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Jay Alan Kaiser

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Supercritical Fluid Extraction

Of

2,3 Butanediol With CO_2:

The Construction of Equipment

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Jay Alan Kaiser

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ABSTRACT

A visual flow through apparatus has been constructed and used to determine the high pressure VLE data of an ethanol-ethane system and a 2,3 butanediol-CO_2 system. The ethanol-ethane data were compared to the literature to assure that the equipment produced accurate data. Data from the 2,3 butanediol system can be used to evaluate the feasability of extracting the diol from a fermentation broth using supercritical CO_2. This apparatus can be used at temperatures ranging from 295 K to 365 K. Pressures from ~1,000 psia to 5,000 psia can be examined. The equipment can be easily adapted to handle a solid - fluid system.

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I. INTRODUCTION

Rising petroleum prices and the vagaries of petroleum producers have caused renewed interest in the bioproduction of feedstocks for chemical processes. Many potential feedstocks produced by fermentations were evaluated during World War II. As petroleum became cheap and abundant in the postwar era, these fermentations became economically unfeasible. One of the extensively investigated fermentations was the production of 2,3 butanediol (diol) from several different organisms (Ledingham and Neish, 1954; Jansen, Flickinger, and Tsao, 1984). It was hoped that the diol could be used to produce synthetic rubber. This fermentation was abandoned because an energy intensive steam stripping process was required to remove the diol from the fermentation broth. A 1984 economic evaluation of the diol production indicates that the fermentation may be feasible in spite of the energy intensive stripping process (Landgrebe, 1984). The present work establishes the equilibrium data neccessary to begin evaluating supercritical fluid extraction as a separation process for the diol fermentation. Basic vapor liquid equilibrium (VLE) data have been determined for the CO_2 - Diol system. Data on H_2O - Diol systems are found in the literature (Ledingham, and Neish) along with some incomplete data on the

solubility of 1,4 butanediol in CO_2 at high temperatures and pressures (Semenova, et al., 1981; Jelinek, et al., 1976). No VLE data on the CO_2 - Diol or CO_2 - H_2O - Diol systems are found in the literature. In order to compare supercritical fluid extraction (SCFE) with steam stripping and other separation methods, these data are essential. If biologically produced 2,3 butanediol is to compete with petroleum feedstocks in the production of methyl ethyl ketone (MEK) and 1,3 butadiene, the most cost effective separation scheme must be identified and optimized. Therefore, the evaluation of SCFE is crucial to this process.

Objectives

To evaluate the supercritical fluid extraction of 2,3 butanediol with CO2, experimental vapor-liquid equilibrium data on the system are needed. The objectives of the present work are:

1. To construct a flow apparatus for high pressure vapor-liquid equilibrium measurements.

2. To compare data taken with this apparatus to data present in the literature.

3. To obtain some vapor-liquid equilibrium data for the CO_2 - 2,3 butanediol system.

II. BACKGROUND

Supercritical Fluid Extraction Basics

Supercritical fluid extraction (SCFE) is based on well known concepts. Hannay and Hogarth (1879) first reported the solubilities of inorganic salts in supercritical ethanol to the Royal Society of London in 1879. Their contemporary, Gore (1861), investigated the solvent properties of liquid CO_2. In 1888, Villard (1888) published the first review of supercritical fluid solubilities. Later, in the early 1950's, Todd and Elgin (1955) studied the high pressure phase equilibria of several liquid and solid solutes in supercritical ethylene. They proposed exploiting supercritical fluid solubilities as an extraction scheme for solid - fluid systems. Since that time, interest in SCFE has been growing.

In spite of its long history, SCFE is just beginning to be developed commercially. Some of the current applications are; the decaffination of coffee and tea (Zosel, 1978), the deasphalting of heavy oils with supercritical propane (Zhuse, 1960), the deoiling of potato chips (Wolkomir, 1984), and the recovery of vegetable oils from crushed seeds (Stahl, 1978). Other potential commercial applications for SCFE are; the removal of nicotine from tobacco (Hubert, 1978), the

molecular weight fractionation of polymer mixtures (McHugh and Krukonis, 1986), and the removal of organic chemicals from fermentation broths (Willson and Cooney, 1985). This final application is important considering the renewed interest in fermentations and other bioprocesses.

Many potentially valuable products like antibiotics, amino acids, proteins and alcohols can be produced by fermentations. These products are present in the fermentation broths at low concentrations. The separations required for recovery are cost-intensive and technically difficult. For example, many antibiotic separations require 60 to 100 processing stages using liquid-liquid extraction (LLE). Often, a difficult precipitation or an expensive distillation is required to recover the antibiotic from the solvent. In addition to the process difficulties, many of the LLE solvents used are toxic. This necessitates extensive, expensive washing procedures before the antibiotic is safe for use. A supercritical solvent that could extract the antibiotic directly from the broth and allow recovery of the antibiotic with a pressure or temperature drop, would offer distinct advantages over conventional separation methods.

Many biological compounds, like antibiotics, degrade when exposed to high temperature. The operating temperature of a supercritical fluid extraction is controlled by the critical temperature of the solvent selected. Many supercritical solvents, like CO_2, have critical temperatures near ambient conditions. This protects

thermally labile compounds and helps make SCFE less energy-intensive than distillation.

Supercritical fluid solvents exploit the physical properties of the critical region to offer several advantages over conventional solvents. These advantages can be summarized:

1. Combine gas like transport properties with liquid-like solvent powers.
2. Offer moderate operating temperatures.
3. Utilize non- toxic gases as solvents.
4. Dissolve non-volatiles.
5. Provide for efficient product recovery (Krukonis and McHugh, 1986).

Basic VLE data and accurate models are needed to determine if supercritical fluid extraction's advantages can be turned into a cost effective commercial separation. Some of these data have been obtained for the 2,3-butanediol-CO_2 system. Some common approaches to making high pressure VLE measurements are outlined below.

Equipment

There are three common methods for taking high pressure thermodynamic data reported in literature. These methods fall into two broad classes, static and flow apparatus. Classically,

thermodynamic VLE data were taken using static equipment. Kay and Connally (Connally, 1962) pioneered a static capillary method of determining dew and bubble pressures. A small sample of known mass and composition was confined above mercury in a capillary outfitted with a small stainless steel ball. The dew pressure was recorded when the first trace of liquid appeared at the intersection of the capillary wall and the stainless steel ball. The bubble pressure was recorded when the gas phase disappeared. This type of apparatus is well suited to temperature-stable hydrocarbon systems and multiple component systems. At high temperatures, the long residence time in the cappillary would thermally degrade temperature sensitive biological compounds. As lab equipment became better suited to high temperatures and pressures, batch methods which recirculated a fluid phase in equilibrium with a liquid phase were developed (Kuk and Montagna, 1983). The equilibrium cell was charged with a liquid of known mass and composition and CO_2 was pumped into the cell until the desired pressure was reached. The fluid and liquid phases were circulated until equilibrium was established. Then both phases were sampled and analyzed with a gas chromatograph. The amount of CO_2 charged to the equilibrium cell could be determined by using a calibrated gas meter if necessary. Sampling of the circulation lines caused small perturbations in equilibrium and some difficulty in sampling. Like other batch methods, this type system is not suitable for thermally labile compounds.

The need for VLE data on temperature sensitive compounds led to the development of flow systems for high pressure VLE measurements. Grayson and Streed (1963) developed an early flow system for high pressure VLE measurements. As interest in SCFE has developed, a number of flow systems have been reported in the literature (Lin and Chao, 1985; Lin, et al., 1985; Radoz, 1985; Inomato Arai and Saito, 1986). A generalized diagram of this class of apparatus appears in Figure 1. The solvent delivery system pumps the supercritical solvent into apparatus. The solvents are often pumped as liquids or delivered with a suitable compressor. The liquid delivery system is usually either a liquid chromatoghraphy or a similar type lab scale pump. The liquid and fluid components are pumped together, mixed and allowed to come to equilibrium. The well mixed components split into liquid and gas vapor phases in the separation cell. The liquid and fluid streams must be pumped through the separation cell at flow rates slow enough to allow diffusive mass transfer equilibrium to be reached. After the flowing system is stabilized at a particular pressure, the gas and liquid streams are sampled to detemine their equilibrium compositions.

Flow through apparatus offer two distinct advantages for biological systems. Since the fluids are flowing through the equipment, residence times can be controlled and thermal degradation minimized. Systems which exhibit low solubility in a supercritical solvent can be sampled accurately by extending the sampling time. Another advantage of flow through systems is the fact

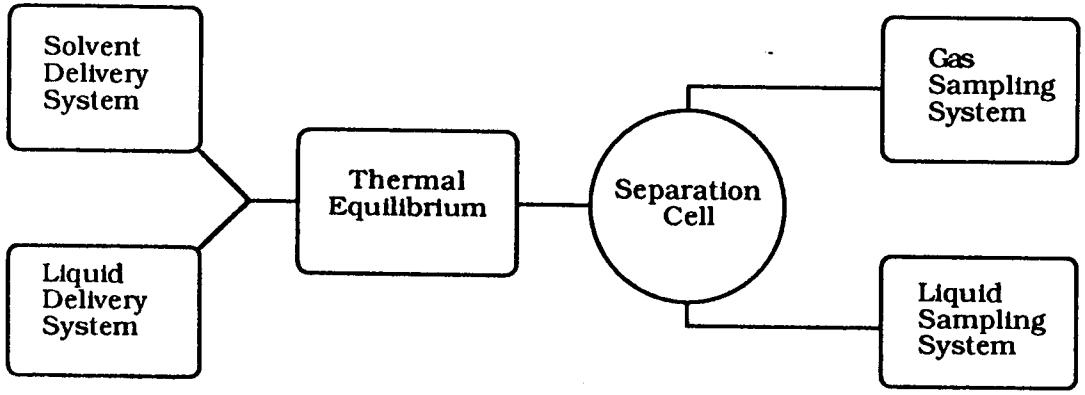

Figure 1: Generalized Diagram of SCFE Apparatus

that sampling does not perturb equilibrium. The main disadvantages of flow systems are the fact that they are difficult to stabilize near the mixture critical point and must be held at steady state for extended periods of time.

Since the study of a wide range of biological systems is planned, a flow through apparatus based on the equipment of Lin, et al. (1985) has been built to conduct these experiments. This visual flow through apparatus will allow the study of thermally liable systems and systems with low solubilities in the supercritical fluid phase. An added advantage of a visual system is the fact that phase behavior in the separation cell can be observed. This equipment can be easily adapted to study a solid and supercritical fluid system.

III. THEORY

Literature

Several excellent discussions of supercritical fluid solubility exist in literature (Franck, 1983; Schnieder, 1976; Johnston et al.,1982; Schnieder, 1978) Several review papers provide abbreviated but accurate discussion of SCFE theory (Randall, 1982; Reid, 1981; Williams, 1981). **Supercritical Fluid Extraction, Principles and Practice** by McHugh and Krukonis (1986) offers an excellent discussion of supercritical solubility and supercritical phase behavior.

Supercritical fluid extraction exploits the pressure - density relationships of the critical region to allow fluids like CO_2 to function as solvents. The shaded region of Figure 2 is the critical region. Isotherms at reduced temperatures of 1.0 and 1.1 are plotted on the graph. Isotherms in this region have flattened out with respect to pressure. As the pressure approaches the critical pressure of CO_2, the partial derivitive of pressure with respect to volume at constant temperature goes to zero.

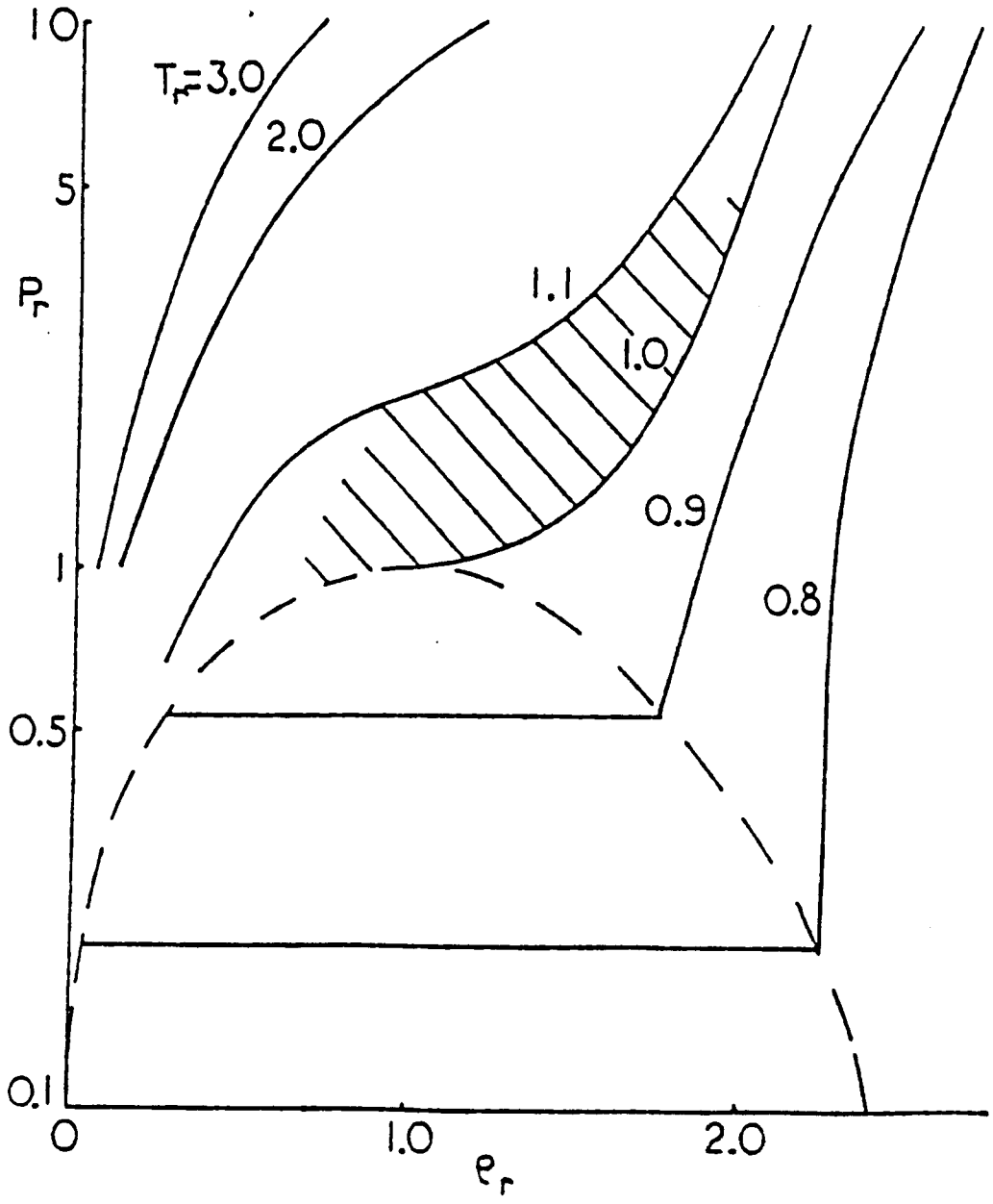

Figure 2: Phase Diagram for CO_2

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T = 0 \qquad (1)$$

Near the critical point, small changes in pressure correspond to large changes in volume or density. These changes in volume allow a supercritical fluid to be an effective solvent.

Several transport phenomena also change in the critical region. Diffusivities decrease with increasing pressure. Although diffusivity decreases with increased pressure, the diffusivity of CO_2 remains an order of magnitude higher than the diffusivities of typical liquid solvents. Viscosity, like diffusivity, changes rapidly in the critical region. Viscosity increases with increasing pressure, but even at high pressures of 400 atm., the viscosity of CO_2 does not exceed .09 centipoise (McHugh and Krukonis, 1986). These viscosities are an order of magnitude below the viscosities for typical liquid solvents.

The physical relationship of pressure and volume in the critical region allows CO_2 to function as a supercritical solvent. Since CO_2 is safe and cheap, there is a great deal of interest in it as a supercritical solvent.

Model

In order to evaluate CO_2 as a solvent for a particular solute, it is necessary to model solubility in the critical region. There are several

approaches to modeling pressure, volume and temperature (PVT) relationships in the critical region. Models can be established using activity coefficients, cubic equations of state (EOS) or a statistical mechanical approach. The simplest computational approach is offered by using either the activity coefficient or EOS approach. An EOS approach using the Peng-Robinson (1976) or Soave equations (1972) offers the advantage of a single fitted parameter, k_{ij}, which accounts for binary interactions in mixtures. In order to utilize an activity coefficient model, two fitted parameters, k_{ij} and the infinite dilution activity coefficient must be known. This work will utilize an EOS model, because it is computationally straight forward. A cubic equation of state models systems well up to moderate pressures. Agreement between the data and model within 10-20% can be expected in this experimental system.

Many other approaches to modeling supercritical fluid solubility appear in the literature. Hard sphere perturbation theory has been applied to supercritical systems by Joshi and Prausnitz (1984) and Uno et al. (1976). The Kirkwood Buff theory has been applied to supercritical fluid systems by Pfund and coworkers (1986) and an augmented van der Waals EOS by Johnston, Ziger and Eckert (1982). The solubility parameter approach has also been used to predict solubilities in supercritical fluids (Gitterman and Procaccia, 1983).

The phase behavior of high pressure liquid - vapor systems can be described by using fugacity coefficients, Φ, predicted from the Peng-Robinson EOS to model the equilibrium of the liquid and vapor

phases. The fugacities of the liquid and vapor phases are equal at equilibrium and can be described by the following equations.

$$f_i^V = y_i \Phi_i^V P \quad (2)$$

$$f_i^L = x_i \Phi_i^L P \quad (3)$$

At equilibrium

$$f_i^L = f_i^V \quad (4)$$

The fugacity coefficients in equations 2 and 3 can be determined using the Peng Robinson equation of state. The Peng-Robinson EOS has the following form:

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \quad (5)$$

Where:

v= molar volume ($cm^3/gmol$)

R= universal gas constant $\left(\frac{cm^3\ atm}{gmol\ °K}\right)$

T= temperature (°K)

P= pressure (atm)

a(T)= temperature dependent interaction parameter $\left(\frac{atm\ gmol^2}{cm^6}\right)$

b= molecular size difference parameter $\left(\frac{cm^3}{gmol}\right)$

The parameter $a(T)_i$ accounts for the attractive interactions between species in the mixture and is given by the product of two parameters (Walas, 1985):

$$a(T)_i = a(T_{ci})_i \cdot a(T_{Ri},\omega_i)$$

$$a(T_{ci})_i = 0.45724(R^2T_{ci}^2/P_{ci})$$

$$a(T_{Ri},\omega_i) = (1+m(1-T_{Ri}^{.5}))^2$$

$$m = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

The parameter b_i accounts for the repulsive interactions between the constituients of the mixture and is related to the critical properties.

$$b_i = 0.07780\left(\frac{RT_{ci}}{P_{ci}}\right)$$

In order to apply the Peng Robinson equation to a supercritical fluid mixture, it is necessary to establish mixing rules for the parameters $a(T)_i$ and b_i. For $a(T)_i$, the following mixing rule has proved suitable (Peng and Robinson, 1976b):

$$a(T)_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \qquad (6)$$

where:

$$a_{ij} = (1 - k_{ij})\sqrt{(a(T)_i\, a(T)_j)}$$

An experimental fitting parameter, k_{ij}, is obtained by regressing the data of interest. The parameter b can be described by the simple mixing rule:

$$b_m = \sum_{i-1}^{n} x_i b_i \qquad (7)$$

The Peng - Robinson EOS can be rewritten in terms of the compressibility factor, Z (Peng and Robinson, 1976).

$$Z^3 - (1 - B)Z^2 + (A^3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad (8)$$

Where:

$$A = a(T)_m\left(\frac{P}{R^2T^2}\right)$$

$$B = b_m\left(\frac{P}{RT}\right)$$

$$Z = \frac{Pv}{RT}$$

This form of the Peng - Robinson equation of state can be substituted into the following equation presented by Prausnitz (1969) to get an expression for the fugacity coefficient.

$$\ln(\phi) = \frac{1}{RT}\int_{V}^{\infty}\left(\left(\frac{\partial P}{\partial N}\right)_{T,N_i} - \frac{RT}{V}\right)dv \qquad (9)$$

Substituting the Peng-Robinson equation (8) into equation 9 yields the following expression for the fugacity coefficient for a

component i, in terms of Z. The Z form of the equation was utilized because it can be easily adapted to fit different situations. Pressure, temperature or compositions can be varied using this form of the Peng - Robinson EOS (Walas, 1985).

$$\ln \phi_i = \frac{b_i}{b_m}(Z-1) - \ln(Z-b_m) - \left(\frac{A}{2.828\ B}\right)\left(\frac{2\Sigma x_i a_{ij}}{a} - \frac{b_i}{b_m}\right)$$

$$\ln\left(\frac{Z + 2.414\ B}{Z - 0.414\ B}\right) \qquad (10)$$

These fugacity coefficients can now be used with equation 3 to predict the vapor phase mole fraction of component y_i and the liquid phase mole fraction, x_i, for a given temperature and pressure. These calculations are iterative and were performed with a Fortran program that appears in the appendix. Figure 3 presents a flowsheet of this program. This program was also used to generate PVT isotherms for the 2,3-butanediol- CO_2 system.

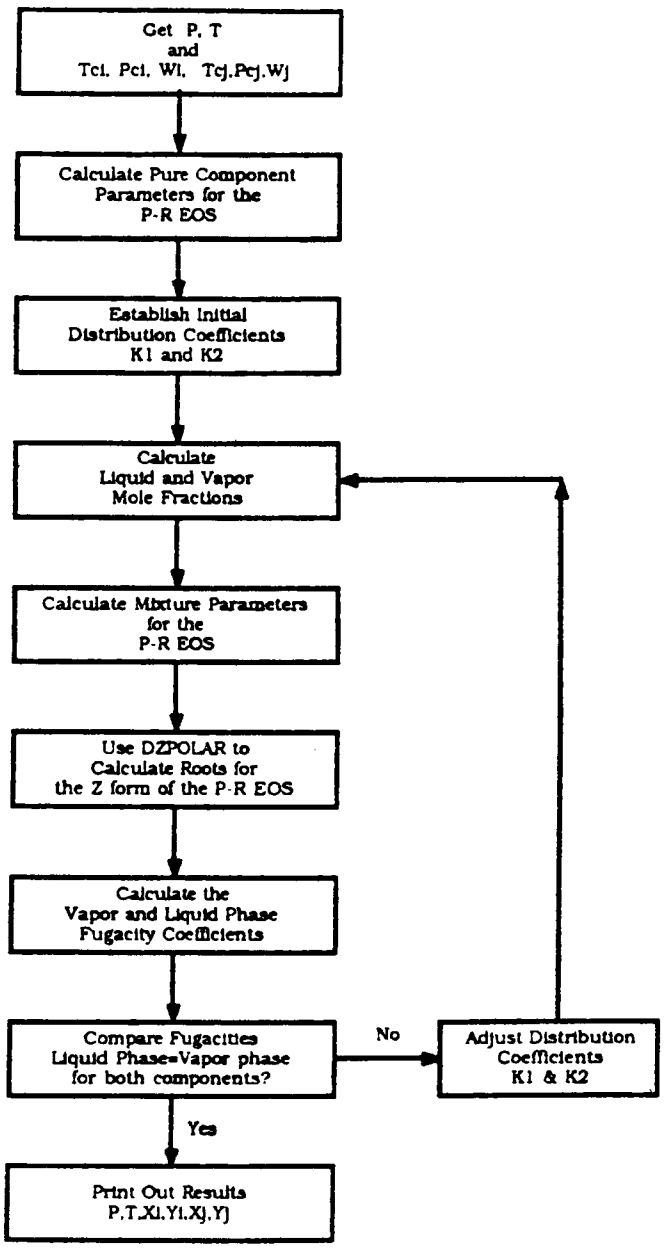

Figure 3: Flow Chart of Peng - Robinson Program for Mole Fraction Prediction

IV. EQUIPMENT

Basic Principles

The flow apparatus designed and built for these experiments is based on concepts developed by Lin and Chao (1985), and Lin et al. (1985). These researchers built a flow apparatus for the examination of the VLE properties of hydrogen in heavy coal liquification solvents. At high temperature and pressure, these compounds are thermally liable. The short residence time offered by a flow through apparatus was crucial to minimize thermal degradation of the compounds being investigated. Other researchers have used the same concepts to measure the solubility of nonvolitiles in supercritical fluids with great success (Radoz, 1985; Inomata, Arai, and Saito, 1986; Konrad, Swaid, and Schneider, 1983; Kurnik, Holla and, Reid, 1981; Theis and Paulaitis, 1984; Van Leer and Paulaitis, 1980).

The equipment constructed by Lin and Chao (1985) uses a Matheson gas blender combined with a Hofer compressor to deliver the gas streams. The gas blender allows mixtures of solvents to be tested. The liquid solute is delivered by a Hills-McCanna metering pump. The solute and solvent are pumped through a heated $\frac{1}{4}$ inch tube containing a spiraled notched ribbon. This tube and ribbon are

used to ensure good mixing and thermal equilibrium. The tube is kept within 1° C of the separation cell.

Lin and Chao (1985) use two separation cells. One, a blind cell, is used for non-conducting systems. In this cell, a capacitor connected to an oscilliscope monitors the liquid level in the cell. For aqueous or conducting systems, Lin and Chao's (1985) capacitor doesn't work. These systems require a visual cell. Monitoring of the liquid meniscus is allowed by sapphire windows. All pressure and temperature measurements are made at the separation cell.

On the blind cell, the gas exit streams are outfitted with a detrainer to prevent the entrainment of liquid droplets in the fluid phase. On either cell, the exit streams are controlled with metering valves which affect both the pressure in the cell and the flowrate from the cell. Other researchers utilize back pressure regulators connected to the separation cell to provide better control of the pressure and flowrate of the apparatus (Radoz, 1985; and Inomata, Arai, and Saito, 1986).

The gas sampling system consists of dropping the system pressure and collecting the solute in an appropriate trap for weighing. The gas volume is measured with a wet test meter or a mass flowmeter. The liquid sampling system consists of collecting the liquid in a graduated cylinder and trapping the dissolved gas over

water. From these data, Lin and Chao (1985) calculate the desired solubilities.

Current System

The original equipment designed for these experiments is diagramed in Figure 4. Some initial experimentation dictated changes in the system. These appear in Figure 5. The equipment in the system will be summarized section by section. The adaptations will be outlined and the limitations of the apparatus will be discussed.

The CO_2 delivery system consists of an inverted gas cylinder to deliver the CO_2 as a liquid and an LDC/ Milton Roy dual head positive displacement mini pump, model number 2396-89. The pump capacity ranges from a minimum of 46 ml/hr to a maximum of 920 ml/hr. (±0.3%/hr.) The maximum delivery pressure for the pump is 6000 psig. The heads of the pump are maintained at a constant temperature by a head cooler. Originally, the pump was operated without the head cooler. However, as the pump motor heats up, so do the pump heads. This warming causes a loss of pressure in the system during operation due to an extreme loss of pumping efficiency as the liquid CO_2 vaporizes on the suction stroke of the pump. The change in pumping efficiency with time is unacceptable if steady state is to be maintained for extended periods. The pump heads are wrapped with $\frac{1}{8}$ inch copper tubing and insulated. A water - ethylene glycol solution

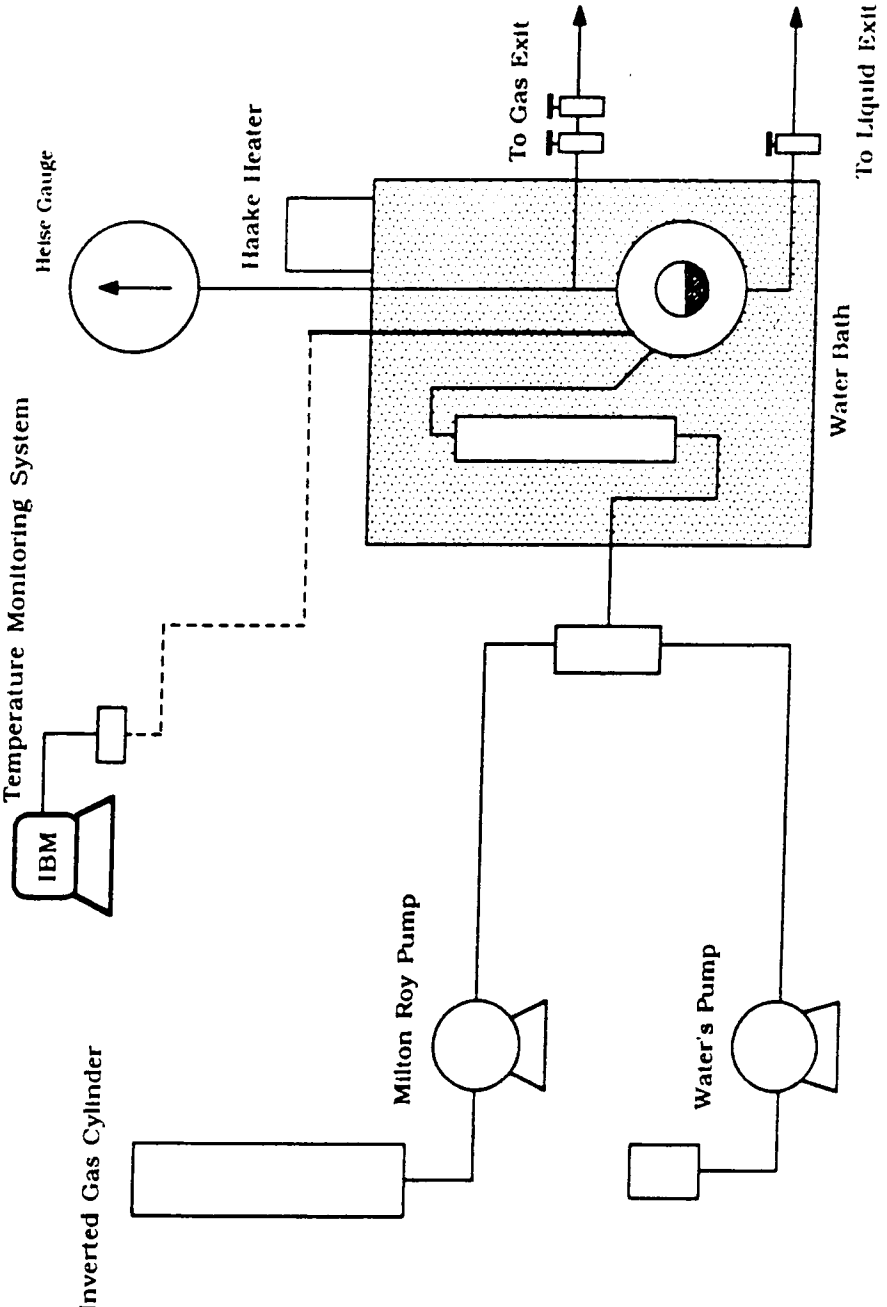

Figure 4: Original Experimental Equipment

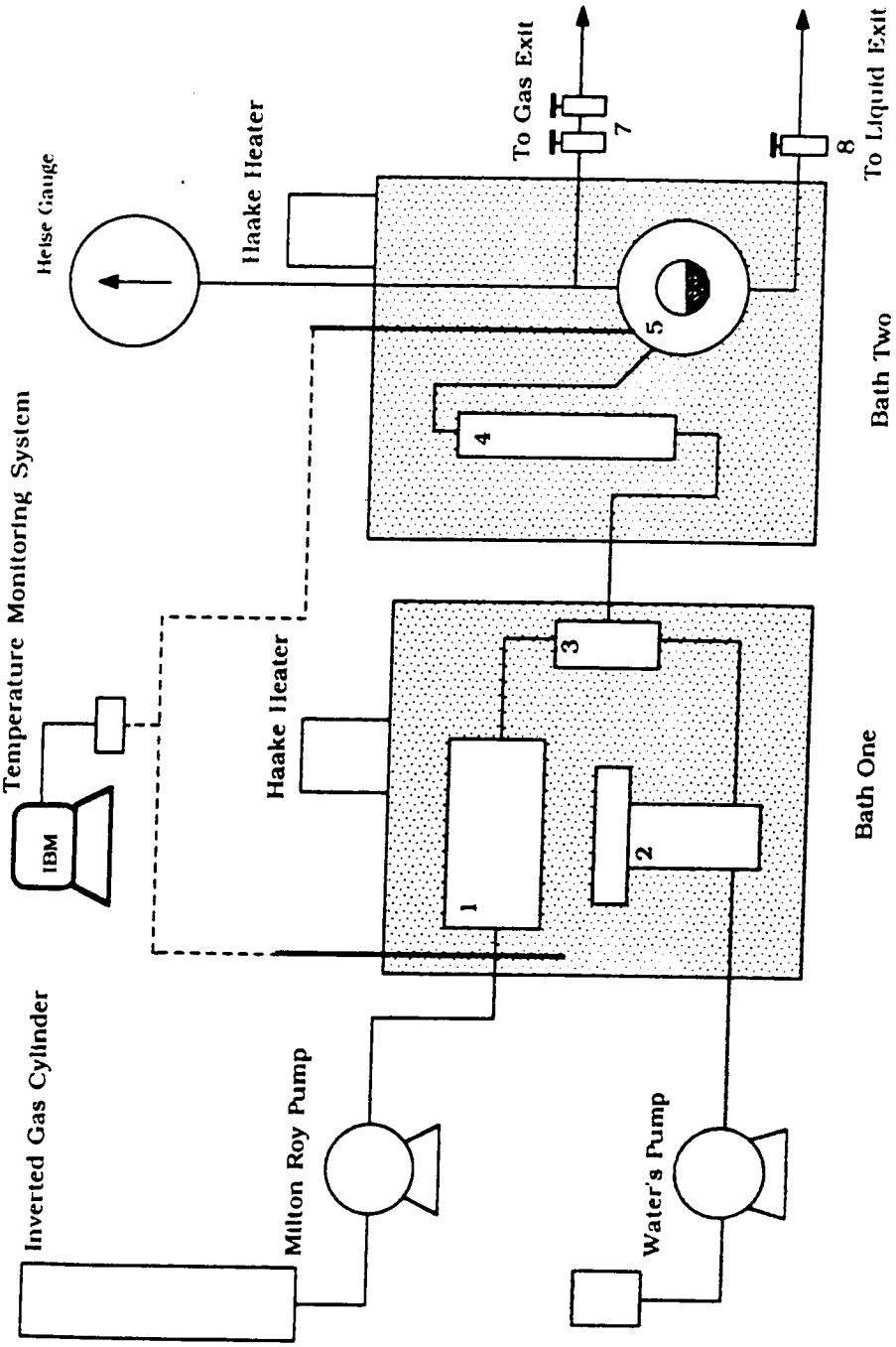

Figure 5: Modified Experimental Equipment

is circulated through an ice bath and the copper tubing surrounding the pump heads. This head cooler effectively eliminates the problems associated with temperature changes in the pump heads.

The Milton Roy is a positive displacement pump. At high pressures, the pressure pulsations due to pumping caused oscillations in the system pressure of 10-15 psig. In order to damp out these pulsations, a 500 cm^3 dead volume (1) was installed in the gas line prior to mixing the solvent and solute. This diminished the effects of pumping on the system. The pulsations in the system are below the detectibility limit of the Heise gauge employed.

This solvent delivery system has a limited pressure range. The lower limit is dictated by the VLE characteristics of the solvent. The lowest possible delivery pressure will be slightly above the saturation pressure for the solvent at the ambient temperature. The minimum pressure possible using CO_2 was ~1000 psig. Pressures below the saturation pressure of the solvent could be reached by righting the gas cylinder and using a high pressure gas regulator to deliver the solvent. The upper pressure limit, 6000 psig, is dictated by the pump itself.

Another disadvantage of this delivery system is the fact that it cannot presently deliver mixed solvents. A compressor combined with a mass blender would allow two fluid streams to be combined at a specific composition and compressed to the desired pressure.

Entrained co-solvents could be utilized with this type solvent delivery equipment.

The liquid delivery system is a Waters Associates Liquid Chromatography Pump, Model 6000A. The capacity of this pump ranges from 0.1 ml/min. up to 9.9 ml/min (±0.1%). The pump is capable of operating pressures up to 6000 psig. The Waters pump is also a positive displacement pump. To assure that pulsations due to pumping the liquid would not affect the system pressure, the pulse dampener diagrammed in Figure 6 has been built. The vertical cell has 75 cm^3 internal volume. A steel plug lined with a $\frac{1}{16}$ inch thick sheet of teflon separates the liquid in the bottom of the cell from a gas in the top of the cell. Pulsations due to the liquid pumping are dampened by the compressible gas. The plug separating the gas and liquid prevents the gas from dissolving into the liquid. The cell can be charged with the solvent gas to a pressure below the bottom of the pressure range being investigated. In these experiments, CO_2 was used.

The solvent and solute are mixed in a tee (3) and pumped into the bottom of a vertical cylinder (4) packed with glass beads. The purpose of the vertical cell is to ensure good mixing and thermal equilibrium. The mixing tee, along with both pulse dampeners, is immersed in a constant temperature water bath that is kept below, but within 1°C of the equilibrium temperature. The vertical cell is in a temperature controlled water bath with the separation cell (5). This

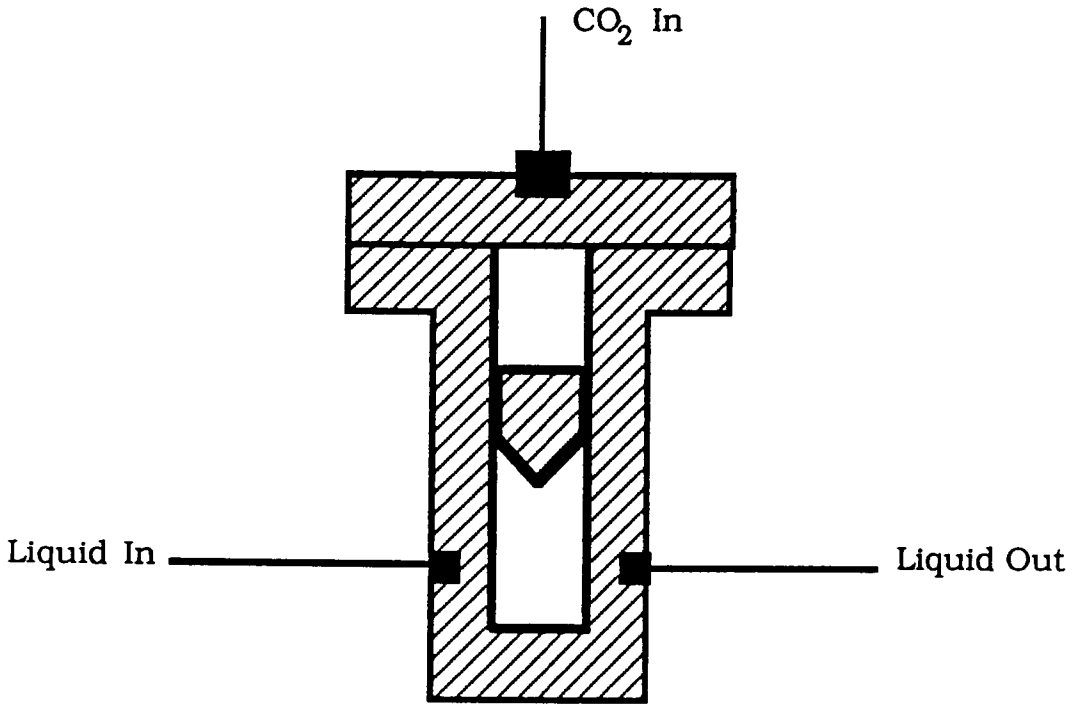

Figure 6: Pulse Dampener for Liquid Pumping

water bath is kept at the experimental temperature. The temperatures in both water bathes are maintained by Haake E3 Immersion Circulators. These heaters have a working temperature range of 25 to 140°C. The temperature control accuracy is rated at ±0.02°C. A nine hour temperature trace of the baths had an average temperature of 61.65°C. The standard deviation was .007. The air-water surfaces of both baths are covered with thermally insulating plastic balls. The balls limit evaporative losses from the baths and provide additional temperature stability.

Temperature measurements are made with five resistance thermometers (RTDs) connected to a Keithley 195A Digital Multimeter. The multimeter is sensitive to ±0.01°C. Temperatures are logged on an IBM XT using a Metrabyte GPIB IEEE−488 interface card connected to a Keithley 705 Scanner. The Keithley instruments have an internal drift of ±0.16°C/day. The internal drift is eliminated by scanning a reference RTD in an electronic cold junction and the RTD's being used for temperature measurements. The RTD's are zeroed every ten seconds by using the difference between the reference RTD and 0.00°C. The resistance of the cold junction was measured. If the junction had a resistance of greater than 0.001 ohms, the reading was disregarded. This eliminates the instantaneous drift of the Keithely instruments. The RTD's have been calibrated with the Chemical Engineering Department's N.B.S. calibrated platinum resistance thermometer. The N.B.S. probe's resistance at 0°C is checked regularly and compared to the value supplied with the probe.

The values agree within ±1 milliohm. Temperatures can be measured to a ±0.04°C accuracy using this apparatus.

Pressure measurements are made with a 16" Heise Bourdon Tube gauge (Model #CMM–61633). This gauge has a pressure limit of 5000 psig with 5 psig divisions. The accuracy is ±0.1% of full scale. The sensitivity is ±0.01% of full scale. The gauge was calibrated by Heise using a dead weight pressure tester. There were no deviations from the 5 psig tolerance in the full range of the calibration. The maximum hysterisis was under 5 psig. The gauge utilizes Heise's patented 'thermal compensator' to correct for changes in ambient temperature. The Heise gauge is connected to the separation cell.

The separation cell (Figure 7) is stainless steel and has an internal volume of 72.4 cm^3. Its sapphire windows are 1 inch in diameter and 1 inch thick and are rated to 15,000 psi. The window seals are made with a gold and copper O-ring combination. This combination is fused into a single gasket by tightening the bolts on the face of the separation cell. The copper O-ring had to be notched so that the gasket could be removed without damaging the machined surfaces of the separation cell. The gasket proved suitable in service up to 5,000 psig at temperatures up to 96° C.

The metering valves used to control the streams leaving the separation cell are manufactured by Autoclave Engineers, model number 10VRMM2812. The valves use a finely tapered stem in a

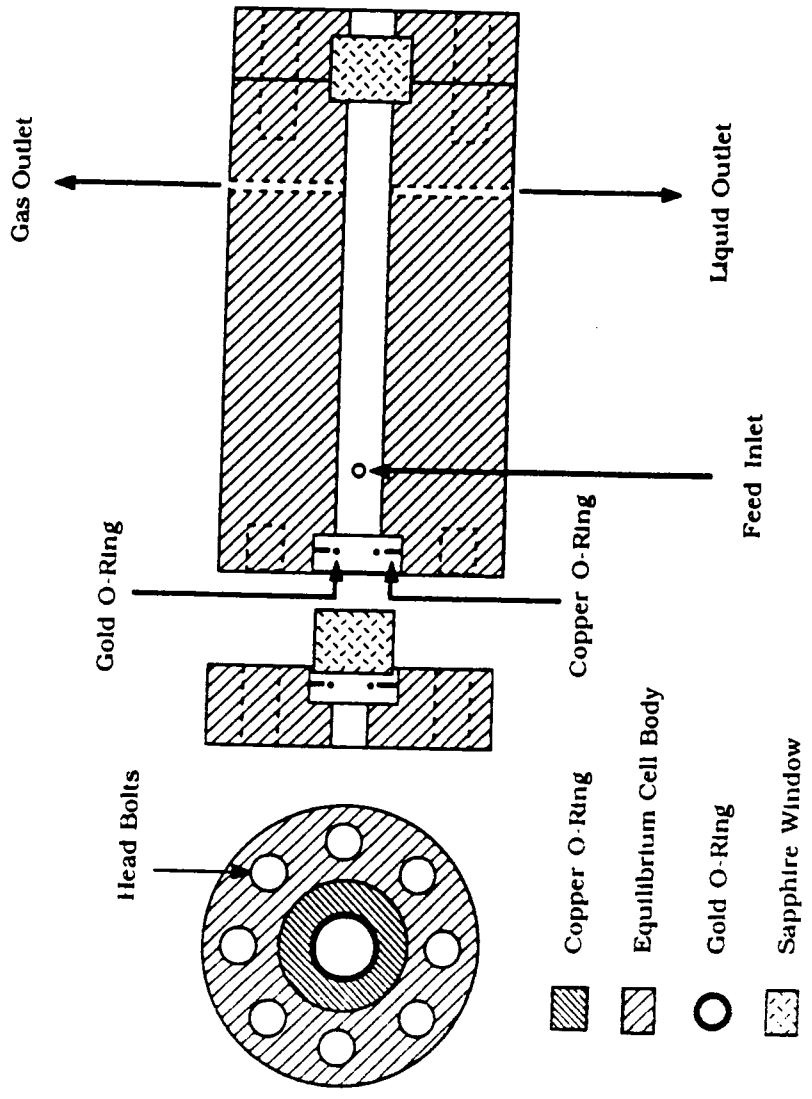

Figure 7: Equilibrium Cell

replaceable seat to effectively meter slow flows at high pressure. A single metering valve was used on the liquid exit (8) of the separation cell. On the gas exit (7), the pressure was dropped across two metering valves in series. These valves effectively controlled flowrate, but were of limited usefulness for controlling pressure. Minute changes in the valve setting led to large changes in pressure. The most effective strategy for controlling pressure was to set the valves and adjust the pumps to reach the appropriate pressure. At the zero setting, the metering valves allow a minimum flow. They are followed by an Autoclave shutoff valve (Model # 10V-2071). All valves are fitted with $\frac{1}{8}$ inch AE Speedbite connections. All tubing used in the apparatus was supplied by Autoclave Engineers. All tubing leaving the water bath is wrapped in heating tape and maintained at a temperature above the boiling point of the solute with Variacs.

The exit systems (Figure 8) for the apparatus are versatile and easily adapted to suit different experimental situations. The gas exit system consists of a cold trap to collect the solute and a wet test meter to measure the volume of gas leaving the separation cell. The wet test meter is an American AL-171 1 liter Wet Test Meter. One revolution of the meter is equivalent to one liter of gas, with divisions of 0.01 liter. The stated accuracy of the meter is 0.5% of the range. The meter requires flowrates from 0.015 LPM to 5.0 LPM. The wet test meter was calibrated by the Metrology Research and Development Laboratory at Martin Marietta. Volumes from wet test meters must be corrected for the temperature of the meter and the pressure drop

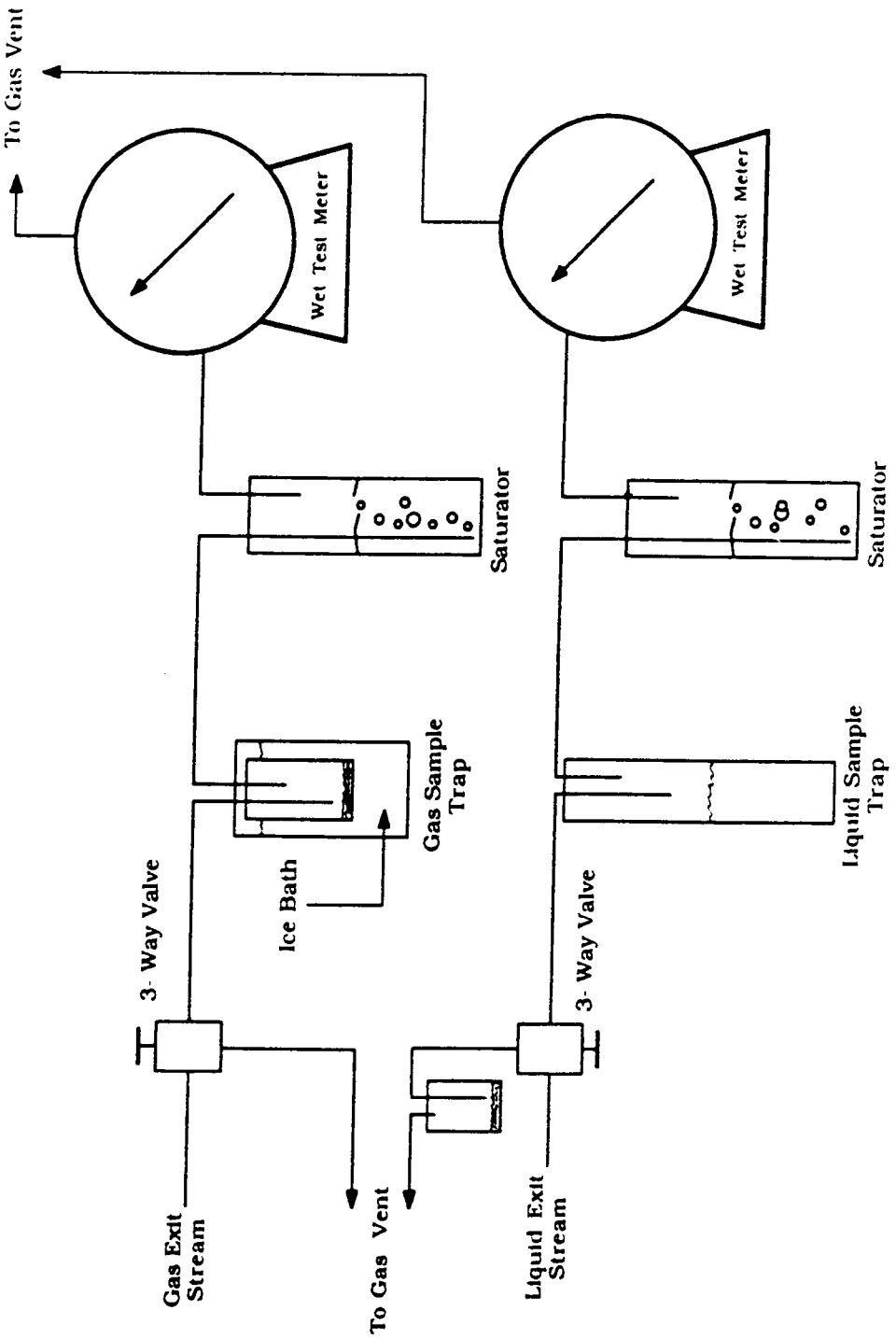

Figure 8: Gas and Liquid Exit Systems

across the meter. Flows used in this experiment did not cause a significant pressure drop across the wet test meter. The temperature corrections and calibration data are in the appendix.

In the liquid exit system, the liquid flows into a graduated cylinder and is collected for weighing. The CO_2 in the liquid stream is measured with a second wet test meter. This wet test meter was calibrated using a calibrated Matheson Flow controller. Nitrogen leaving the flow controller was saturated and flowed through the wet test meter. The run was timed and the volume of gas passed through the wet test meter was determined by the flowrate and time. These data are in the appendix.

Accurate sample weights are needed. Weights of butanediol in the cold trap are determined with a Metler AE 163 four place balance. The Metler balance is accurate to ±0.01%. The weight of liquid butanediol in the graduate is determined with a Sartorius two place balance (Model #1409) with a percent error of ±0.06%. The Sartorius balance will handle weights up to 599.99 grams.

Summary

There are advantages and disadvantages built into flow apparatus for high pressure VLE measurements. This equipment was selected because of the advantages that flow systems offer for biological

compounds. The construction of the current apparatus places some constraints on the systems and data ranges that can be investigated.

The limitations of this apparatus can be summarized as follows:

1. The gas delivery system limits the range of pressures and solvents that can be investigated. This system's minimum pressure is ~1000 psig for CO_2. The maximum pressure is 5000 psig.

2. The system pressure is difficult to control. The low flowrates used in these experiments caused small changes (<1.0%) in the valve setting to result in large changes in pressure.

3. The experimental temperatures are limited to those attainable in a water bath. The temperature range of the apparatus could be extended with an oil bath.

A Heise gauge or pressure transducer with a 10,000 psig range would allow a larger pressure range to be examined. A compressor would allow solvents to be delivered in this pressure range. A 10,000 psig liquid chromatography pump would bring the liquid delivery system into the same pressure range. Pressures in this range might require a revamping of the seal on the separation cell.

There are two approaches to making the system pressure more controllable. The first is to add some pressure control in the form of a back pressure regulator. The second is to move to higher temperatures. The system pressure is easier to stabilize and maintain at higher temperatures.

The advantages of this apparatus can be summarized as follows:

1. Flow systems allow accurate sampling in systems with limited solubility.

2. The sampling scheme does not disturb equilibrium.

3. The low residence time allows the investigation of thermally labile compounds.

4. The system can be easily adapted to handle a solid-fluid system.

5. The veiw cell allows the observation of phase behavior during experiments.

Comparison to Literature System

This equipment was verified by running an ethanol-ethane system whose data are available in the literature. The data produced by this flow system matched the literature data. Figures 9 and 10 illustrate the data of McHugh, Mallet and Kohn (1983). The black individual points on Figure 10 were taken using this apparatus. Data taken on this apparatus agrees well with the literature data. Data were taken by increasing the pressure from one point to the next and while decreasing pressure from point to point. The average deviation was 1.69%. The deviation between the literature and experimental mole fraction of ethane in the liquid phase is defined as:

$$\% \text{ Error} = \frac{x_{\text{lit.}} - x_{\text{expt.}}}{x_{\text{lit.}}} * 100 \qquad (11)$$

Purity of Chemicals

The gases used in this work were used as supplied by M.G. Industries. The C.P. grade bone dry CO_2 had a minimum purity of 99.8%. The C.P. grade ethane had a minimum purity of 99.0%.

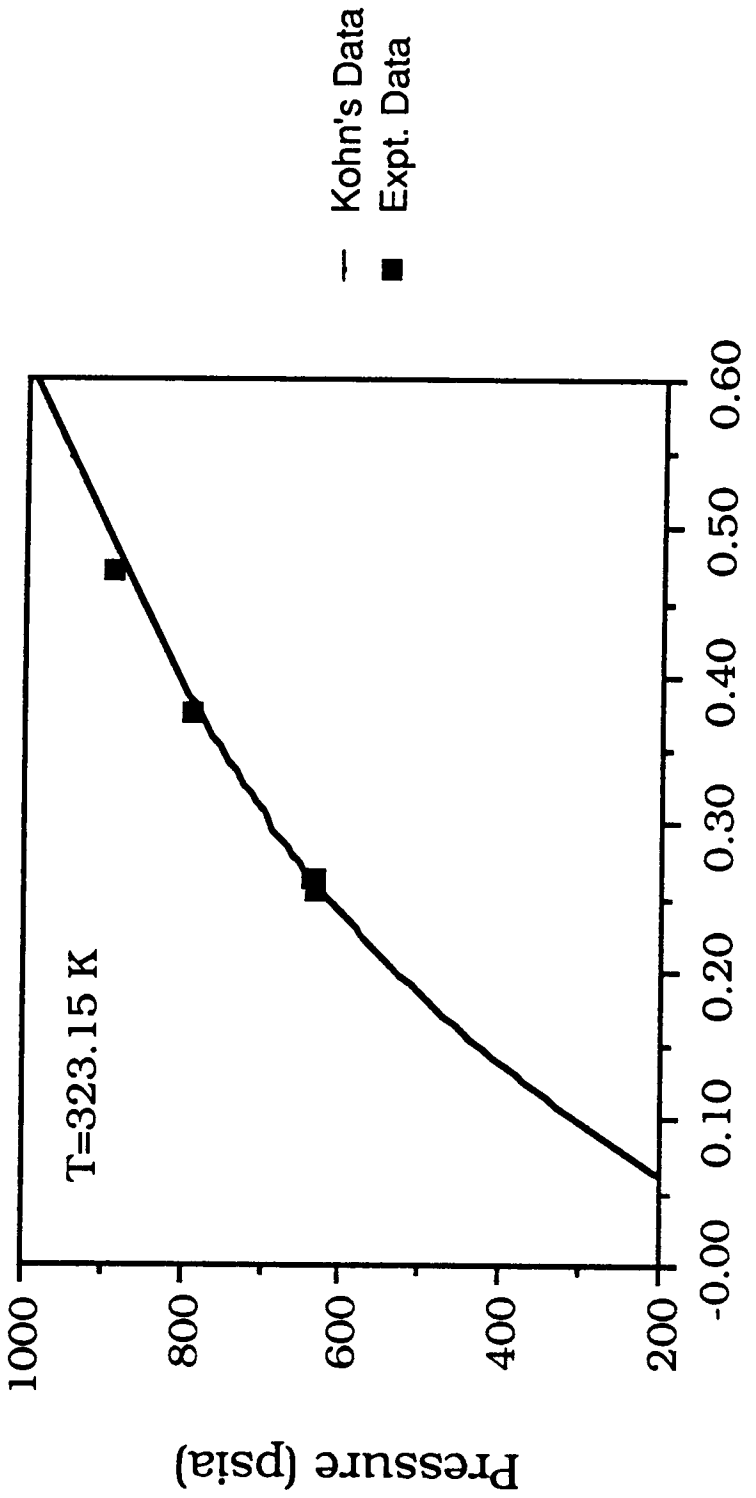

Figure 9: Comparison of Literature and Experimental Data

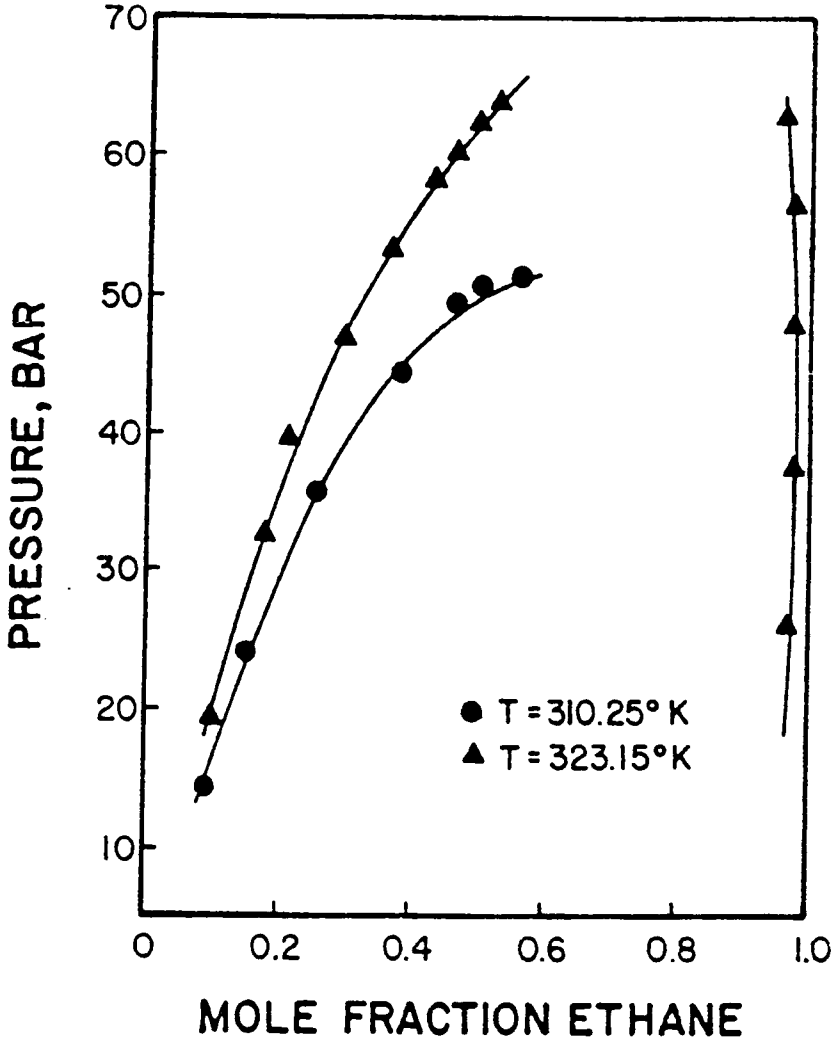

Figure 10: Data of McHugh, Mallet, and Kohn

The ethanol used was supplied by by U.S. Industrial Chemicals. The 200 proof ethanol was 99.9% pure and was used as supplied. The 2,3 butanediol was supplied by Pfaltz and Bauer at a 98.0% purity. The diol was further purified by distillation. The first 15% (by volume) of the distillate was discarded. The final 15% of the original volume was left in the boiling flask. The fraction of diol used had a boiling point of 181.8°C. The literature value for the boiling point of 2,3 butanediol is 182°C.

Experimental Procedure

The data are collected by the following procedure. Allow the water baths to reach the experimental temperature. Check the temperatures of the exit lines. They must be maintained above the boiling point of the solute. Ice the gas inlet lines and start the head cooler for the Milton Roy pump. The position of the metering valves is checked. While starting the apparatus, all metering valves should be at or near the zero setting. If the bath temperatures are stable, start CO_2 flow. The valve of the inverted gas cylinder is opened and the pressure rises slowly until the critical pressure is passed. As the pressure rises to within 750 psig of the desired pressure, open the gas metering valves until a gas flowrate of 1.0 to 0.50 LPM is reached. Within 500 psig of the desired experimental operating pressure, start the Waters pump at a flowrate of 4.0 to 5.0 milliliters per minute. (ml/min.) When a meniscus forms in the separation cell, slow the

liquid flowrate to 2.0 ml/min. Slowly begin to open the liquid metering valve to 3 to 4 % open. The system pressure should be rising at approximately 4 psig per minute. If the pressure is rising at a faster rate, crack the gas metering valve open **very** slightly. The pressure should stop rising for a moment. After a short time, the pressure should begin to rise slowly. A sudden drop in system pressure indicates too much of a change in the gas metering valve. Slow the rate at which the Milton-Roy pump adds CO_2 to the system until the pressure stabilizes. The liquid meniscus is best controlled by setting the metering valve and adjusting the rate at which liquid is being pumped in. Stabilizing the system is best accomplished at low flows and with few valve changes.

In the gas stream, the average liquid sample weighed 1.31 grams. The average volume of CO2 measured was 33.40 liters. The average weight of liquid collected on the liquid side was 16.44 grams. The average volume of gas collected from the liquid stream was 2.59 liters.

The temperature of the system was held within ±0.05°C of the experimental temperature. The pressure varied by ±10 psig from the average value.

When changing systems, pass N_2 through the system overnight at a flow rate of 1.0 LPM to insure that the previous solute is removed from the lines. Pump 500 to 600 milliliters of the new solute solution

through the system to insure none of the original solute remains in the lines. It is best to remove the liquid side pressure dampener and flush it clean with distilled water. If the new system is not an aqueous one, dry the pulse dampener with compressed air prior to its reinstallation.

V. RESULTS AND DISCUSSION

Results

The data in Table 1 were calculated from the raw data in the appendix, using a computer program. Figure 11 is a flowsheet of the program. The wet test meter corrections and calibrations were handled first. The final function of the program was to correct the experimental data for the solubility of butanediol in CO_2 at room temperature and pressure. The atmospheric pressure solubility was approximated using Raoult's Law. At the gas exit the temperature of the ice bath is used in the correction. On the liquid side, room temperature is used in the calculations. The values calculated from Raoult's law are compared to values calculated from the Peng-Robinson equation with the experimental k_{ij} in Table 2.

The Raoult's Law predictions were reasonable corrections for the liquid phase samples. There was a great deal of deviation from the ideal in the gas phase. Alternate corrections may need to be evaluated for the gas streams in the exit system.

The program also calculates the enhancement factor for the vapor phase mole fraction of butanediol.

Table 1: Experimental Data

Pressure psia	Bath Temp. K	M. F. Diol in Liquid Phase	M. F. Diol in Vapor Phase
2,024	319.4	0.6295	0.00950
2711	319.4	0.5969	0.01099
2,021	334.8	0.6374	0.00460
2,332	334.8	0.6137	0.00902
3,472	334.8	0.5677	0.02025
4,085	334.8	0.5081	0.02432
4,481	334.8	0.5054	0.02842
2,908	334.8	0.5671	0.01483
1,221	334.6	0.7340	0.00196
1,437	334.6	0.7149	0.00399
1,755	334.6	0.6756	0.00247
1,087	334.7	0.7444	0.00477
2,281	349.6	0.6280	0.00832
2,918	349.6	0.5605	0.01328
3,962	349.6	0.5073	0.00227
4,471	349.6	0.4775	0.00330
4,077	349.6	0.4964	0.02705
4,756	349.7	0.4584	0.03578
1,638	349.6	0.7166	0.00200
1,399	349.6	0.7387	0.00150
1,304	349.6	0.7458	0.00140
1,095	349.6	0.7858	0.00112
4,953	364.7	0.4309	0.05868
1,509	364.7	0.7120	0.00253
2,399	364.7	0.6245	0.00715
2,841	364.7	0.5749	0.01284
1,885	364.7	0.6911	0.00365
3,400	364.7	0.5233	0.01874

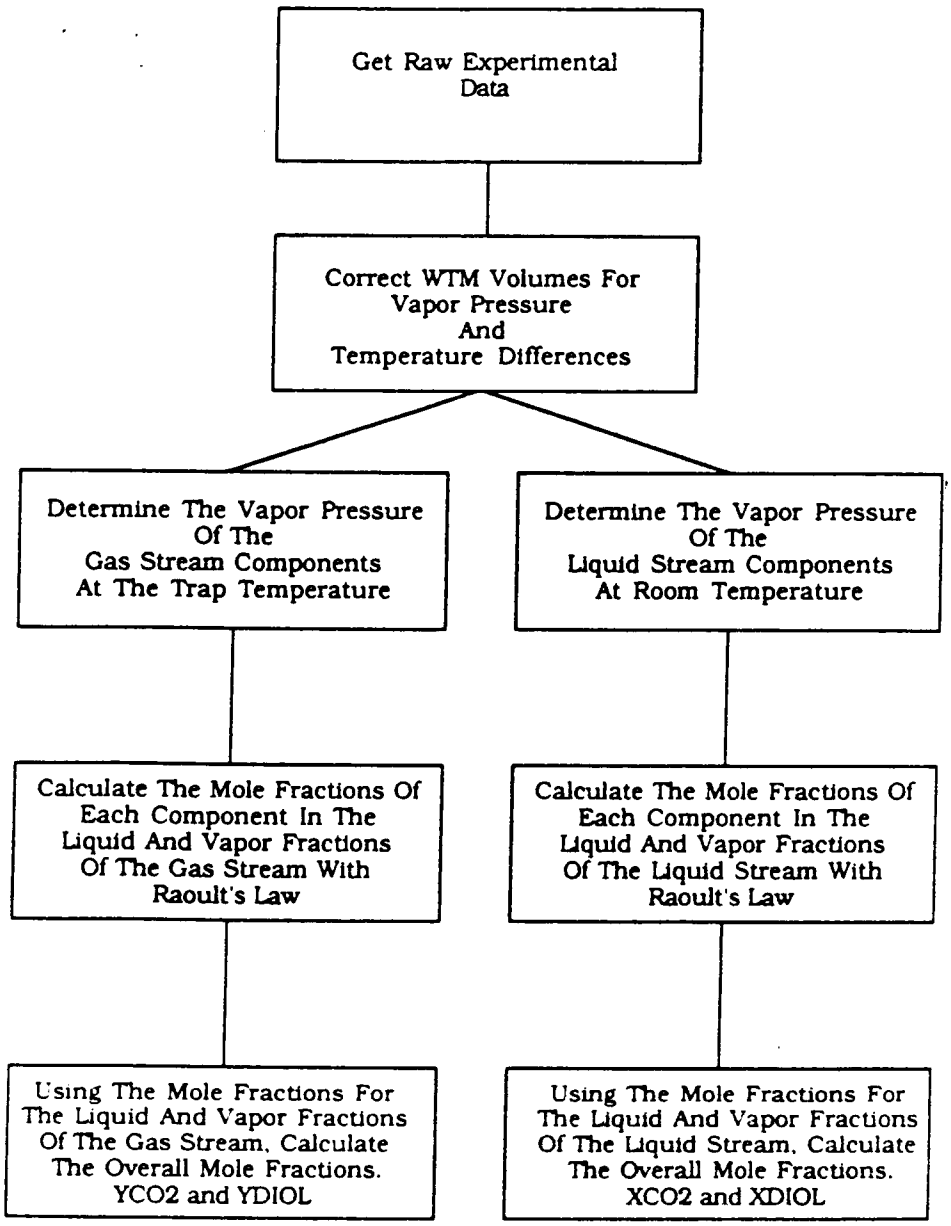

Figure 11: Flowsheet for Data Calculation Program

Table 2: Comparision of Mole Fractions Calculated from Raoult's Law and the Peng - Robinson EOS.

	Liquid Exit		Gas Exit	
	X_{Diol}	Y_{Diol}	X_{Diol}	Y_{Diol}
Raoult's	.9849	$7.7 \cdot 10^{-4}$	.9726	$2.3 \cdot 10^{-4}$
P-R EOS	.9942	$1.3 \cdot 10^{-4}$	.9916	$7.8 \cdot 10^{-6}$
% Error	.93%	492%	1.92%	2849%

The actual data range from a low temperature of 334.6 K to a high temperature of 365.0 K. The maximum 2,3-butanediol mole fraction in supercritical CO_2 was .0587. It occurred in the 365.0 K isotherm at a pressure of 4953 psia. The experimental data and model results for each isotherm are presented in Figures 12 through 15. The pressure vs. mole fraction isotherms predicted by the Peng - Robinson model are plotted in Figure 16. Figure 17 is a plot of the enhancement factor vs. pressure. The enhancement factor is defined as the experimental vapor phase mole fraction of the diol divided by the ideal mole fraction predicted from Raoult's Law and the vapor pressure, P_{sat}.

$$E = \frac{Y_{expt}}{Y_{ideal}} \tag{12}$$

$$Y_{ideal} = \frac{X \cdot P_{sat}}{P} \tag{13}$$

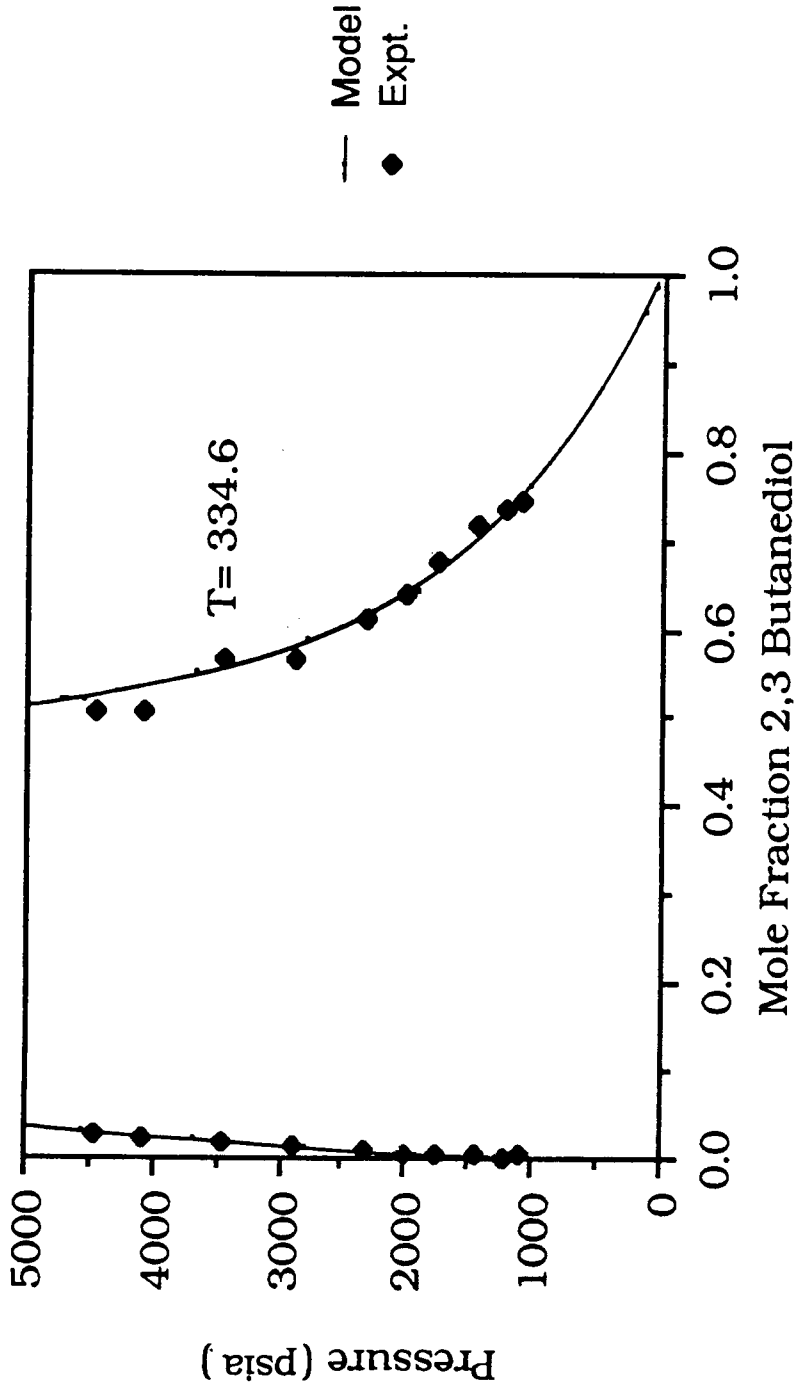

Figure 12: Mole Fraction 2,3 Butanediol vs. Pressure at T= 334.6 K

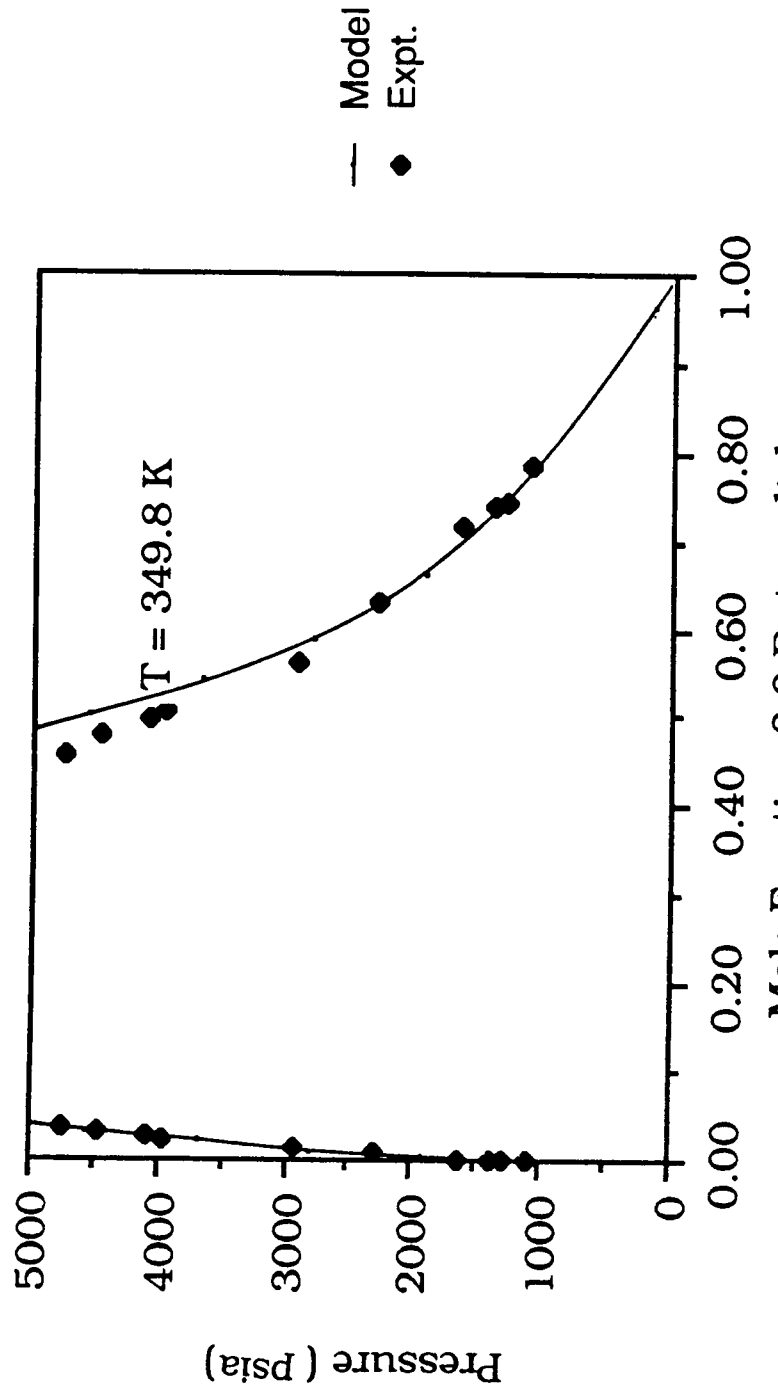

Figure 13: Mole Fraction 2,3 Butanediol vs. Pressure at T= 349.8 K

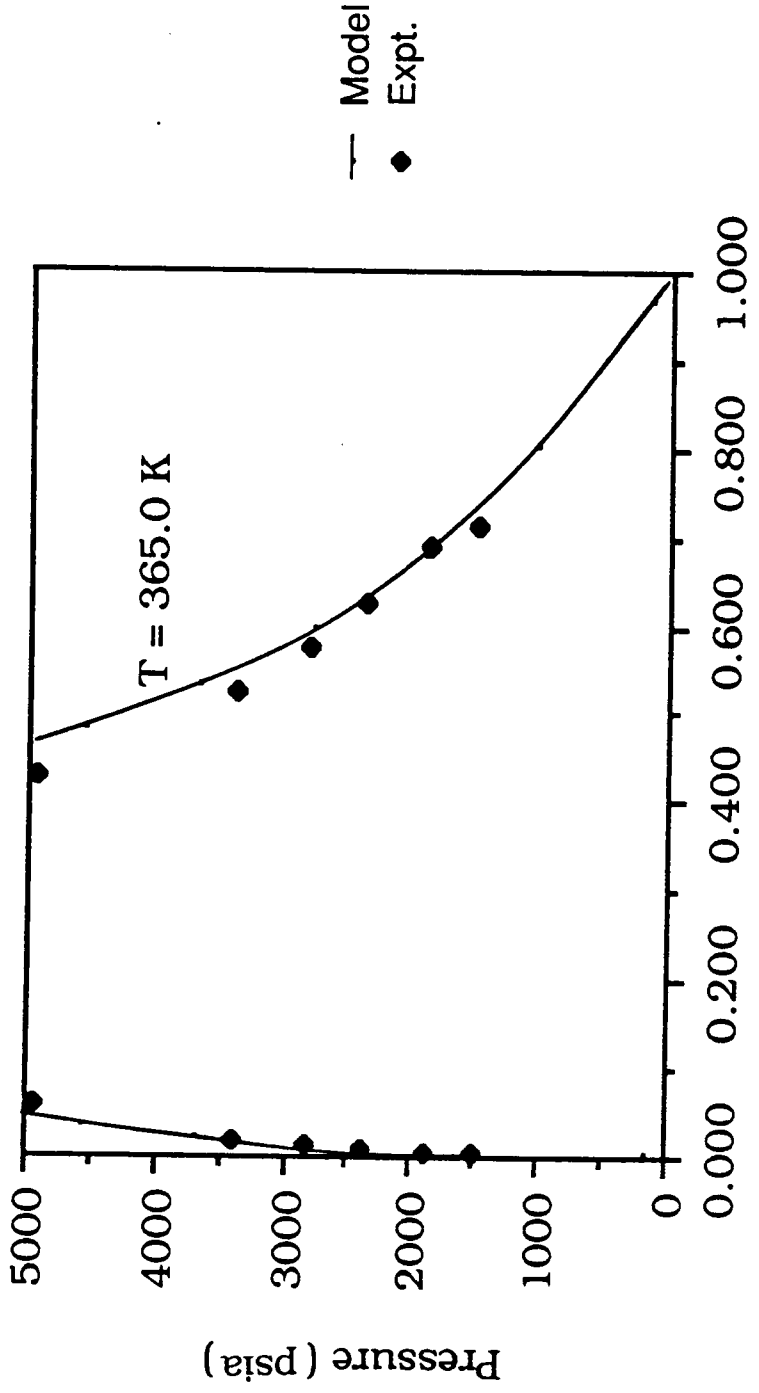

Figure 14: Mole Fraction 2,3 Butanediol vs. Pressure at T= 365.0 K

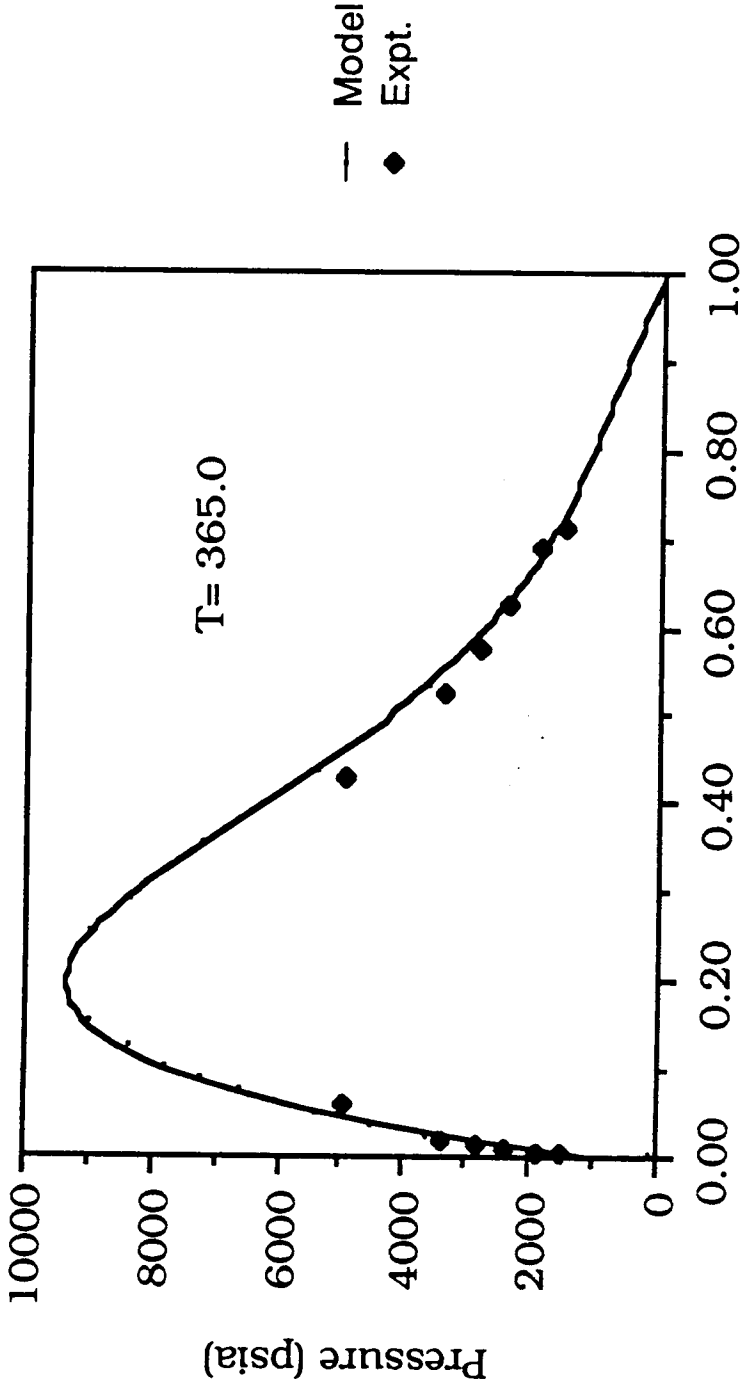

Figure 15: Model Predicted Isotherm at T= 365.0

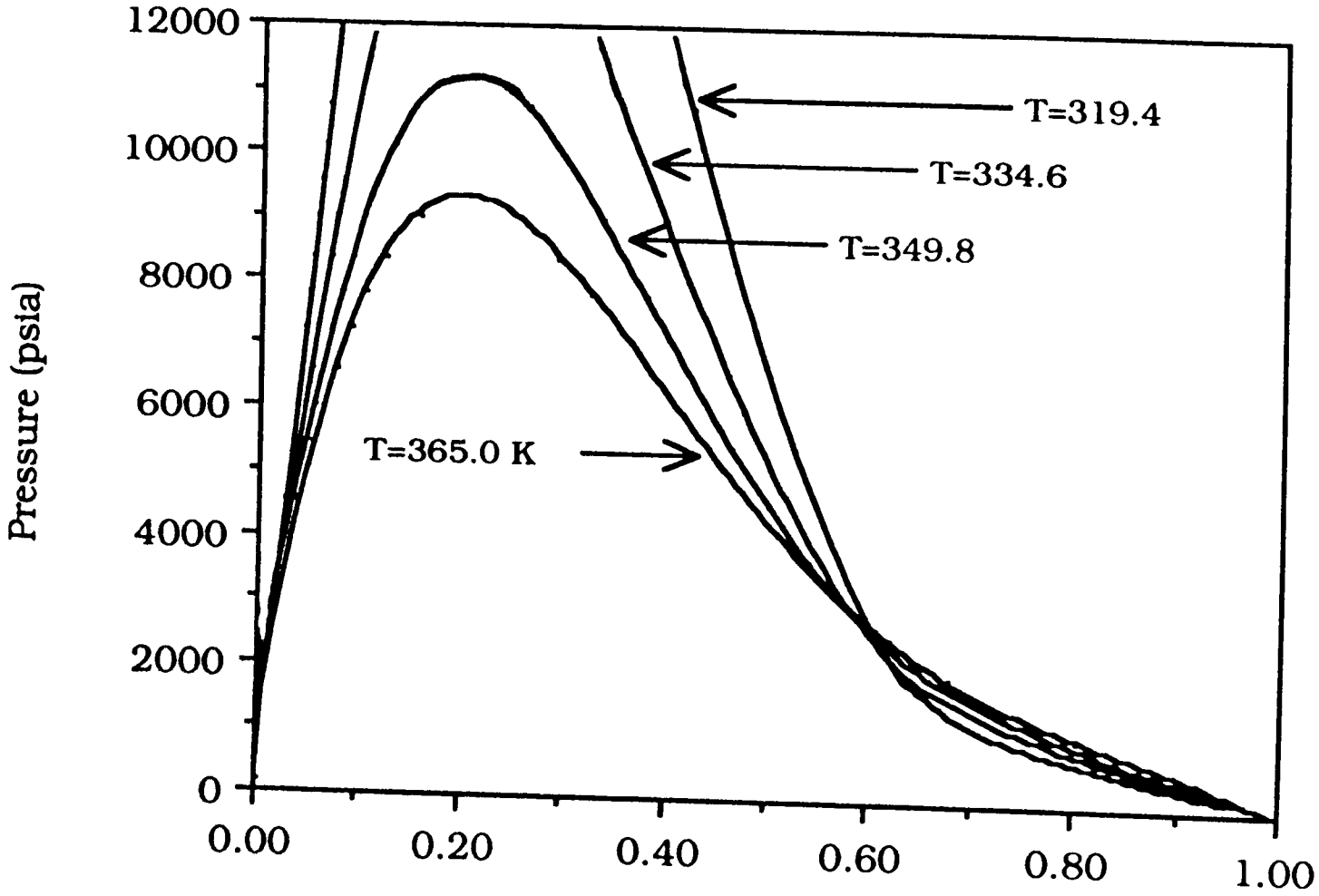

Figure 16: Model Predictions for All Isotherms

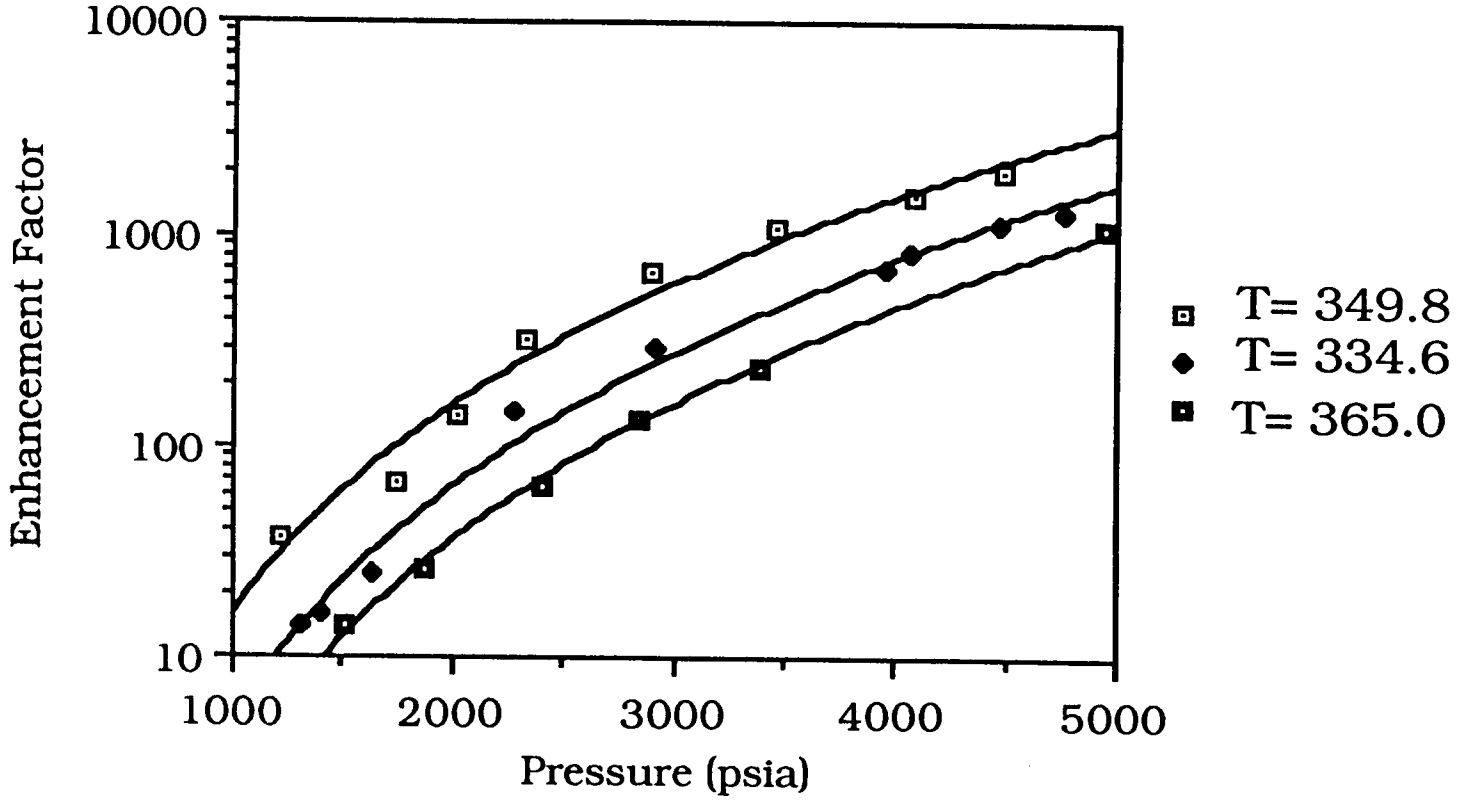

Figure 17: Plot of Enhancement Factor vs Pressure

The difference between ideal and actual solubility is easily seen in Figure 18, both the actual and ideal mole fraction of diol in the vapor phase are plotted against pressure.

Discussion of Model

Modeling the butanediol system required the estimation of criticals for 2,3-butanediol. Reid (1987) presents several different approaches to critical estimation. In many biological systems, critical data cannot be found. These estimations are of paramount importance when a cubic equation of state is being used.

Criticals for 2,3 butanediol were predicted by methods developed by Lyderson, Joback, and Ambrose. All three of these methods are group contribution estimations. Joback's revision of Lyderson's method gave a critical pressure of 738.1 psia and a critical temperature of 613.3°K. Ambrose gave a higher critical temperature of 687.6°K. Data from the method developed by Joback were used because they resulted in the lowest overall errors. They were calculated from the following equations (Reid, 1987):

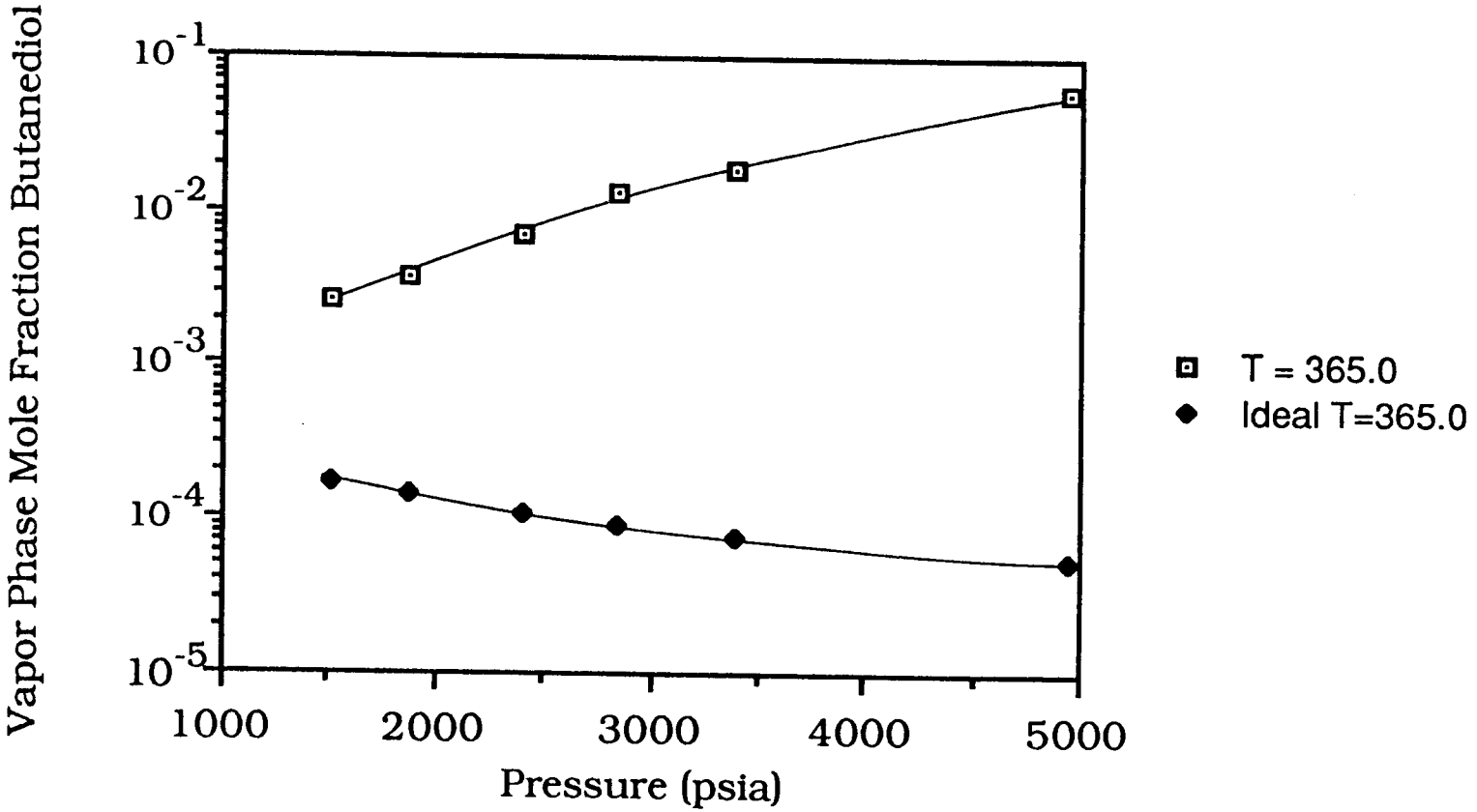

Figure 18: Mole Fraction Butanediol in the Vapor Phase vs. Pressure

$$T_c = T_b(1 + (1.242 + \Sigma \Delta_T)^{-1} \quad (14)$$

$$P_c = M(0.339 + \Sigma\Delta_P)^{-2} \quad (15)$$

where:

T_b = boiling temperature, K

M = molecular weight, $\left(\frac{g}{gmol}\right)$

$\Sigma\Delta_T$ = group contribution parameter

$\Sigma\Delta_P$ = group contribution parameter

The critcals for CO_2 were obtained from the International Thermodynamic Tables of The Fluid State of Carbon Dioxide (1955). The critical pressure for CO_2 is 72.8 atm., the critical temperature is 304.2 K, and the accentric factor is 0.225.

The Peng-Robinson equation also requires the acentric factor, ω, for 2,3 butanediol. The acentric factor is defined:

$$\omega = - \log P_R^{sat} - 1.00 \quad (16)$$

Where:

P_R^{sat} = reduced vapor pressure at a reduced temperature, T_r=0.70.

The vapor pressure data for 2,3 butanediol are plotted in the appendix. From this vapor pressure data, the ω calculated for 2,3-butanediol is 1.056.

The results of this experiment indicate that the 2,3-butanediol-CO2 system can be modeled by a cubic equation of state at high pressures. The k_{ij} for the system was determined by minimizing the average absolute deviation (AARD) for both the liquid and vapor phases mole fractions. The AARD is defined:

$$AARD = \frac{1}{N} \sum_{N}^{i=1} Abs\left(\frac{X^{calc.} - X^{expt.}}{X^{expt.}}\right) \qquad (17)$$

The k_{ij} for all data was 0.067 and gave rise to an average 30.2% AARD for the system. For most systems, the values of k_{ij} range from 0 to .15 (Walas, 1985). Kim, Bae, and Hong (1987) have applied the Peng Robinson equation of state to many solid - fluid systems. They minimized the vapor phase AARD and found k_{ij}'s for seventy systems. They report good agreement between the model and the experimental data. In this data, the Peng-Robinson model provides a mediocre fit for the data. The primary cause of the poor fit is questionable data in the low temperature and pressure region seen in Figure 17, a plot of enhancement factor vs. pressure. The 334.6 K isotherm is extremely irrregular at low pressures. This is due to the small sample of diol collected on the gas side in these runs (0.300g). The Peng-Robinson

equation should be able to fit this data within 15-20 %. A better fit than this is not likely, because the 2,3 butanediol system is polar.

McClellan (1974) reports a dipole moment of 2.1 Debye for 2,3-butanediol. The naphthalene - CO_2 system is a classical SCFE system that is well modeled by a cubic equation of state (Kim, Bae, and Han, 1987; McHugh and Krukonis, 1986). In contrast to the butanediol system, naphthalene has no dipole moment. The effects of a polar solute are difficult to quantify with a simple cubic equation of state. A statistical mechanical approach utilizing the BACK equation of state (Lee and Chao, 1986) or an augmented van der Waals treatment (Johnston, Ziger, and Eckert, 1982) may model a polar system better than a simple cubic equation of state.

VI. RECOMMENDATIONS AND CONCLUSIONS

Recommendations

This experimental work leads to several recommendations. Adaptations of the equipment will be discussed along with direction for additional work.

When Figures 12 - 15 are examined, the most obvious system limits are the 1000 psig minimum solvent delivery pressure and the maximum pressure of 5000 psig, dictated by the Heise gauge. Solubility in the range of 1000 to 5000 psig is not extremely pressure or temperature dependent. If experimental data useful in the development of theoretical models are desired, a larger pressure and temperature range is needed. The low pressure data can be obtained by using a high pressure gas regulator to deliver the solvent. The higher pressures are limited by the Heise gauge at 5000 psig and by both pumps at 6000 psig. A pressure transducer that could handle pressures up to 10000 psig and interface with the existing computer data collection system would solve the pressure measurement problem. A compressor for solvent delivery would allow higher system pressures. It could also be combined with a mass blender to greatly expand the number of systems that can be handled on the apparatus.

Custom binary solvent mixtures could be designed and tested. High pressure liquid chromatography pumps capable of delivering a liquid solvent at pressures higher than 6000 psig and at the required low, accurate flowrates would have to be obtained to deliver the liquid solute at this higher pressure. The current pressure limit offers direction in terms of future work.

Data for the low pressure range (0 - 1000 psig) are needed for the 2,3-butanediol system. This data can be taken on the current system with the addition of a high pressure gas regulator. Accurate data for the low temperature and mid-range pressures are also needed. These data could be obtained by operating the existing apparatus at higher flowrates.

If solid- fluid systems are to be evaluated with this equipment, the aquarium which serves as a water bath must be replaced. The replacement bath should be metal, so that the metering valves can be mounted on it. There are two problems associated with the valves. First, if mounted outside the bath, temperature drops cause some solute to drop out. The fine taper of the valve allows these minute amounts of solute to plug the metering valve. This plugging causes fluctuations in pressure that disrupt steady state operation. The second problem associated with the current configuration of the valves is the fact that the exit lines must run uphill to leave the aquarium. In a solid - fluid system, these uphill lines will cause problems as the solid solute drops out. Ideally, the water level of the bath should be

maintained just below the exit of the valve and the sampling system should be below the valve. The exit lines from a metal bath could run down hill immediately. The current lines must first run up and over the edge of the aquarium before they can run into the exit system. This invites plugging problems in a solid fluid system. A metal bath could also provide some protection from the high pressure parts of the system. The difficulty with a metal bath is sealing the window which must be present so that the equilibrium cell can be viewed. This might prove tricky, but is far from impossible.

Conclusions

The apparatus constructed for these experiments is suitable for evaluating SCFE systems in the range 2000 to 5000 psig. The range of 1000 to 2000 psig must be investigated further. Faster CO_2 flowrates should provide the larger liquid samples needed on the gas side to insure accurate data.

A high pressure gas regulator and a compressor would make the solvent delivery system much more versatile. The addition of the regulator would give the current apparratus a range from 0 to 5000 psig. If higher pressures are to be investigated, the pressure measuring capability must be upgraded.

This work provides the vapor liquid equilibrium data necessary to approximate a rough cost of SCFE for a 2,3- butanediol fermentation. A better model and broader range of data are needed. The apparatus constructed for these experiments can be adapted to handle a solid-supercritical fluid system. The Peng - Robinson model can be used to examine other systems of interest. Data taken on this apparatus from judiciously selected systems would prove useful in establishing a better model for biological systems like CO_2 - 2,3 - butanediol.

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APPENDIXES

APPENDIX A

RAW DATA

	A	B	C	D	E	F	G	H	I	J	K	L
1					Table of Raw	Data						
2												
3					Gas Phase	Gas Phase	Gas Side	Liquid Phase	Liquid Phase	Liquid Side	Room Temp	Flowrate
4	Pressure	Bath Temp.	M. F. Diol In	M. F. Diol In	Vol. CO2	Wt. Diol	Wet Test Mtr.	Vol. CO2	diol collected	Wet Test MTR.		
5	PSIA	K	Liquid Phase	Vapor Phase	Liters	grams	K	Liters	grams	K	K	LPM
6												
7					Tr=1.05							
8												
9	2,023.70	319.41	0.6295	0.00948	37.47	1.32	294.75	1.64	10.66	293.65	296.75	1.25
10	2,710.70	319.39	0.5969	0.01099	34.05	1.39	295.25	1.65	9.32	294.45	296.65	1.13
11					Tr=1.10							
12	2,020.70	334.76	0.6374	0.0046	30.07	0.49	295.55	2.01	13.70	294.15	293.85	0.75
13	2,331.70	334.78	0.6137	0.00902	34.23	1.13	294.45	1.65	9.97	296.15	297.75	1.00
14	3,471.70	334.80	0.5677	0.02025	43.86	3.35	296.55	1.39	6.96	295.15	295.98	1.46
15	4,084.70	334.79	0.5081	0.02432	26.16	2.41	296.15	3.34	13.12	294.95	295.50	1.05
16	4,480.70	334.79	0.5054	0.02842	23.86	2.58	297.25	2.48	9.59	296.15	296.73	0.99
17	2,907.70	334.80	0.5671	0.01483	36.72	2.04	296.15	2.44	12.18	295.65	296.17	1.52
18	1,220.70	334.58	0.734	0.00196	49.36	0.32	295.15	1.90	20.58	294.45	295.00	1.65
19	1,436.70	334.56	0.7149	0.00399	73.57	1.04	294.65	0.84	8.32	293.75	292.76	2.46
20	1,754.70	334.56	0.6756	0.00247	45.17	0.38	294.05	2.19	17.93	293.05	292.07	1.77
21	1,086.70	334.89	0.7444	0.00477	36.23	0.62	296.85	1.92	21.95	295.15	295.53	1.22
22					Tr=1.15							
23	2,281.10	349.56	0.628	0.00832	38.30	1.10	299.95	1.91	11.77	299.35	297.85	1.51
24	2,918.20	349.57	0.5805	0.01328	53.89	2.52	300.35	3.22	14.94	299.95	298.15	1.37
25	3,961.70	349.61	0.5073	0.00227	12.82	1.09	298.15	3.31	12.98	299.95	295.15	0.36
26	4,471.10	349.64	0.4775	0.0033	23.50	2.84	297.85	5.56	18.41	296.35	296.65	0.37
27	4,077.10	349.57	0.4964	0.02705	7.37	0.73	297.85	3.43	12.19	295.85	298.25	0.51
28	4,756.10	349.70	0.4584	0.03578	10.38	1.36	298.15	2.13	6.48	296.15	298.45	0.60
29	1,637.70	349.57	0.7166	0.002	32.68	0.22	295.15	1.23	12.21	293.85	294.15	0.56
30	1,396.70	349.63	0.7397	0.0015	26.05	0.12	295.55	2.41	26.85	294.25	294.45	0.80
31	1,303.70	349.66	0.7458	0.0014	38.17	0.16	298.15	2.65	30.47	296.55	296.05	1.31
32	1,094.70	349.64	0.7858	0.00112	32.65	0.11	295.95	3.01	43.76	297.95	296.25	0.82
33					Tr=1.20							
34	4,952.70	364.67	0.4309	0.05868	18.40	4.31	294.15	1.56	4.50	296.25	293.85	0.93
35	1,508.70	364.69	0.712	0.00253	30.05	0.26	296.65	1.72	16.60	299.75	295.15	1.54
36	2,398.70	364.66	0.6245	0.00715	30.66	0.80	295.15	3.19	20.57	293.35	293.43	1.22
37	2,840.70	364.65	0.5749	0.01284	40.80	1.95	294.65	4.67	24.39	293.05	293.06	1.36
38	1,884.70	364.66	0.6911	0.00365	47.49	0.61	296.05	2.68	23.35	293.95	294.82	1.90
39	3,399.70	364.66	0.5233	0.01874	21.16	1.49	295.95	6.28	26.46	294.05	293.45	0.85

	A	B	C	D	E	F	G	H	I	J	K	L
1						Table of Raw	ETOH/Ethane	Data				
2												
3					Gas side	Gas Side	Gas Side	Liquid Side	Liquid Side	Liquid Side	Room	FLOWRATE
4	Pressure	Temperature	M.F. ETOH	M.F. ETOH	WTM Vol	Weight ETOH	WTM Temp.	WTM Vol.	Weight ETOH	WTM Temp.	Temperature	LPM
5	PSIA	K	in Liquid	in Vapor	Liters	Grams	K	Liters	Grams	K	K	
6												
7	631	323.25	0.7463	0.01217	46.728	0.9121	297.75	11.35	68.43	297.15	296.06	0.53
8	632.2	323.25	0.7367	0.01196	52.274	0.99053	298.35	12.01	68.34	297.45	296.42	0.59
9	786.7	323.25	0.624	0.01362	101.532	2.2964	297.95	20.43	65.26	297.15	297.35	1.19
10	640	323.25	0.7373	0.01152	115.506	2.1506	298.45	7.45	42.31	297.55	297.15	1.93
11	888.5	323.25	0.5282	0.01918	54.226	1.8153	298.15	9.94	20.57	298.05	298.05	1.76

APPENDIX B

COMPUTER PROGRAMS

```
C       This program calculates the P-V diagram for Binary systems
C       THE PROGRAM USES DOUBLE PRECISION VARIABLES. THE DOUBLE PRECISION
C       IMSL ROOT FINDING ROUTINE, DZPORC, IS USED. THE IMSL LIBRARY MUST BE
C       SPECIFIED WHEN THE PROGRAM IS LINKED.

C       DECLARE VARIABLES
 REAL*8 TC1,TC2,PC1,PC2,OMEGA1,OMEGA2,X1,X2,Y1,Y2,ATC1,ATC2,A1,A2
 REAL*8 TR1,TR2,TFAC1,TFAC2,B1,B2,ALPHA1,ALPHA2,P,T,R,ZZV,ZZL
 REAL*8 BVM,BVZ,AVZ,AVM,VMIX2,VMIX1,BLM,BLZ,ALM,ALZ,LMIX1,LMIX2
 REAL*8 KIJ,K1,K2,CV(4),CL(4),PHIV1,PHIV2,PHIL1,PHIL2,MVV,MVL
 REAL*16 CR(3)
 COMPLEX*16 ZV(3),ZL(3)
 INTEGER IER1,IER2,NDEG


C       ENTER THE CRITICAL DATA CO2=2, 2,3-BDIOL=1
C       ENTER R IN (CM^3*ATM)/(GMOL*K) AND T IN K

 DATA TC2,PC2,OMEGA2/304.2,72.8,0.225/
 DATA TC1,PC1,OMEGA1/613.32,50.21,1.056/
 DATA R,T,KIJ/82.05,319.4,0.067/

C       OPEN OUTPUT FILES
 OPEN(UNIT=8,FILE='K105.DAT',STATUS='NEW')
 WRITE(8,*) ' '

 OPEN(UNIT=7,FILE='MODMV.DAT',STATUS='NEW')
 WRITE(7,*) ' '

C       THE PENG-ROBINSON EQUATION WILL BE USED IN THE FORM
C       Z^3-(1-B)*Z^2+(A-3*B^2-2*B)*Z-(A*B-B^2-B^3)=0
C       A AND B WILL BE DETERMINED BY THE USUAL MIXING RULES,
C       FROM THE PURE COMPONENT INFORMATION.


C       CALCULATING THE PURE COMPONENT A'S (LITTLE A'S) AND B'S
C       FOR THE PR-EOS

 ATC1=0.45724*R**2*TC1**2/PC1
 ATC2=0.45724*R**2*TC2**2/PC2

 TFAC1=.37464-1.54226*OMEGA1-.26992*OMEGA1**2
 TFAC2=.37464-1.54226*OMEGA2-.26992*OMEGA2**2

 TR1=T/TC1
 TR2=T/TC2

 ALPHA1=(1-TFAC1*(1.0-TR1**.5))**2
 ALPHA2=(1-TFAC2*(1.0-TR2**.5))**2

 A1=ATC1*ALPHA1
 A2=ATC2*ALPHA2
```

```
C       CALCULATING THE B'S FOR PR-EOS

 B1=0.0778*R*TC1/PC1
 B2=0.0778*R*TC2/PC2


C       ESTABLISH THE INITIAL DISTRIBUTION COEFFICIENTS FOR THE SYSTEM
 K1=0.1
 K2=3.0

C       ESTABLISH DO LOOP THAT WILL CALCULATE THE EQUIB MOLE FRACTIONS
C       FOR A RANGE OF PRESSURES

 DO 5000 P=10,760,20

C       CALCULATE THE MOLE FRACTIONS FROM THE GIVEN INITIAL K-VALUES
1000    X1=(1.0-K2)/(K1-K2)
 X2=1.0-X1
 Y1=X1*K1
 Y2=1.0-Y1
 ZZV=0.0
 ZZL=0.0

C       DEBUG STATEMENTS
C       WRITE(8,1010)X1,X2,Y1,Y2
C1010   FORMAT(1X,'X1=',D16.5,1X,'X2= ',D16.5,1X,'Y1,Y2= ',D16.5,1X,D16.5)

C       CALCULATE THE CONSTANTS FOR PR EOS USING MIXING RULES
C       VAPOR PHASE CONSTANTS

 AVIJ=Y1*Y2*(1.0-KIJ)*(A1*A2)**.5
 AVM=Y1**2*A1-2*AVIJ-Y2**2*A2

 BVM=B1*Y1-B2*Y2

C       LIQUID PHASE CONSTANTS

 ALIJ=X1*X2*(1.0-KIJ)*(A1*A2)**.5
 ALM=X1**2*A1-2*ALIJ-X2**2*A2

 BLM=B1*X1-B2*X2

C       CONVERT AVM,BVM AND ALM,BLM INTO APPROPRIATE FORM FOR THE Z
C       FORM OF THE PR EOS

 AVZ=AVM*P/(R*T)**2
 BVZ=BVM*P/(R*T)

 ALZ=ALM*P/(R*T)**2
 BLZ=BLM*P/(R*T)

C       ESTABLISH THE COEFFICIENTS FOR THE VAPOR PHASE PR-EOS
C      CV4=1.0, CV3=-(1.0-BVZ), CV2=(AVZ-3*BVZ**2-2*BVZ)
C       CV1=-(AVZ*BVZ-BVZ**2-BVZ**3)
```

```
      CV(4)=1.0
      CV(3)=-(1.0-BVZ)
      CV(2)=AVZ-3*BVZ**2-2*BVZ
      CV(1)=-(AVZ*BVZ-BVZ**2-BVZ**3
C           DEBUG STAEMENTS
C           WRITE(8,1020)CV(1),CV(2),CV(3),CV(4)
C1020       FORMAT(1X,'CV1=',D16.8,' CV2=',D16.8,' CV3=',D16.8,' CV4',D16.8)

C           SET ZPOLAR ERROR CODE TO ZERO
      IER1=0.0
C           SET NDEG FOR ZZPOC EQUAL TO THREE FOR CUBIC EQUATION
      NDEG=3

C           CALL DZPORC AND SOLVE FOR THE VAPOR PHASE Z

      CALL DZPORC(NDEG,CV,ZV,IER1)

      IF (IER1.NE.0) THEN
           PRINT *,'IER1=',IER1
      END IF

C           THIS LOOP CHECKS FOR COMPLEX ROOTS AND PRINT AN ERROR
C           MESSAGE IF COMPLEX ROOTS ARE FOUND

      DO 1500 I=1,3,1
      CR(I)=DIMAG(ZV(I))
      IF (CR(I).GT.1.0E-7.OR.CR(I).LT.-1.0E-7) THEN
           ZV(I)=(0.0,0.0)
      END IF
1500       CONTINUE

C           THESE STATEMENTS SELECT THE HIGH VALUE OF ZV
C           MUST FIRST CONVERT Z'S TO REAL NUMBER, BECAUSE YOU
C           CAN'T PERFORM LOGICAL OPERATIONS ON COMPLEX NUMBERS
      ZV1=REAL(ZV(1))
      ZV2=REAL(ZV(2))
      ZV3=REAL(ZV(3))

      IF (ZV1.GT.ZV2.AND.ZV1.GT.0) THEN
           ZZV=ZV1
      END IF
      IF (ZV2.GT.ZZV.AND.ZV2.GT.0.0) THEN
           ZZV=ZV2
      END IF
      IF (ZZV.LT.ZV3.AND.ZV3.GT.0) THEN
           ZZV=ZV3
      END IF

C           DEBUG STATEMENTS
C           WRITE(8,1505) ZZV
C1505       FORMAT(1X,'ZZV= ',D16.8)
```

```
C         CALCULATE THE LIQUID PHASE COEFFICIENTS FOR THE PR EOS
C         THEY CORRESPOND TO THE VAPOR COEFF'S DEFINED ABOVE

 CL(4)=1.0
 CL(3)=-(1.0-BLZ)
 CL(2)=ALZ-3*BLZ**2-2*BLZ
 CL(1)=-(ALZ*BLZ-BLZ**2-BLZ**3)
C
C         ZERO THE ERROR FUNCTION FOR ZPOLAR
 IER2=0
C         DEBUG STATEMENTS
C         WRITE(8,*)CL(1),CL(2),CL(3),CL(4)

C         CALL DZPORC AND SOLVE FOR THE LIQUID PHASE Z

 CALL DZPORC(NDEG,CL,ZL,IER2)
 IF (IER2.NE.0) THEN
         PRINT *,'IER2=',IER2
 END IF

C         THIS LOOP CHECKS ZL FOR IMAGINARY ROOTS AND
C         SUBSTITUTES 0.0,0.0 FOR COMPLEX ROOTS

 DO 1750 I=1,3
 CR(I)=DIMAG(ZL(I))
 IF (CR(I).GT.1.0E-7.OR.CR(I).LT.-1.0E-7) THEN
         ZL(I)=0.0
 END IF
 1750    CONTINUE
C         WRITE(8,*) ZL(1),ZL(2),ZL(3)

C         THIS LOOP SELECTS THE LOW ROOT FOR ZL
C         CONVERT IMAGINARY ZL(I)'S INTO REAL ZL1-ZL3

 ZL1=REAL(ZL(1))
 ZL2=REAL(ZL(2))
 ZL3=REAL(ZL(3))

 IF (ZL1.LT.ZL2.OR.ZL1.GT.0.0) THEN
         ZZL=ZL1
 END IF
 IF (ZL2.LT.ZZL.AND.ZL2.GT.0.0) THEN
         ZZL=ZL2
 END IF
 IF (ZL3.LT.ZZL.AND.ZL3.GT.0.0) THEN
         ZZL=ZL3
         END IF
 IF (ZZL.LE.0.0) THEN
         ZZL=ZL3
 END IF

C         CALL SUBROUTINE LNPHI TO CALCULATE THE NATURAL LOG OF THE
C         LIQUID AND VAPOR PHASE FUGACITY COEFFICIENTS
```

```
C
C         FOR THE VAPOR PHASE FUGACITY COEFFICIENT FOR COMPONENT 1

 VMIX1=Y1*A1+Y2*(1.0-KIJ)*(A1*A2)**0.50
 CALL LNFUGCF(B1,BVM,ZZV,BVZ,AVZ,AVM,VMIX1,PHIV1,K1,K2)

C         FOR THE VAPOR PHASE FUGACITY COEFFICIENT OF COMPONENT 2

 VMIX2=Y2*A2+Y1*(1.0-KIJ)*(A1*A2)**0.50
 CALL LNFUGCF(B2,BVM,ZZV,BVZ,AVZ,AVM,VMIX2,PHIV2,K1,K2)

C         FOR THE LIQUID PHASE FUGACITY COEFFICIENT OF COMPONENT 1

 LMIX1=X1*A1+X2*(1.0-KIJ)*(A1*A2)**0.50
 CALL LNFUGCF(B1,BLM,ZZL,BLZ,ALZ,ALM,LMIX1,PHIL1,K1,K2)

C         FOR THE LIQUID PHASE FUGACITY COEFFICIENT OF COMPONENT 2

 LMIX2=X2*A2+X1*(1.0-KIJ)*(A1*A2)**0.50
 CALL LNFUGCF(B2,BLM,ZZL,BLZ,ALZ,ALM,LMIX2,PHIL2,K1,K2)


C         CALCULATE THE FUGACITIES FOR COMPONENTS 1 & 2 IN THE VAPOR PHASE

 FV1=Y1*P*EXP(PHIV1)
 FV2=Y2*P*EXP(PHIV2)


C         CALCULATE THE LIQUID PHASE FUGACITIES FOR COMPONENTS 1 & 2

 FL1=X1*P*EXP(PHIL1)
 FL2=X2*P*EXP(PHIL2)

C         CHECK THE FUGACITIES OF EACH COMPONENT
C         IF FL1=FV1 AND FL2=FV2 THEN EQULIBRIUM HAS BEEN REACHED AND
C         VALUES SHOULD BE WRITTEN TO AN OUTPUT FILE.

 Q1=FL1/FV1
 Q2=FL2/FV2
 TEST1=Q1-1.0
 TEST2=Q2-1.0

 IF (ABS(TEST1).GT.0.0001.AND.ABS(TEST2).GT.0.0001) THEN
                 K1=K1*Q1
                 K2=K2*Q2
                 CK1=K1
                 CK2=K2
GOTO 1000
         ELSE
         PRINT *,'OUTPUT FILED'
PP=P*14.7
WRITE(8,*) X1,PP,T
WRITE(8,*) Y1,PP,T
```

```
C       CALCULATE MOLAR VOLUMES FROM ZZV AND ZZL
 MVV=ZZV*R*T/P
 MLV=ZZL*R*T/P
 WRITE(7,*) MVV,PP,T
 WRITE(7,*) MLV,PP,T

       END IF
5000   CONTINUE
 END


C       THIS SUBROUTINE CALCULATES THE FUGACITY COEFFICIENTS FROM THE
C       PENG ROBINSON EQUATION OF STATE

 SUBROUTINE LNFUGCF(B,BM,Z,BZ,AZ,AM,MIX,LNPHI,K1,K2)
 CHARACTER Y$
 REAL*8 B,BM,Z,BZ,AZ,AM,MIX,LNPHI,K1,K2
 REAL*8 T1,T2,T3,T4

C       THIS IF LOOP KEEPS THE PROGRAM FROM CRASHING IF THE
C       GUESS FOR K1 AND K2 WAS BAD.

 IF (Z.LT.BZ) THEN
 PRINT *,'Z IS LESS THAN BZ, GIVING AN ERROR IN LNFUGCF'
 PRINT *,'DO YOU WANT TO ADJUST DISTRIBUTION COEFFICIENTS?'
 PRINT *,'ENTER Y'
 READ *,Y$
 IF (Y$.EQ.'Y') GO TO 501
 CONTINUE
 ELSE

 T1=B/BM*(Z-1.0)-DLOG(Z-BZ)
 T2=AZ/(2.828*BZ)
 T3=2.0/AM*MIX-B/BM
 T4=DLOG((Z-2.414*BZ)/(Z-0.414*BZ))
 LNPHI=T1-T2*T3*T4

 END IF
 GO TO 502
501     PRINT *,'ENTER NEW DISTRIBUTION COEFFICIENTS: K1,K2'
 READ *,K1,K2
502     END
```

```
C       This program calculates the P-V diagram for Binary systems
C       WHILE VARYING THE VALUE OF KIJ, THE EXPERIMENTAL FITTING FACTOR
C       FOR THE PENG-ROBINSON EQUATION. THE SUM OF ACTUAL MOLE FRACTION
C       MINUS THE SUM OF THE EXPERIMENTAL MOLE FRACTION IS REPORTED.
C       THIS ALLOWS AN OPTIMIZATION OF KIJ.
C       THE PROGRAM USES DOUBLE PRECISION VARIABLES. THE DOUBLE PRECISION
C       IMSL ROOT FINDING ROUTINE, DZPORC, IS USED. THE IMSL LIBRARY MUST BE
C       SPECIFIED WHEN THE PROGRAM IS LINKED.

C       DECLARE VARIABLES
        REAL*8 TC1,TC2,PC1,PC2,OMEGA1,OMEGA2,X1,X2,Y1,Y2,ATC1,ATC2,A1,A2
        REAL*8 TR1,TR2,TFAC1,TFAC2,B1,B2,ALPHA1,ALPHA2,P,T,R,ZZV,ZZL
        REAL*8 BVM,BVZ,AVZ,AVM,VMIX2,VMIX1,BLM,BLZ,ALM,ALZ,LMIX1,LMIX2
        REAL*8 KIJ,K1,K2,CV(4),CL(4),PHIV1,PHIV2,PHIL1,PHIL2,MVV,MVL
        REAL*8 TAARD,VAARD,LAARD,DX,DY,SDX,SDY,AX2(40),AY2(40)
        REAL*8 PP(40),TT(40),INC,KMAX,KMIN
        REAL*16 CK(3)
        COMPLEX*16 ZV(3),ZL(3)
        INTEGER IER1,IER2,NDEG


C       ENTER THE CRITICAL DATA CO2=2, 2,3-BDIOL=1
C       ENTER R IN (CM^3*ATM)/(GMOL*K) AND T IN K

        DATA TC2,PC2,OMEGA2/304.2,72.8,0.225/
        DATA TC1,PC1,OMEGA1/613.32,50.21,1.056/
        DATA R,N/82.05,30/

        OPEN (UNIT=8,FILE='minallt.DAT',STATUS='NEW')
        WRITE(8,*) ' '

        OPEN(UNIT=7,FILE='MV.DAT',STATUS='NEW')
        WRITE(7,*) ' '

C       ENTER THE MOLE FRACTION DATA IN TERMS OF CO2
        DATA PP(1),AX2(1),AY2(1),TT(1)/2023.7,.6295,.00948,319.41/
        DATA PP(2),AX2(2),AY2(2),TT(2)/2710.7,.5969,.01098,319.39/
        DATA PP(3),AX2(3),AY2(3),TT(3)/2020.7,.6374,.00460,334.76/
        DATA PP(4),AX2(4),AY2(4),TT(4)/2331.7,.6137,.00902,334.77/
        DATA PP(5),AX2(5),AY2(5),TT(5)/3471.7,.5677,.02025,334.79/
        DATA PP(6),AX2(6),AY2(6),TT(6)/4084.7,.5081,.02432,334.79/
        DATA PP(7),AX2(7),AY2(7),TT(7)/4480.7,.5054,.02842,334.79/
        DATA PP(8),AX2(8),AY2(8),TT(8)/2907.7,.5671,.01483,334.80/
        DATA PP(9),AX2(9),AY2(9),TT(9)/1220.7,.7340,.00196,334.58/
        DATA PP(10),AX2(10),AY2(10),TT(10)/1436.7,.7149,.00399,334.56/
        DATA PP(11),AX2(11),AY2(11),TT(11)/1754.7,.6756,.00247,334.56/
        DATA PP(12),AX2(12),AY2(12),TT(12)/1086.7,.7444,.00477,334.89/
        DATA PP(13),AX2(13),AY2(13),TT(13)/2291.1,.6280,.00832,349.56/
        DATA PP(14),AX2(14),AY2(14),TT(14)/2918.2,.5605,.01328,349.57/
        DATA PP(15),AX2(15),AY2(15),TT(15)/3961.7,.5073,.02274,349.61/
        DATA PP(16),AX2(16),AY2(16),TT(16)/4471.1,.4775,.03302,349.64/
        DATA PP(17),AX2(17),AY2(17),TT(17)/4077.1,.4964,.02705,349.57/
        DATA PP(18),AX2(18),AY2(18),TT(18)/4756.1,.4584,.03578,349.70/
        DATA PP(19),AX2(19),AY2(19),TT(19)/2098.7,.6483,.00122,349.60/
        DATA PP(20),AX2(20),AY2(20),TT(20)/1869.7,.6812,.00139,349.63/
        DATA PP(21),AX2(21),AY2(21),TT(21)/1637.7,.7166,.00200,349.57/
        DATA PP(22),AX2(22),AY2(22),TT(22)/1396.7,.7387,.00149,349.63/
        DATA PP(23),AX2(23),AY2(23),TT(23)/1303.7,.7458,.00140,349.66/
        DATA PP(24),AX2(24),AY2(24),TT(24)/1094.7,.7858,.00111,349.64/
        DATA PP(25),AX2(25),AY2(25),TT(25)/4952.7,.4309,.05868,364.67/
        DATA PP(26),AX2(26),AY2(26),TT(26)/1508.7,.7120,.00253,364.69/
        DATA PP(27),AX2(27),AY2(27),TT(27)/2398.7,.6244,.00715,364.66/
        DATA PP(28),AX2(28),AY2(28),TT(28)/2840.7,.5749,.01284,364.65/
        DATA PP(29),AX2(29),AY2(29),TT(29)/1884.7,.6911,.00365,364.66/
        DATA PP(30),AX2(30),AY2(30),TT(30)/3399.7,.5233,.01874,364.66/
```

```
      jl=0
      DO 111 I=1,N,1
      jl=jl-1
      PP(I)=PP(I)/14.7
111   CONTINUE

C     THESE STATEMENTS DETERMINE THE RANGES OF KIJ TO BE
C     TESTED. A MINIMUM AND MAXIMUM MUST BE ENTERED.
      PRINT *,'ENTER THE RANGE OF KIJS TO BE EXAMINED.'
      PRINT *,'ENTER MIN,MAX,INCREMENT'
      PRINT *,'KIJS SHOULD RANGE FROM 0 TO .20'
      READ *,KMIN,KMAX,INC
C     ECHO PRINT VALUES
      PRINT *,'KMAX=',KMAX,' KMIN=',KMIN,' INCREMENT=',INC

C     THESE LOOPS REGRESS KIJ
      I=0
      DO 7777 KIJ=KMIN,KMAX,INC
      WRITE(8,*) '*****************************************************'
      I=I+1
      SDX=0
      SDY=0

      WRITE(8,*) ' '
      WRITE(8,*) 'KIJ=',KIJ,' OMEGA1=',OMEGA1
      PRINT *,'KIJ= ',KIJ
            DO 6666 J=1,N,1
            P=PP(J)
            T=TT(J)
C           PRINT *,'P=',PP(J)*14.7,' T=',TT(J)
C     THE PENG-ROBINSON EQUATION WILL BE USED IN THE FORM
C     Z^3-(1-B)*Z^2-(A-3*B^2-2*B)*Z-(A*B-B^2-B^3)=0
C     A AND B WILL BE DETERMINED BY THE USUAL MIXING RULES,
C     FROM THE PURE COMPONENT INFORMATION.


C     CALCULATING THE PURE COMPONENT A'S (LITTLE A'S) AND B'S
C     FOR THE PR-EOS

      ATC1=0.45724*R**2*TC1**2/PC1
      ATC2=0.45724*R**2*TC2**2/PC2

      TFAC1=.37464+1.54226*OMEGA1-.26992*OMEGA1**2
      TFAC2=.37464+1.54226*OMEGA2-.26992*OMEGA2**2

      TR1=T/TC1
      TR2=T/TC2

      ALPHA1=(1+TFAC1*(1.0-TR1**.5))**2
      ALPHA2=(1+TFAC2*(1.0-TR2**.5))**2

      A1=ATC1*ALPHA1
      A2=ATC2*ALPHA2


C     CALCULATING THE B'S FOR PR-EOS

      B1=0.0778*R*TC1/PC1
      B2=0.0778*R*TC2/PC2


C     ESTABLISH THE INITIAL DISTRIBUTION COEFFICIENTS FOR THE SYSTEM
      K1=0.1
      K2=3.0
```

```
C       CALCULATE THE MOLE FRACTIONS FROM THE GIVEN INITIAL K-VALUES
1000    X1=(1.0-K2)/(K1-K2)
        X2=1.0-X1
        Y1=X1*K1
        Y2=1.0-Y1
        ZZV=0.0
        ZZL=0.0


C       DEBUG STATEMENTS
C       WRITE(8,1010)X1,X2,Y1,Y2
C1010   FORMAT(1X,'X1=',D16.5,1X,'X2= ',D16.5,1X,'Y1,Y2= ',D16.5,1X,D16.5)

C       CALCULATE THE CONSTANTS FOR PR EOS USING MIXING RULES
C       VAPOR PHASE CONSTANTS

        AVIJ=Y1*Y2*(1.0-KIJ)*(A1*A2)**.5
        AVM=Y1**2*A1+2*AVIJ+Y2**2*A2

        BVM=B1*Y1+B2*Y2

C       LIQUID PHASE CONSTANTS

        ALIJ=X1*X2*(1.0-KIJ)*(A1*A2)**.5
        ALM=X1**2*A1+2*ALIJ+X2**2*A2

        BLM=B1*X1+B2*X2

C       CONVERT AVM,BVM AND ALM,BLM INTO APPROPRIATE FORM FOR THE Z
C       FORM OF THE PR EOS

        AVZ=AVM*P/(R*T)**2
        BVZ=BVM*P/(R*T)

        ALZ=ALM*P/(R*T)**2
        BLZ=BLM*P/(R*T)

C       ESTABLISH THE COEFFICIENTS FOR THE VAPOR PHASE PR-EOS
C       CV4=1.0, CV3=-(1.0-BVZ), CV2=(AVZ-3*BVZ**2-2*BVZ)
C       CV1=-(AVZ*BVZ-BVZ**2-BVZ**3)

        CV(4)=1.0
        CV(3)=-(1.0-BVZ)
        CV(2)=AVZ-3*BVZ**2-2*BVZ
        CV(1)=-(AVZ*BVZ-BVZ**2-BVZ**3)

C       DEBUG STAEMENTS
C       WRITE(8,1020)CV(1),CV(2),CV(3),CV(4)
C1020   FORMAT(1X,'CV1=',D16.8,' CV2=',D16.8,' CV3=',D16.8,' CV4',D16.8)


C       SET ZPOLAR ERROR CODE TO ZERO
        IER1=0.0
C       SET NDEG FOR ZZPOC EQUAL TO THREE FOR CUBIC EQUATION
        NDEG=3

C       CALL DZPORC AND SOLVE FOR THE VAPOR PHASE Z

        CALL DZPORC(NDEG,CV,ZV,IER1)

        IF (IER1.NE.0) THEN
              PRINT *,'IER1=',IER1
        END IF

C       THIS LOOP CHECKS FOR COMPLEX ROOTS AND PRINT AN ERROR
C       MESSAGE IF COMPLEX ROOTS ARE FOUND
```

```
      DO 1500 I=1,3,1
      CR(I)=DIMAG(ZV(I))
      IF (CR(I).GT.1.0E-7.OR.CR(I).LT.-1.0E-7) THEN
            ZV(I)=(0.0,0.0)
      END IF
1500  CONTINUE

C     THESE STATEMENTS SELECT THE HIGH VALUE OF ZV
C     MUST FIRST CONVERT Z'S TO REAL NUMBER, BECAUSE YOU
C     CAN'T PERFORM LOGICAL OPERATIONS ON COMPLEX NUMBERS
      ZV1=REAL(ZV(1))
      ZV2=REAL(ZV(2))
      ZV3=REAL(ZV(3))

      IF (ZV1.GT.ZV2.AND.ZV1.GT.0) THEN
            ZZV=ZV1
      END IF
      IF (ZV2.GT.ZZV.AND.ZV2.GT.0.0) THEN
            ZZV=ZV2
      END IF
      IF (ZZV.LT.ZV3.AND.ZV3.GT.0) THEN
            ZZV=ZV3
      END IF

C     DEBUG STATEMENTS
C     WRITE(8,1505) ZZV
C1505 FORMAT(1X,'ZZV= ',D16.8)

C     CALCULATE THE LIQUID PHASE COEFFICIENTS FOR THE PR EOS
C     THEY CORRESPOND TO THE VAPOR COEFF'S DEFINED ABOVE

      CL(4)=1.0
      CL(3)=-(1.0-BLZ)
      CL(2)=ALZ-3*BLZ**2-2*BLZ
      CL(1)=-(ALZ*BLZ-BLZ**2-BLZ**3)
C
C     ZERO THE ERROR FUNCTION FOR ZPOLAR
      IER2=0
C     DEBUG STATEMENTS
C     WRITE(8,*)CL(1),CL(2),CL(3),CL(4)

C     CALL DZPORC AND SOLVE FOR THE LIQUID PHASE Z

      CALL DZPORC(NDEG,CL,ZL,IER2)
      IF (IER2.NE.0) THEN
            PRINT *,'IER2=',IER2
      END IF

C     THIS LOOP CHECKS ZL FOR IMAGINARY ROOTS AND
C     SUBSTITUTES 0.0,0.0 FOR COMPLEX ROOTS

      DO 1750 I=1,3
      CR(I)=DIMAG(ZL(I))
      IF (CR(I).GT.1.0E-7.OR.CR(I).LT.-1.0E-7) THEN
            ZL(I)=0.0
      END IF
1750  CONTINUE
C     WRITE(8,*) ZL(1),ZL(2),ZL(3)

C     THIS LOOP SELECTS THE LOW ROOT FOR ZL
C     CONVERT IMAGINARY ZL(I)'S INTO REAL ZL1-ZL3

      ZL1=REAL(ZL(1))
      ZL2=REAL(ZL(2))
      ZL3=REAL(ZL(3))
```

```
      IF (ZL1.LT.ZL2.OR.ZL1.GT.0.0) THEN
            ZZL=ZL1
      END IF
      IF (ZL2.LT.ZZL.AND.ZL2.GT.0.0) THEN
            ZZL=ZL2
      END IF
      IF (ZL3.LT.ZZL.AND.ZL3.GT.0.0) THEN
            ZZL=ZL3
            END IF
      IF (ZZL.LE.0.0) THEN
            ZZL=ZL3
      END IF

C     CALL SUBROUTINE LNPHI TO CALCULATE THE NATURAL LOG OF THE
C     LIQUID AND VAPOR PHASE FUGACITY COEFFICIENTS
C
C     FOR THE VAPOR PHASE FUGACITY COEFFICIENT FOR COMPONENT 1

      VMIX1=Y1*A1+Y2*(1.0-KIJ)*(A1*A2)**0.50
      CALL LNFUGCF(B1,BVM,ZZV,BVZ,AVZ,AVM,VMIX1,PHIV1,K1,K2)

C     FOR THE VAPOR PHASE FUGACITY COEFFICIENT OF COMPONENT 2

      VMIX2=Y2*A2-Y1*(1.0-KIJ)*(A1*A2)**0.50
      CALL LNFUGCF(B2,BVM,ZZV,BVZ,AVZ,AVM,VMIX2,PHIV2,K1,K2)

C     FOR THE LIQUID PHASE FUGACITY COEFFICIENT OF COMPONENT 1

      LMIX1=X1*A1-X2*(1.0-KIJ)*(A1*A2)**0.50
      CALL LNFUGCF(B1,BLM,ZZL,BLZ,ALZ,ALM,LMIX1,PHIL1,K1,K2)

C     FOR THE LIQUID PHASE FUGACITY COEFFICIENT OF COMPONENT 2

      LMIX2=X2*A2-X1*(1.0-KIJ)*(A1*A2)**0.50
      CALL LNFUGCF(B2,BLM,ZZL,BLZ,ALZ,ALM,LMIX2,PHIL2,K1,K2)

C     CALCULATE THE FUGACITIES FOR COMPONENTS 1 & 2 IN THE VAPOR PHASE

      FV1=Y1*P*EXP(PHIV1)
      FV2=Y2*P*EXP(PHIV2)

C     CALCULATE THE LIQUID PHASE FUGACITIES FOR COMPONENTS 1 & 2

      FL1=X1*P*EXP(PHIL1)
      FL2=X2*P*EXP(PHIL2)

C     CHECK THE FUGACITIES OF EACH COMPONENT
C     IF FL1=FV1 AND FL2=FV2 THEN EQULIBRIUM HAS BEEN REACHED AND
C     VALUES SHOULD BE WRITTEN TO AN OUTPUT FILE.

      Q1=FL1/FV1
      Q2=FL2/FV2
      TEST1=Q1-1.0
      TEST2=Q2-1.0

      IF (ABS(TEST1).GT.0.0001.AND.ABS(TEST2).GT.0.0001) THEN
                  K1=K1*Q1
                  K2=K2*Q2
                  CK1=K1
                  CK2=K2
GOTO 1000
       ELSE
```

```
C       CALCULATE MOLAR VOLUMES FROM ZZV AND ZZL
        MVV=ZZV*R*T/P
        MLV=ZZL*R*T/P
        WRITE(7,*) MVV,P,T,ZZV
        WRITE(7,*) MLV,P,T,ZZL

        END IF
5000    CONTINUE

C       SUM THE ABS DEVIATIONS

        DX=ABS((X1-AX2(J))/AX2(J))
        SDX=SDX+DX

        DY=ABS((Y1-AY2(J))/AY2(J))
        SDY=SDY-DY

6666    CONTINUE

C       CALCULATE THE ABS AVERAGE DEVIATION

        LAARD=SDX/N
        VAARD=SDY/N
        TAARD=(SDY+SDX)/N

        WRITE(8,*)
        WRITE(8,*) ' LIQUID PHASE AARD=',LAARD
        WRITE(8,*) ' VAPOR PHASE AARD=',VAARD
        WRITE(8,*) ' THE AVERAGE ABSOLUTE DEVIATION =',TAARD
        WRITE(8,*) '*******************************************************'
7777    CONTINUE
        END


C       THIS SUBROUTINE CALCULATES THE FUGACITY COEFFICIENTS FROM THE
C       PENG ROBINSON EQUATION OF STATE

        SUBROUTINE LNFUGCF(B,BM,Z,BZ,AZ,AM,MIX,LNPHI,K1,K2)

C       DECLARE SUBROUTINE VARIABLES
        REAL*8 B,BM,BZ,AZ,AM,MIX,LNPHI,Z
        REAL*8 T1,T2,T3,T4,K1,K2

        CHARACTER Y$

C       THIS IF LOOP KEEPS THE PROGRAM FROM CRASHING IF THE
C       GUESS FOR K1 AND K2 WAS BAD.

        IF (Z.LT.BZ) THEN
        PRINT *,'Z IS LESS THAN BZ, GIVING AN ERROR IN LNFUGCF'
        PRINT *,'DO YOU WANT TO ADJUST DISTRIBUTION COEFFICIENTS?'
        PRINT *,'ENTER Y'
        READ *,Y$
        IF (Y$.EQ.'Y') GO TO 501
        CONTINUE
        ELSE

        T1=B/BM*(Z-1.0)-DLOG(Z-BZ)
        T2=AZ/(2.828*BZ)
        T3=2.0/AM*MIX-B/BM
        T4=DLOG((Z-2.414*BZ)/(Z-0.414*BZ))
        LNPHI=T1-T2*T3*T4

        END IF
        GO TO 502
501     PRINT *,'ENTER NEW DISTRIBUTION COEFFICIENTS: K1,K2'

        READ *,K1,K2
502     END
```

```
REM THIS PROGRAM CALCULATES MOLE FRACTIONS FROM RAW DATA
REM FOR USE WITH CO2 AND BUTANEDIOL
REM THESE LINES GET GENERAL DATA
10 INPUT"ENTER THE RUN NUMBER";RUN$
INPUT"ENTER THE RUN PRESSURE (psig)";RPG
INPUT"ENTER THE BATH TEMPERATURE (CELCIUS)";T
INPUT"ENTER THE ROOM TEMPERATURE IN DEGREES C";RT
INPUT"ENTER THE TEMPERATURE OF THE COL  TRAP in K";TT#
INPUT"ENTER THE ATMOSPHERIC PRESSURE IN ATM.";AP
PRINT"ROOM TEMP="RT;"Patm=";AP;" RUN #="RUN$
RPA=RPG+AP*14.7

REM THESE LINES GET DATA FOR THE GAS SIDE
INPUT"ENTER THE VOLUME OF GAS PASSED THROUGH THE GAS SIDE WTM (L)";GV
INPUT"ENTER THE Wt. OF Bdiol COLLECTED ON THE GAS SIDE (grams)";GW
Input"Enter The Temperature Of The Gas Side Wet Test Meter (C):";GWT

REM THESE LINES GET DATA FOR THE LIQUID SIDE
INPUT"ENTER THE Wt OF Diol COLLECTED ON THE LIQUID SIDE";LW
INPUT"ENTER THE VOLUME OF GAS PASSED THROUGH THE LIQUID SIDE WTM (L)";LV
INPUT"ENTER THE TEMPERATURE OF THE LIQUID SIDE WTM (C)";LWT

REM THESE LINES CORRECT THE WTM READINGS FOR DIFFERENCES IN TEMP.
REM AND VAPOR PRESSURE

REM CONVERT TO ABSOLUTE TEMP.
GWT=GWT+273.15
LWT=LWT+273.15
RT=RT+273.15

REM CORRECTION FOR DIFFERENCE BETWEEN ROOM T AND WTM T

GV1=GV*(RT/GWT)
LV1=LV*(RT/LWT)

REM CORRECTION VAPOR PRESSURE DIFFERENCE, VAPOR PRESSURE REGRESSED FROM
REM VP=4.666E-10*10^(.0262*T) DATA FROM 56TH EDITION CRC HANDBOOK

GVP=4.666E-10*10^(.0262*GWT)
LVP=4.666E-10*10^(.0262*LWT)
RVP=4.666E-10*10^(.0262*RT)

GV2=GV1*((AP-GVP)/(AP-RVP))
LV2=LV1*((AP-LVP)/(AP-RVP))

REM CORRECTION FOR WTM CALIBRATIONS
REM FOR THE GAS SIDE WET TEST METER

GV3=-.0019+0.996*(GV2)

REM FOR THE LIQUID SIDE WET TEST METER

LV3=.0012+.9636*(LV2)

REM THESE CORRECTIONS ACCOUNT FOR SOLUBILITY OF BDIOL IN CO2 AT
REM ATMOSPHERIC PRESSURE AND THE TRAP TEMPERATURE 0 C OR 273.15 K

REM GET VAPOR PRESSURES FOR CO2 AND DIOL AT 273.15 K
REM EQUATIONS REGRESSED FROM DATA IN PERRY'S AND CRC

CVP=-276.4922+4.0641*TT#-.0206*TT#^2+3.630E-5*TT#^3

BVP#=4.569E-7*10^(0.0205*TT#)
BVP#=BVP#/760.0
```

```
print BVP#
REM FOR THE GAS SIDE SAMPLES CALCULATE MOLE FRACTIONS

REM CALCULATE VOL PER MOLE OF AN IDEAL GAS AT ROOM T AND P
REM T IN KELVIN, P IN ATM, AND VOLUME IN LITERS

VPM=(.082056*(RT))/AP

REM CORRECT GAS SIDE MOLE FRACTION CALCULATIONS USING THE VAPOR PRESSURES
REM OF CO2 AND BUTANEDIOL AT THE TEMPERATURE OF THE COLD TRAP

REM CALCULATE THE MOLE FRACTION BDIOL IN THE GAS SIDE LIQUID SAMPLE

GXD=((1.0-CVP/AP)/(BVP#/AP-CVP/AP))
GXC=1.0-GXD

REM CALCULATE THE MOLE FRACTION CO2 IN THE GAS SIDE VAPOR SAMPLE

GYD=GXD*BVP#/AP
GYC=1.0-GYD

REM CALCULATE THE TOTAL MOLES IN GAS SIDE LIQUID SAMPLE

GML=GW/(GXD*90.0+GXC*44.0)

REM CALCULATE THE TOTAL MOLES IN THE GAS SIDE VAPOR SAMPLE
REM CONVERT THE VOLUME OF CO2 TO MOLES

GMCO2=GV3/VPM
GMV=GMCO2/GYC

REM CALCULATE THE GAS SIDE MOLE FRACTIONS

YD=(GMV*GYD + GML*GXD)/(GMV+GML)
YC=(GMV*GYC + GML*GXC)/(GMV+GML)

REM CALCULATE THE MOLE FRACTIONS DIOL AND CO2 IN LIQUID SIDE SAMPLES
REM CALCULATE THE CO2 AND DIOL VP'S AT PATM AND ROOM T

LCVP=-276.4922+4.0641*RT-.0206*RT^2-3.630E-5*RT^3
LBVP#=4.569E-7*10^(0.0205*RT)
LBVP#=LBVP#/760
PRINT"lcvp=";LCVP,"LBVP#=";LBVP#
LXD=((1.0-LCVP/AP)/(LBVP#/AP-LCVP/AP))
LXC=1.0-LXD

LYD=LXD*LBVP#/AP
LYC=1.0-LYD

REM CALCULATE THE TOTAL MOLES IN LIQUID SIDE LIQUID SAMPLE

LML=LW/(LXD*90.0+LXC*44.0)

REM CALCULATE THE TOTAL MOLES IN THE LIQUID SIDE VAPOR SAMPLE

LMV=LV/LYC/VPM

REM CALCULATE THE MOLE FRACTIONS FOR THE LIQUID SIDE

XD=(LMV*LYD + LML*LXD)/(LML+LMV)
XC=(LMV*LYC + LML*LXC)/(LML+LMV)
PRINT"GXD, GYD=",GXD,GYD
PRINT"LXD,LXC,LYD,LYC"; LXD,LXC,LYD,LYC
PRINT"TOT M L=";LML,"TOT M V=";LMV
SUMY=YC+YD
```

```
SUMX=XD+XC

REM WARNING STATEMENT
IF SUMY>1.001 OR SUMX>1.001 THEN PRINT"***** WARNING SUM OF MOLE FRACTIONS
IF SUMY<.998 OR SUMX<.998 THEN PRINT"****** WARNING SUM OF MOLE FRACTIONS <

REM OUTPUT STATEMENTS
PRINT "MOLE FRACTIONS"
PRINT"YCO2="YC;" YDIOL="YD;" SUMY="SUMY
PRINT"XCO2="XC;" XDIOL="XD;" SUMX="SUMX
pRINT"GV="GV,GV1,GV2,GV3
PRINT"LV="LV,LV1,LV2,LV3

REM THESE STATEMENTS CALCULATE THE ENHANCEMENT FACTOR E=YACTUAL/YIDEAL
REM fIND THE VAPOR PRESSURE OF DIOL AT EXPERITMENTAL T
T=T+273.15
BVP=4.569E-7*10^(.0205*T)
REM CONVERT BVP FROM MMHG TO PSI
BVP=BVP*.019342
REM CALCULATE YIDEAL (YID)
YID=BVP/RPA
PRINT "YID=";YID
REM CALC E
E=YD/YID
PRINT "E=";E
OPEN "C:\Kaiser\thsisdat\erckmf.DAT" FOR APPEND AS #1
Print#1, " "
print#1, "Run #= ";Run$
PRINT#1, RPA; XD;T
print#1, RPA; YD;T
Print#1,
CLOSE#1
OPEN "C:\Kaiser\thsisdat\errckt.DAT" FOR APPEND AS #2
PRINT#2, RPA;T;XD;YD;GV;GW;GWT;LV;LW;LWT;RT
CLOSE#2
OPEN "C:\Kaiser\thsisdat\Erckyid.DAT" FOR APPEND AS #3
PRINT#3, E,YD,YID,RPA,T
CLOSE#3

INPUT"ANOTHER RUN?";Y$
IF Y$="Y"THEN 10 ELSE END
```

APPENDIX C

CALIBRATION AND CORRECTION DATA

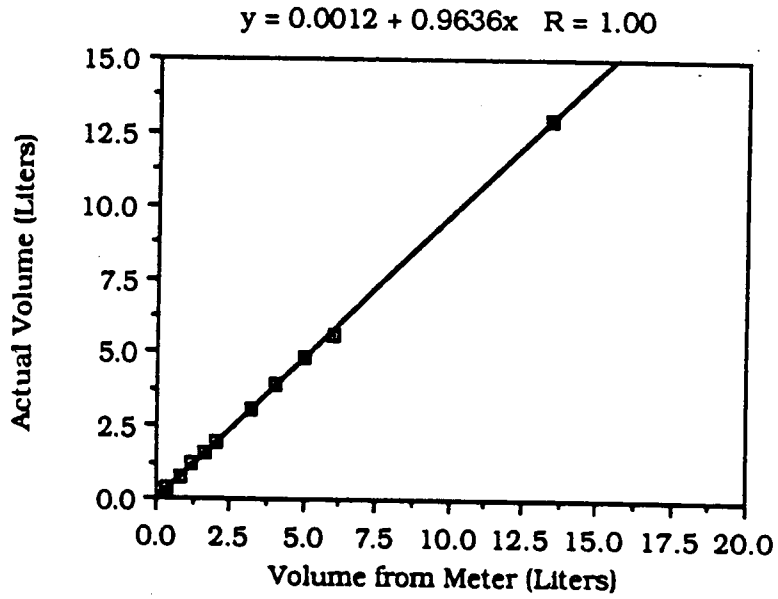

Figure 19: Calibration Curve for the 3 Liter Wet Test Meter

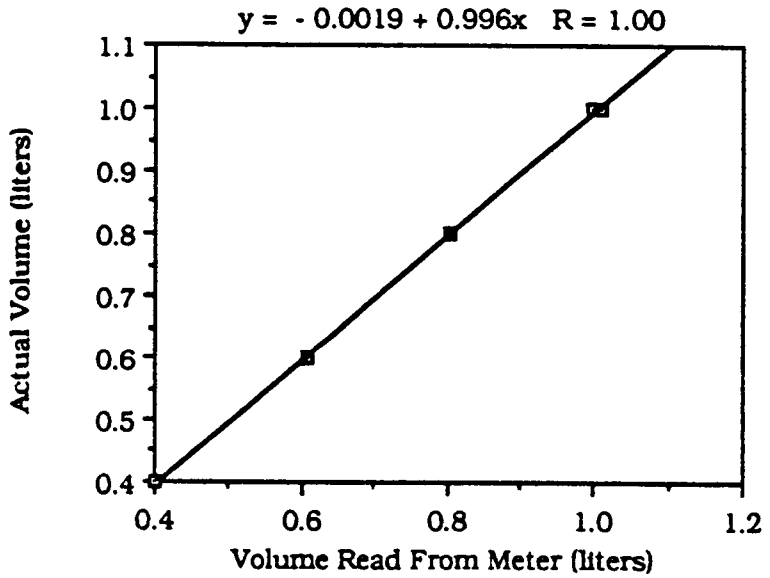

Figure 20: Calibration Curve for the 1 Liter Wet Test Meter

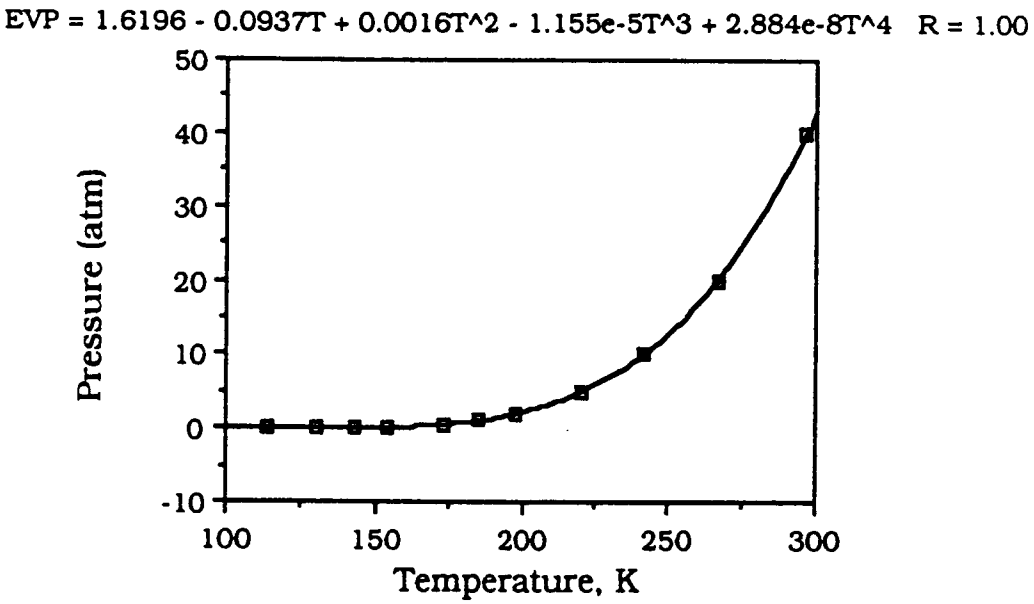

Figure 21: Vapor Pressure of Ethane vs. Temperature

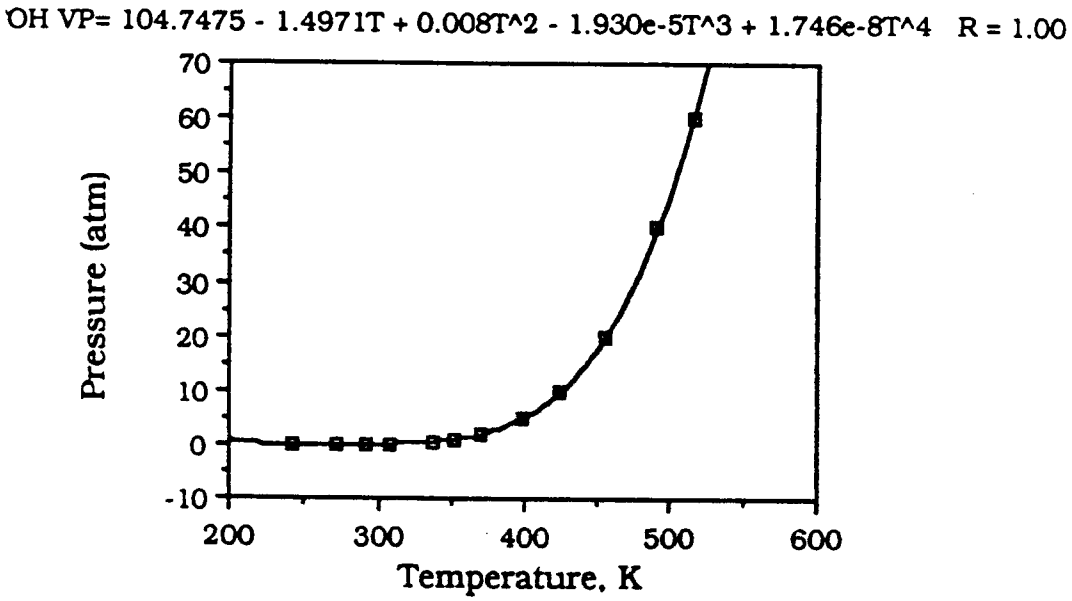

Figure 22: Vapor Pressure of Ethanol vs. Temperature

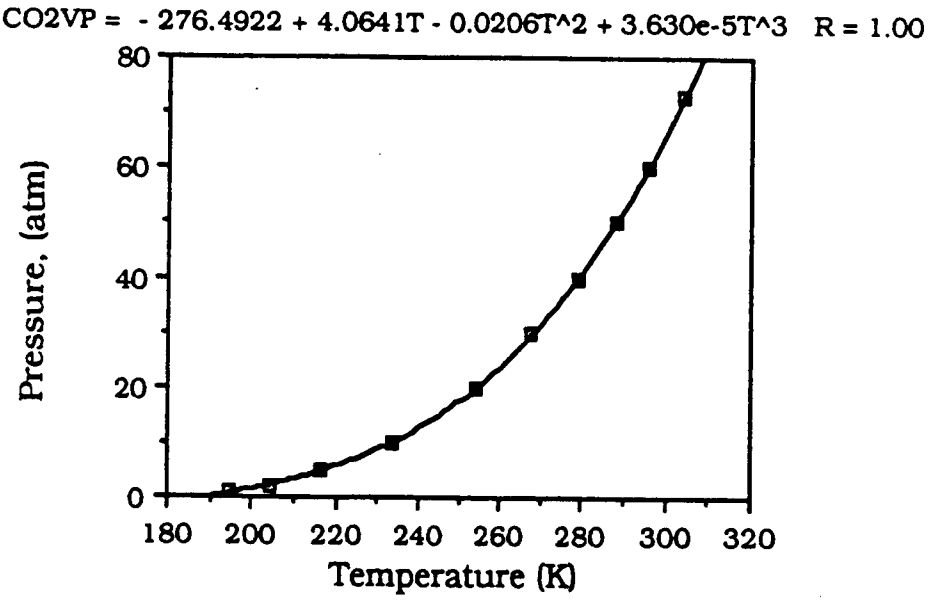

Figure 23: Vapor Pressure of CO_2 vs. Temperature

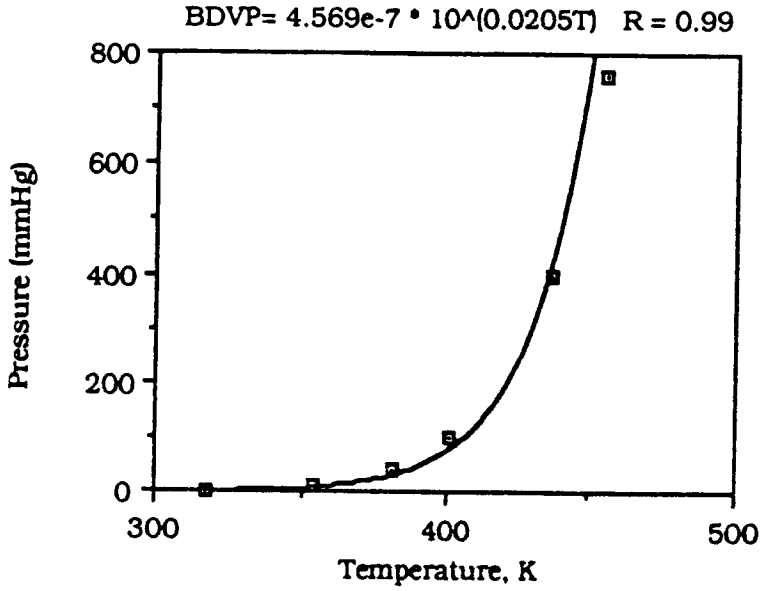

Figure 24: Vapor Pressure of Butanediol vs. Temperature

VITA

Jay Alan Kaiser was born in Pittsburgh, Pennsylvania on December 8, 1960. He attended public school in Memphis, Tennessee and graduated from Ridgeway High School in May 1979. The following September he entered The University of Tennessee. Through the Co-op program of the university, he worked for the Buckeye Cellulose Corp. for two years. In March 1985 he received a Bachelor of Science degree in Chemical Engineering.