	Argon	Water	795.68	738.37	115.64	118.68	196.23	.0002358	.03025	.02771	44730
38	Argon	Water	837.87	770.60	115.64	119.69	195.22	.0002508	.03098	.02839	43670
39	Argon	Propanol	800.36	735.46	567.08	570.62	195.73	.001843	.2379	.2179	1369.

*Ostwald and Bunsen Coefficients

APPENDIX F

APPENDIX F

EQUIPMENT LIST

Main System

1. Powerstat - The Superior Electric Company - Type 116 - Output voltage 0-140 volts
2. Heating Mantle - Glas-Col Apparatus Co. - Three liter round bottom mantle - Iron Constantan - 450°C maximum
3. Condensor - Ace Glas Incorporated - Item # 5930-14
4. Ball Joints - Westglass Corporation - W-1553-V; W-1560
5. Transducer - Consolidated Electrodynamics Corporation (CEC) - Type 4-313-0002 - Range 0-20 psia
6. Chamber Adapter for Transducer - CEC - Type 4-008-44
7. Electrical Connector for Transducer - CEC - Type 38323-0018
8. Potentiometer - Leeds and Northrup Company - Type K-5, 7555-A-11
9. Potentiometer - H. Tinsley and Co., Ltd. - Diesselhorst Thermo-Electric Free Potentiometer - Type 3589R
10. Pressure Regulator - The Matheson Company, Inc. - Model 3300
11. Swadgelock Fittings - Ben McKalip Co., Tulsa, Okla. - Part No. 400-1-4-316; 400-7-2-316; 400-6-316
12. Stopcocks - Ace Glass Incorporated - Type 8194-05; 8172-08; 8289-06
13. Kovar to Glass Seal - Ace Glass Incorporated - Type 7675-12
15. Syringes (vacuum) - Laboratory Supplies Co., Inc. - Catalog No. P-105 - Models C and D.

Electrical System

15. Power Supply - Hewlett-Packard - Model 6201B
16. Power Supply - Hewlett-Packard - Model 801C
17. Resistors - Leeds and Northrup Co. - one ohm and 2000 ohm precision standard resistors

Heating and Cooling System

18. Temperature Controller - Fisher Scientific Co. - Proportional Controller - Model 22
19. Chiller - E. H. Sargent and Co. - Water Bath Cooler - Cat. No. S-84890
20. Strip Heater - Edwin L. Wiegand Co., Pittsburgh, Pa. - S-802 - 250 watts

Vacuum System

21. Vacuum Pump - The Welch Scientific Co. - Model 1402
22. McCleod Vacuum Gage - Ace Glass Incorporated - Item # 8726-04

APPENDIX G

APPENDIX G

NOMENCLATURE

General

- l - Ostwald Coefficient
- α - Bunsen Coefficient
- H - Henry's Law Constant
- V_g - Volume of gas absorbed at the temperature and pressure of the measurement
- V_s - Volume of solvent at the temperature and pressure of the measurement
- T - Temperature of measurement ($^{\circ}\text{K}$)
- p^* - Partial pressure of the gas
- x_g - Mole fraction of gas in solvent
- R - Gas constant
- \ln - Natural logarithm
- \log - Common logarithm

Gjaldbaek and Niemann

- x_2 - Solubility of gas in mole fraction
- x_2^i - "Ideal" solubility of gas
- \bar{v}_2 - Partial molar volume of the dissolved gas
- v_1 - Molar volume of the solvent
- δ_1 - Solubility parameter of the solvent
- δ_1^* - Corrected δ_1 for non-polar gases in polar solvents

- δ_2 - Solubility parameter of the gas
- α - Polarizability of the gas
- ϵ_0 - Dielectric constant of the gas

Prausnitz and Shair

- x_2 - Mole fraction of gas in liquid phase
- f_2^L - Fugacity of hypothetical liquid at one atmosphere
- f_2^0 - Fugacity of pure gas at initial conditions of one atmosphere
- γ_2 - Activity coefficient of gas
- P_c - Critical pressure
- v_2 - Molar volume of gas
- δ_2 - Solubility parameter of the gas

Loeffler and McKetta

- A - Helmholtz free energy
- c_i - Concentration of species i
- a_0 - Activity
- E - Energy
- f^{oL} - Fugacity of hypothetical liquid at one atmosphere
- K - Association equilibrium constant
- K' - $K v_1$
- n - Number of moles
- x - Mole fraction
- ϕ - Volume fraction
- S - Entropy
- v_T - Volume of one "true" mole of solution
- v_x - Volume of one stoichiometric mole of solution

v - Molar volume

Subscripts

o - Gas

l - Alcohol monomer

i - Degree of alcohol polymerization

a - Alcohol

v - Constant volume

Superscripts

o - Pure component property

- - Partial molal quantity

Lin and Chao

α - Polarizability of the gas

e_c - Energy required for creation of a cavity

e_i - Interaction energy of a solute molecule with the solvent

A_u - Surface area of group of type u

λ - Surface energy density of u -group and gas interaction

S - Total surface area of gas molecule

E - Energy of vaporization

ρ_E - Energy density

σ - Diameter of a gas molecule

H - Henry's Law Constant

H^o - "Hard sphere" Henry's Law Constant

v - Molar volume of the solvent

χ - Energy of a dissolved molecule of gas = $e_c + e_i$

k - Boltzman constant

Error Analysis

ϵ_y - Expected error in property y

n - Number of moles

x_i - Independent variables

ΔP - Pressure drop in gas reservoir during typical run

ΔP_x - Pressure drop during expansion from V_1 to $(V_1 + V_A)$

V - Volume of total gas reservoir

V_A - Volume of Bulb A

V_B - Volume of Bulb B

V_ℓ - Volume of tubing in gas reservoir

V_1 - Unknown volume ($V_B + V_\ell$)

VITA

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