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**CARBON DIOXIDE EXTRACTION OF ETHANOL FROM WATER AT
ELEVATED PRESSURES**

The University of Oklahoma

PH.D. 1982

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THE UNIVERSTIY OF OKLAHOMA
GRADUATE COLLEGE

CARBON DIOXIDE EXTRACTION
OF ETHANOL FROM WATER
AT ELEVATED PRESSURES

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

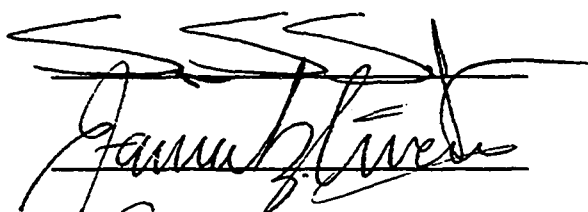
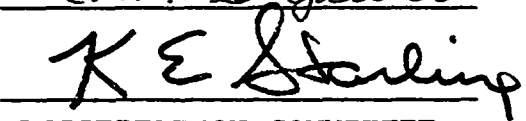
By
ALAN SPENCER PEGUES

Norman, Oklahoma

1982

CARBON DIOXIDE EXTRACTION
OF ETHANOL FROM WATER
AT ELEVATED PRESURES

APPROVED BY


C. M. Shepcevic

K E Sterling
DISSERTATION COMMITTEE

ABSTRACT

A growing national need exists for new and innovative separation processes using a new classification of solvents. Current separation techniques often are characterized by high daily energy costs or expensive and often environmentally unsound solvents. Fluids employed at elevated pressures may fill this need for a new class of solvents.

Carbon dioxide at ambient temperature and elevated pressure of 1000 psia is employed as an extraction solvent for separating ethyl alcohol and water mixtures. A bench apparatus with a 460 ml/hr ethanol/water-feed rate demonstrates the feasibility of continuous operation of the process. The design of the next pilot plant is discussed.

A mass balance on the bench apparatus demonstrates operating conditions closely matching equilibrium conditions due to high mass transfer rates in compressed solvents. Continuously fed bench apparatus operation for extended periods of time was achieved while observing the critical

opalescence of carbon dioxide. Operation at the critical point of carbon dioxide is discussed in relation to process control of high pressure, near critical, and supercritical processes.

The $\text{CO}_2\text{-H}_2\text{O}$ binary is evaluated by a solubility equation incorporating pure component experimental data, and the second virial cross coefficient as intermolecular force contributor to the mixture fugacity coefficient. The solubility equation predicted behavior which was more typical of normal fluids than of the $\text{CO}_2\text{-H}_2\text{O}$ binary.

Experimental results from the continuously fed apparatus demonstrate that a 23.4% conversion of a 49.5 mole% $\text{ETOH-H}_2\text{O}$ feed stream to an 88 mole% $\text{ETOH-H}_2\text{O}$ overhead stream may be accomplished with liquid carbon dioxide at 25°C and 1000 psia, and a solvent (CO_2) to feed (ETOH and H_2O) ratio of 3.12. The resulting bottom stream contained 41.5 mole% ETOH on a CO_2 free basis.

ACKNOWLEDGEMENTS

I would like to express my thanks to the members of my advising committee, my family, and my friends for their encouragement and support throughout this dissertation research.

I would like to thank my advisor, Dr. Sam Sofer, for his insights, creative skills, and direction which he has shared with me.

I would also like to thank members of my final dissertation committee for their great efforts in this dissertation research. Dr. Cedomir Silepcevic, Dr. Kenneth Starling, and Dr. Faruk Civan have been an enormous contribution to my development, for which I am thankful.

Many lessons were received from my Doctoral Candidacy committee members, Dr. Rodrick McCallum, Dr. Arthur Aldag, and Dr. Jay Radovich, for which I am appreciative.

I would like to thank my parents and family for their constant encouragement and support through the many efforts of this dissertation. I would especially like to thank my brother Guy and my sister Sara for the efforts in both technical and preparative work.

I would like to thank the First National Bank of Decatur, Texas for financial loans necessary in the final phase of the dissertation effort.

William Kastens and Dave Defenders deserve much thanks for their efforts in turning pencil drawings into graphic illustrations and figures. Margaret Williford is much appreciated for her typing skill so put to the test by this dissertation. I am also appreciative to Elaine Curry for her help in making final corrections.

I would like to thank K. Hudson for a very informative tutorial on skills with machine tools, and for making possible the equipment construction phase of this research. I would also like to thank John Noe for his efforts on the electrical aspect of the equipment.

I would also like to thank Bernard Wire for his detailed and determined assistance on many difficult and possibly dangerous experimental runs.

I would also like to thank my friends for their support Kay, Joe, Sam, Vivek, Rosendo, Jeff, Andrea, Will, Dave, Vic, Tim, Mike, Mary, Jeri, Debbi, Bob, Abraham, Loyd, Jan, Yolanda, Hamant, and the members and associate members of O.U. Ch.E. G.S.C.C.

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CARBON DIOXIDE EXTRACTION
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CHAPTER I

INTRODUCTION

High pressure liquid solvents and supercritical solvents have recently been touted by both the academic and industrial research and development sectors for having enhanced solvation characteristics. The search for a new class of solvents accompanies a national need for energy supplies and more energy efficient processes. The oil glut over the last year cannot overshadow the ten-fold increase in oil prices over the last decade. The national need for a more stable energy supply can partially be offset by more energy efficient technology.

The problems of oil supply in the 1970's has pushed the economic efficiency closer to the maximum thermodynamic efficiency. Solvents separation can improve the efficiency of processes which are traditionally carried out by evaporative techniques. The search for

more energy efficient technology leads to high pressure liquid solvents and supercritical solvents as one of the new, more energy efficient, processes. This dissertation investigates the use of carbon dioxide as a high pressure liquid solvent for the separation of ethanol and water.

Although the experimental phase of this dissertation encompasses only high pressure liquid CO_2 as solvent, supercritical solvents are discussed in great detail. Both high pressure liquid solvents and supercritical solvents have displayed advantages compared to conventional solvents. This dissertation research investigates both high pressure liquid solvents and supercritical solvents, while experimental research is restricted to high pressure liquid carbon dioxide solvent.

The concept of using small molecules (three carbons or less) above the thermodynamic liquid-vapor critical point as solvents was first applied to residual oil recovery. Pilat applied for a patent in 1933 in Poland, and in 1934 in the United States with the Shell Development Company (U.S. pat. 2,315,131 (1943)). This patent has all of the characteristics of current supercritical solvent extraction of residual oil, except for current nomenclature. German authors claim to have invented the technology in 1962, with Dr. K. Zosel at the Max-Planck-Institut für Kohlenforschung [258]. The first symposium

on a novel method of separation, viz. extraction with supercritical gases, was held on June 5 and 6, 1978, at "Haus der Technik", Essen, Germany. Regardless of the identity of the original inventors, the most comprehensive literature source for the full spectrum of "supercritical solvent extraction processes" is found in the proceedings of this symposium. The background section of this dissertation includes an extensive review of the Essen symposium along with other applications of the process being developed or implemented in the United States and Britian. The background survey indicates that most advances outside the realm of residual oil recovery can be attributed to the work cited in the Essen symposium.

This dissertation investigates the operation and thermodynamics of high pressure liquid and supercritical carbon dioxide as a solvent for the separation of ethanol and water. A bench apparatus was constructed to determine if ethanol could be separated from water with a carbon dioxide solvent. The apparatus constructed for this work demonstrates that the ethanol-water separation occurs upon contact with liquid carbon dioxide. The pilot plant used a one stage contactor and gave product streams which closely match the one theoretical stage conditions.

One of the major considerations which presented itself to this author during the initial phases of research was the feasibility of operating a plant near the critical point of a solvent. Many problems arise in the prediction of the vapor-liquid critical region by equations of state, and it was felt that several of these problems, such as mechanical stability and infinite heat capacity, would interfere with successful operation of a "supercritical extraction" plant. Operation of the pilot plant at the critical point of carbon dioxide for sustained periods of time demonstrates that all operational problems are surmountable.

Predictive thermodynamic equations of state (EOS) are also reviewed and considered. The literature does not indicate any EOS which would predict the $\text{CO}_2\text{-H}_2\text{O-ETOH}$ system. The second virial cross coefficient was chosen as a predictive tool for the $\text{CO}_2\text{-H}_2\text{O}$ system. The virial equation was chosen so that assumptions and generalizations made by other authors could be tested. The mixture fugacity coefficient, as given by the virial equation of state truncated after the second virial coefficient, is used in a solubility equation relating the "heavy" and "light" phases. The solubility equation incorporating the second

virial cross coefficient is tested for predictive capabilities on the carbon dioxide and water binary system. Although the predictive capabilities are poor, the methods of analysis produced results which may shed a more informative light on the nature of high pressure liquid and supercritical solvent extraction.

The original and foremost goal of this dissertation work was to determine if "carbon dioxide solvent extraction of ethanol from water" is a viable process. This goal has been successfully met. Specifically, the research goals, subject to the constraint that capital expenditures will not exceed \$500 (1981 dollars), are:

1. To demonstrate that high pressure liquid carbon dioxide can be used as a solvent for the separation of ethanol and water.
2. To construct a small continuously fed pilot plant which would serve as a general model for a commercial process and to determine a need for modification of the apparatus for future investigations.
3. To determine which thermodynamic property modeling method should be used for design purposes.

All the above goals have been successfully accomplished in the course of the research for this dissertation.

The scope of this dissertation research reaches from experimental high pressure pilot plant construction and operation to thermodynamic properties prediction by an equation of state. The study of the $\text{CO}_2\text{-H}_2\text{O-ETOH}$ system could be extended to other high pressure systems with ease; the $\text{CO}_2\text{-H}_2\text{O-Lube Oil}$ system is a system being encountered today in enhanced oil recovery operation and research. The measurement of equilibrium data, although not performed in this dissertation research, is within the scope of projects which can be considered in the future. Incorporation of equilibrium data measurement yields useful information for developing new equations of state and for fitting and testing current models.

Reservoir volume expansion and CO_2 miscibility are other areas within the scope of the type of research discussed in this dissertation. Each of these projects, any many more are 2 to 3 year studies. The overall scope of high pressure liquid and supercritical fluid solvent extraction processes will remain within the scope of Chemical Engineering at least as long as the supply of coal.

CHAPTER II

BACKGROUND: A REVIEW OF SUPERCRITICAL SOLVENT EXTRACTION DESIGNS AND PROCESS VARIABLES

The purpose of this chapter is three-fold. Primarily, it provides a condensation and analysis of the diverse industrial processes and procedures which can be grouped under the title "Supercritical Extraction." The coalescence of these topics under the collective term "Supercritical Extraction" will yield as large a data base as that of distillation.

Secondarily, the material presented here is intended to be food for thought to the reader. Although this chapter places high emphasis on supercritical solvent processes, the technology is applicable to many elevated pressure processes. An important contribution of this chapter is a fresh viewpoint for high pressure process design. Innovative high pressure process designs may result from consideration of supercritical processes.

Lastly, this section serves to bring supercritical extraction out of the specialized realm of thermodynamics and into the realm of commercialized processes.

We begin with a general discussion of the nature of supercritical extraction by viewing the process in its most general pressure-temperature-volume space.

Supercritical Phenomena

Supercritical solvent extraction is a process very similar to liquid-liquid extraction, until the mixture bubble point is reached then the similarity is towards distillation. Retrograde condensation can also be a useful description of the near-critical and supercritical phenomena. To avoid the oblivion of ambiguity, the Katz [108] rules of nomenclature for retrograde condensation will be followed:

"Condensation is interpreted as the formation of a less dense or vapor phase when the system is on or within the border curve for a two-phase fluid system. The term "retrograde" is used to earmark phase changes in which the direction of the temperature or pressure travel causing the phase change is backward from that which causes the phase change for normal cases, such as pure substances or mixtures at low pressure. At atmospheric pressure, a temperature drop or a pressure rise may cause condensation of a vapor to a liquid. A condition may arise above the critical temperature or pressure of a mixture within the limits of the two-phase region in which a rise in temperature at constant pressure or a decrease in pressure at constant temperature causes vapor to change into liquid. This process is con-

densation, but because the conditions of temperature or pressure are changing in a direction opposite to that normally encountered, the condensation is said to be retrograde."

Clarification in terminology is needed. Supercritical solvent extraction is a designation established by several authors [253, 161, 250, 246, 111, 103, 221] to describe some "gas" extractions of solids. The solvent "gas" is a fluid which is above both its critical temperature and its critical pressure, and thus "supercritical." The solvent is usually maintained between the critical temperature and 1.2 times the critical temperature, and between the critical pressure and 2 to 5 times the critical pressure. The fluid density may resemble a gas or a liquid. The region labeled supercritical fluid in Figure 1 depicts the thermodynamic boundaries. Extrapolation of the vapor pressure curve above the critical point bisects the supercritical region into a low density and a high density area. A supercritical process operates in the high solvent density area for solute extraction, and moves to the low density area for solvent recovery.

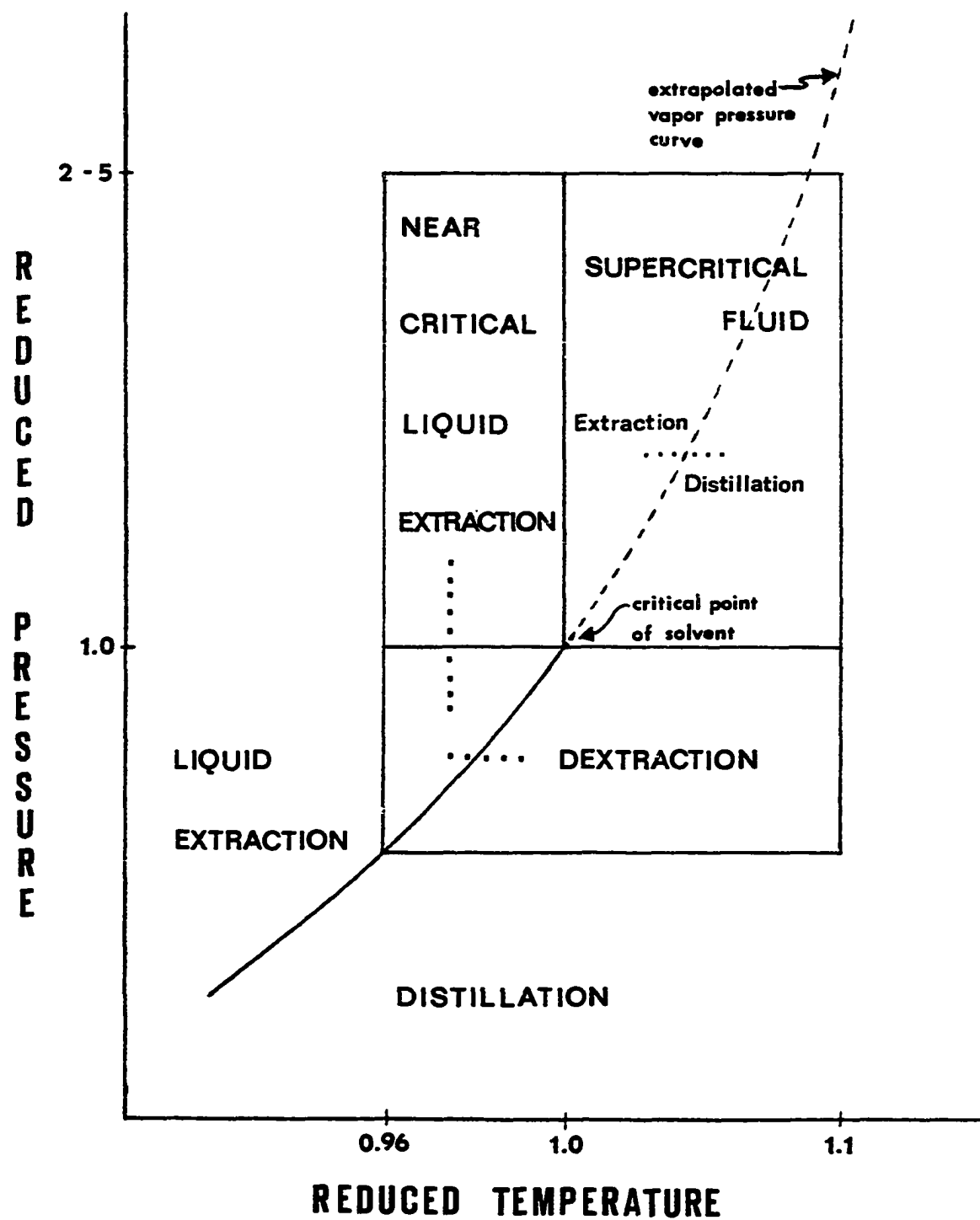
Distillation and liquid extraction are operating regions seen to lie on opposing sides of the vapor-liquid equilibrium curve. The supercritical fluid extraction process is similar to a two-step process involving first a liquid extraction to move solute into the solvent phase,

followed by distillation of the solvent-solute mixture for solvent recovery. The similarity between supercritical fluid extraction (SCF) and a two-step extraction-distillation brought Zosel [253] to designate the SCF process as dextraction. Williams [258] considers dextraction to be derived from the Latin roots "distillare" and "extrahere."

The near critical liquid region is also illustrated in Figure 1. This region is bounded by a lower temperature of 0.96 times the critical, the vapor pressure curve, the critical temperature and 2 to 5 times the critical pressure. Some extraction processes may favor using the near critical liquid region for the extraction; however, for solvent recovery, either the low density supercritical fluid or the distillation areas must be used.

A process using extraction in the near critical liquid region, followed by solvent recovery in the upper distillation region, has not been described in the literature. Dextraction is a label favored by this author for a process of this type. Distillation, liquid extraction, dextraction, supercritical fluid extraction, near critical liquid extraction, and dextraction are all labels which describe the state of the pure solvent and not the state of the solvent-solute-residue mixture. When the solute is a solid, these labels clearly define most mixture properties. If the solute and residues are liquid;

FIGURE 1. PROCESSING IN THE CRITICAL REGION OF A VAPOR PRESSURE CURVE. A broad range of processing strategies is condensed on this single vapor pressure curve, of this single vapor pressure curve, of the pure component solvent. At lower pressures, liquid extraction lies on the high density side of the vapor pressure curve and distillation on the low density side. The "extended" vapor pressure curve divides the supercritical fluid region into a high density region suitable for solute extraction and a low density range suitable for solvent regeneration (distillation). The high density near critical liquid is sometimes used as an extraction solvent. Dextraction refers to a process carried out below the critical point of the solvent, however, still within the critical region. The critical region, as related to separation processes, is bounded by a temperature range of $0.96 T_c$ -solvent to $1.1 T_c$ -solvent and by a pressure range of somewhat below P_c -solvent to 2 (to 5) P_c -solvent.



then these terms begin to lose their descriptive value. Retrograde condensation and double retrograde condensation better describe the multifluid, multiphase mixture properties.

Supercritical fluid and nearcritical liquid will be used in the remainder of this text to describe the thermodynamic state of the pure component solvent. Supercritical and nearcritical will not be used as process or mixture descriptions. The terms destraction and dextraction will be abandoned.

Fluid extraction will be used as a general process term for any process which involves a supercritical fluid or nearcritical liquid solvent.

Fluid Extraction Processes

Supercritical solvents have been used in a wide variety of separation and recovery process. Commercial success has been achieved for some solid solute process. Caffeine extraction from green coffee beans is a notable example [112, 276]. Many processes have been described or proposed in the literature:

1. demetallization in heavy crudes
[58,258].
2. SCF extraction of coal [269].
3. residuum processing [77, 78,
253 , 258].

4. extraction of plant materials containing chemotherapeutic drugs [221].
5. reforming of glucose and wood [163].
6. regeneration of activated charcoal [162].
7. caffeine extraction [258].
8. nicotine, hops, and spice extraction [103].

These processes use a variety of gases as SCF solvents: pentane, propane, water, carbon dioxide, and other low molecular weight solvents. The critical pressure of these solvents is moderate, but this necessitates a high capital cost. High initial investment is offset by either or both of two benefits. The first comes from a promised large reduction in daily utility costs, which is seen most clearly in the Kerr-McGee ROSE process for improving resins. Gearhart and Garwin [77,78], who have developed the ROSE process, note that a unique feature of this process is the more economical recovery of the solvent under SCF conditions, instead of by conventional evaporation, resulting in a utilities savings of 50% over the evaporative method, and an actual savings in investment costs of 20%. Because of its versatility,

the ROSE process now claims to produce highly refined products from the bottom of the oil barrel. This demonstrates the benefits of SCF solvents in recovering and upgrading resources previously considered as waste.

Caffeine Extraction

A German process for the decaffeination of green coffee beans came on stream in 1978-1979. These decaffeinated coffee beans are currently on the U.S. market.

The decaffeination can be carried out by three process configurations [258]. The beans are contacted in a pressure vessel with supercritical CO₂ [process variables are: $p = 160\text{--}220 \text{ ATM} = 2.22 - 3.05 \text{ Pc}$; $\rho = 0.4 \text{ to } 0.62 \text{ g cm}^{-3} = 1 \text{ to } 1.4 \text{ } \rho_{\text{c}}$; $T = 70\text{--}90^{\circ}\text{C} = 1.13 - 1.19 \text{ Tc}$]. The CO₂ is continuously recycled to a wash tower with water at 70-90°C. The extraction process continues for 10 hours (@90°C) or until all the caffeine has been extracted. The wash water is then degassed and distilled to recover the caffeine. The caffeine concentration in the bean is reduced from an initial 0.7 - 3.0% concentration to a "decaffeinated" value of as low as 0.02% [the quality control minimum is 0.08%]. One kilogram of coffee requires from 3 to 5 liters of wash water.

An alternate process approach is to recycle the CO₂ through an activated charcoal bed. The caffeine then

moves from the green bean phase, through the CO₂ phase, and then to the charcoal phase, from which it must later be extracted, for regeneration of the adsorber unit.

A variation on the activated charcoal approach is to mix the green beans with the activated charcoal, in the same pressure vessel. The charcoal pellets are approximately the same size and shape as the bean so that good contact and a short mass transfer path is maintained. One kilogram of charcoal is used per kilogram of bean. This process is said to achieve the required degree of decaffeination after 5 hours. The advantage of this process variation is that no CO₂ recycle is used. The disadvantages are that the activated charcoal must be separated from the green beans, and the caffeine must be re-extracted from the activated charcoal.

Spice Essence

Voyages to frontiers in search of spice led to a new world. Those that did not set out on the initial voyages for spice would eventually set sail for the gold. Thus, it is no wonder that supercritical carbon dioxide solvent extraction would be applied to the spice trade.

The completely "natural" CO₂ is a prime choice in food and pharmaceutical processes, and this solvent

has been given a "non-additive" designation under Federal Germany food legislation. Carbon dioxide is safe for any food processing, as it is completely bio-compatible.

Hubert [103] has summarized the quality control specifications for "food stuffs extraction-grade" carbon dioxide:

1. Odor	neither burnt nor pungent
2. Color	colorless
3. CO ₂ content	minimum 99.9 vol %, measured in the liquid or gas state
4. PH ₃ , H ₂ S and reducing organic substances	not detectable in 100 liters (STP) of gas
5. Foreign acids, e.g. SO ₂ , HCl	not detectable in 100 liters (STP) of gas
6. Carbon monoxide	<2 vol-ppm
7. Oxidizable constituents	max. 1 vol-ppm
8. Evaporation residue	max. 1 vol-ppm

Only air, nitrogen, and distilled or demineralized water are also excluded from the prohibition on additives.

The essence of table spices can be extracted with CO₂ to an extraction degree of 81 to 99% [103]. The extraction of ground chilies gives a red oil which holds 97% of the hot principle, capsaicine alkaloid, from the starting material. Ground black pepper extracts to a yellow paste with a very strong smell of pepper. The

piperine (hot principle) constituent made up 77% of the paste, roughly the same as from other commercial processes. The degree of piperine extracted was 98; three percent above the required 95% yield. Both capsaicine and piperine were extracted with supercritical carbon dioxide and separated from the solvent by reducing temperature and pressure to below the critical. Ground nutmegs can be made to yield a nutmeg butter. The nutmeg butter precipitates from the carbon dioxide solvent at temperatures and pressures above the critical point. One of the importances of spice extraction to the food industry can best be felt by recounting that it is the seeds of the "hot" pepper which cause intestinal distress, not the "hot" essence of the pepper.

Low Nicotine Tobacco

Nicotine or the tobacco aroma, "tar", may be preferentially removed from tobacco leaves [103]. Under normal moisture contents of 10-23%, aroma is removed by CO₂. The moisture content must be increased to up to 25% to favorably extract the nicotine. With two possible outcomes dependent on a third parameter, we now have the opportunity for implementing some process design techniques.

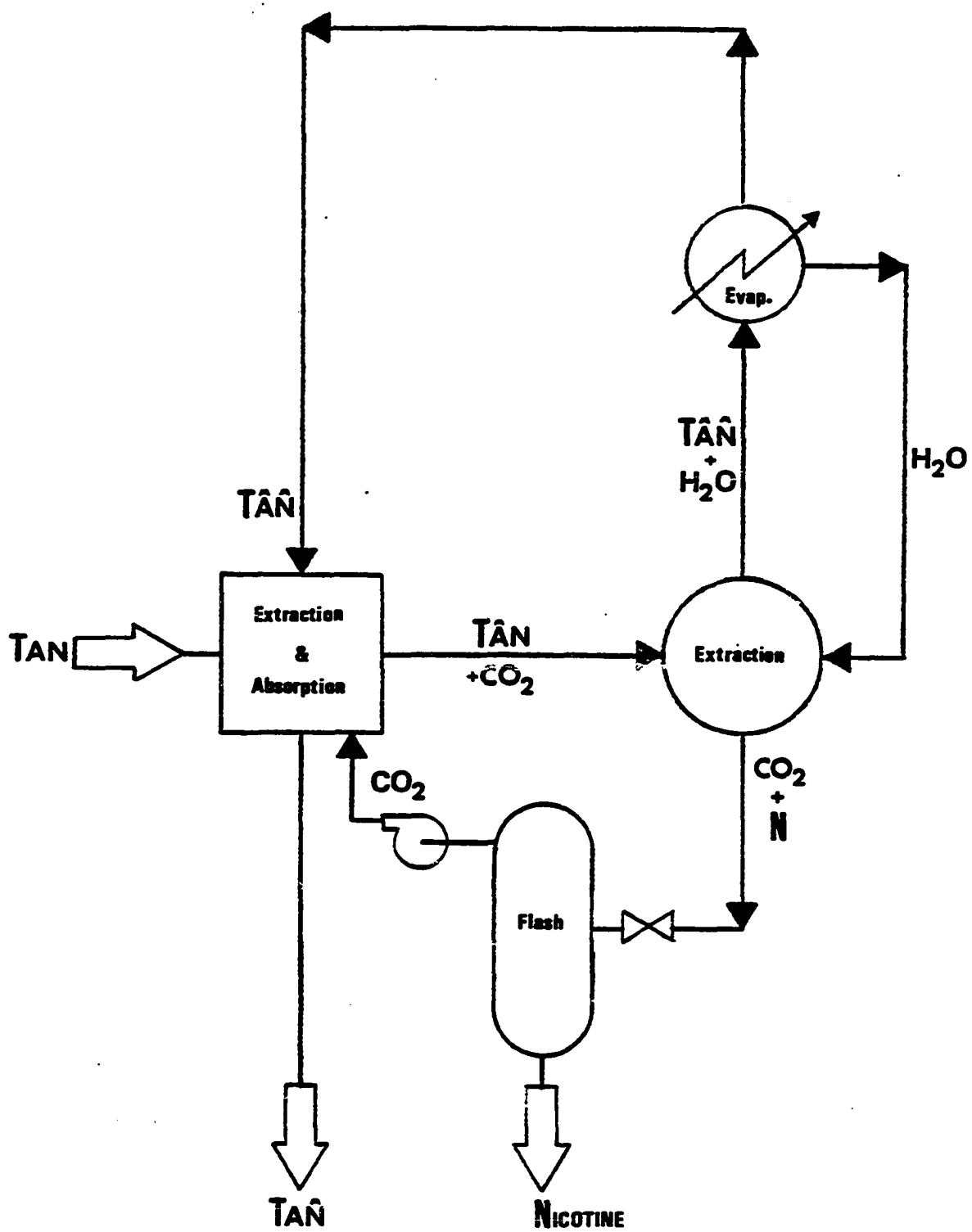
Processing of bulky, leafy material such as tobacco is most easily accomplished in a semicontinuous batch mode. A particular feed batch of tobacco

would remain in its initial pressure vessel for all phases of the processing. The extraction steps of the process require 3 to 6 hours of contact time depending on the source of the tobacco: Virginia, Burley, Orient, etc.

The first stage of processing is to remove the aroma from the fresh tobacco (see Figure 2). The low moisture content of the feed tobacco facilitates removal of the aroma while inhibiting nicotine removal. The solvent for aroma removal is dry supercritical carbon dioxide ($P \approx 300$ bar, $T = T_c$ to 100°C). CO_2 solvent with aroma is cycled to another pressure vessel containing a tobacco which has been both dearomatized and denicotinized. The solvent may be either heated or depressurized so that the aroma is precipitated onto the dearomatized, denicotinized tobacco. The CO_2 is thus regenerated and is cycled back to the pressure vessel containing the fresh tobacco (now partially dearomatized). The semi-batch processing continues until the first pressure vessel contains a dearomatized but fully nicotinized tobacco, and the second pressure vessel contains the final process product, a denicotinized, rearomatized tobacco.

Water must now be added to the first pressure vessel. Supercritical carbon dioxide ($P = 300$ ATM, $T = T_c$ to 100°C) solvent with water as an entrainer will now extract the nicotine from the dearomatized tobacco.

FIGURE 2. TOBACCO DENICOTINIZATION. Stage 1 mixes feed tobacco [tobacco with aroma and nicotine = T_{an}] with processed tobacco from Stage 3 [tobacco without aroma and nicotine = $T_{\bar{a}n}$]. Supercritical CO_2 extracts the aroma from the fresh tobacco. Aroma is adsorbed from the CO_2 by the denicotinized, dearomatized tobacco. The process product exits from Stage 1 as denicotinized, rearomatized tobacco ($T_{\bar{a}n}$). The fresh feed tobacco (T_{an}) leaves Stage 1 as dearomatized tobacco ($T_{\bar{a}n}$), and enters Stage 2. Water is added in Stage 2 to force the CO_2 extraction of nicotine. Nicotine exits Stage 2 with the CO_2 phase. The CO_2 is recycled to Stage 1 after selective sorbents remove the nicotine. Regeneration of the sorbents provides nicotine as a side stream. The denicotinized, dearomatized tobacco ($T_{\bar{a}n}$) is dried in a third stage, then recycled to the first stage. This tobacco ($T_{\bar{a}n}$) is rearomatized in Stage 1, and exits Stage 1 as the product stream, denicotinized-rearomatized tobacco ($T_{\bar{a}n}$).



The CO₂ solvent with water and nicotine is now cycled from the tobacco pressure vessel to a nicotine separation unit; the regenerated CO₂ returns to the tobacco pressure vessel for further nicotine extraction. Denicotinization continues until nicotine concentration drops from the initial value of 1.2 to 4.0% to a denicotinized value of about 0.1% nicotine in the tobacco.

Nicotine is separated from the CO₂ and water mixture with selective sorbents. Regeneration of the sorbents produces nicotine as a side product stream.

The dearomatized tobacco, which has just been denicotinized, still has a high moisture content from the addition of process water. The process water must be evaporated off, so that the proper moisture content for rearomatizing is established. If the water is not removed then the tobacco would be both rearomatized and renicotinized. The dry, dearomatized, and denicotinized tobacco is rearomatized with aroma from fresh tobacco, and the cycle is complete.

Other solvents used for this process also successfully denicotinize the tobacco, but the tobacco produced has a rubbery texture not marketable for esthetic reasons. An added advantage of the supercritical solvent is that the aromas of several tobacco types may be blended to enhance the value of lower grade tobaccos.

Hubert [103] gives a smoke analysis on the treated and untreated tobaccos. The treated tobacco received good marks in all respects; however, a slight expansion of the treated tobacco was noted. Nicotine in the tobacco was reduced 94.7%, and nicotine in the smoke was reduced 94.8%.

One of the major advantages of using supercritical carbon dioxide as a solvent for denicotinization is the sustained quality in texture. The tobacco produced is not rubbery, such as would be the case when using other process solvents.

The denicotinization process is not technically complex. The simplicity in the process design was achieved by dealing with two constraints: 1) a batch process is required to handle tobacco leaves; 2) economic factors consist substantially of marketability of a luxury item.

The batch nature of processing tobacco leaves is dictated by the market place. Denicotinized tobacco leaves must still look like tobacco leaves to the consumer. The tobacco leaves are constrained in baskets inside the pressure vessel during processing. This packing arrangement restricts the degrees of freedom in choosing classical techniques of mass transfer enhancement. This process only uses one technique to enhance mass transfer, the activated charcoal adsorber, which

removes nicotine from the solvent stream. The continuous regeneration of the solvent stream maximizes the concentration driving force for denicotinization.

Marketability studies are beyond the scope of this work. It should be noted however, that the market place supports a tremendous permutation of aroma (Tar) and nicotine concentrations. The advertisement "your low tar, low nicotine cigarette has been processed only by Car-bon Di-oxide, a part of the air we all breathe" ... "instead of Di-methyl-Chlor-ide like ..brand x" may appear in newspapers soon.

Fractionation of C₁₄-C₂₀ α -olefins

Supercritical ethylene serves as another important solvent in fluid extraction. Zosel [258] describes the fractionation of α -olefins with supercritical ethylene. The high degree of fractionation is achieved through reflux established by a "hot" finger at the column top.

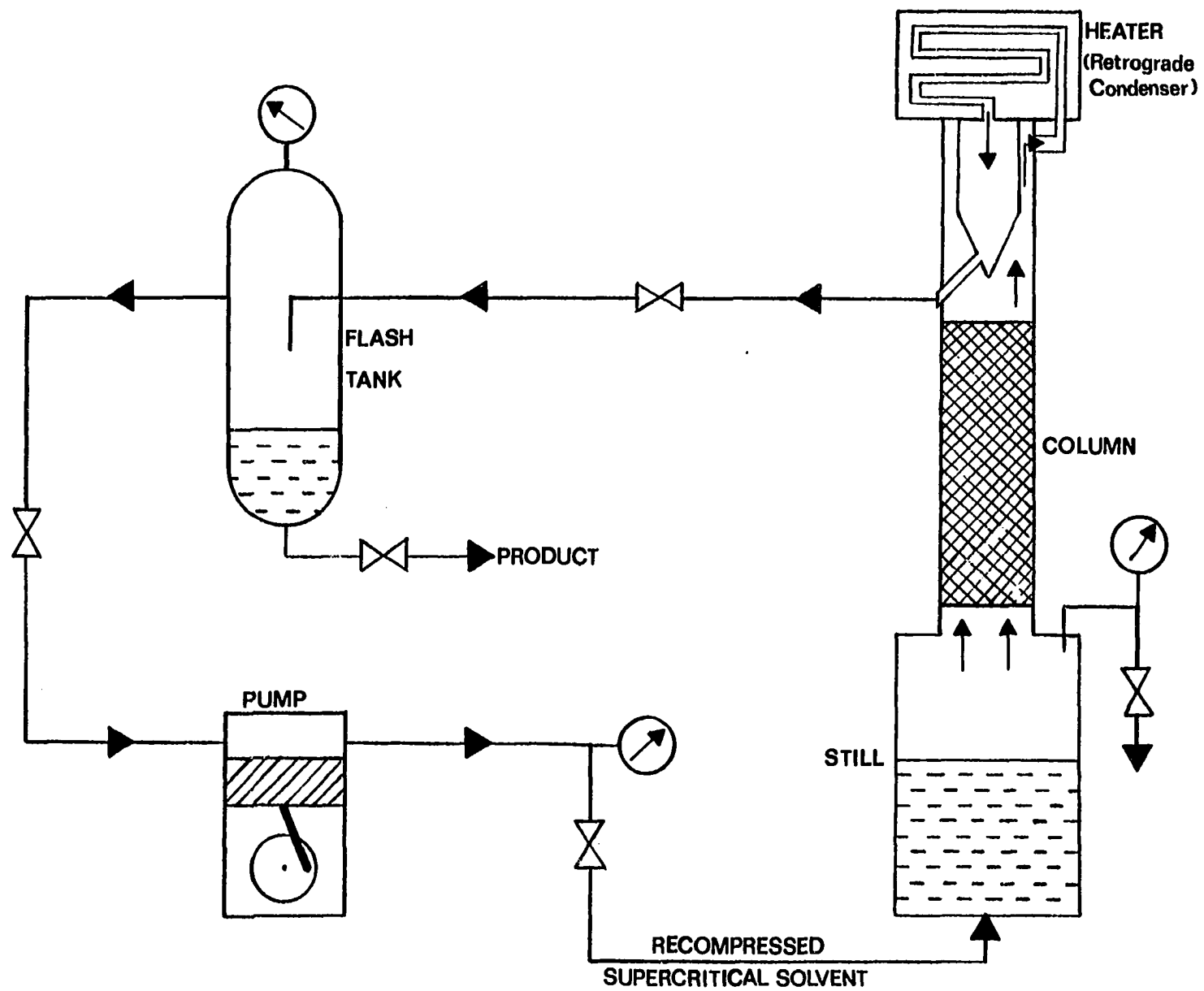
Two phases form when superheated ethylene at 25°C ($T_c = 9^\circ\text{C}$, $P_c = 50 \text{ ATM}$) is contacted with a high boiling mixture of α -olefins (C₁₉ - C₂₀). As the system pressure is increased, the ethylene dissolves in the liquid. At the critical pressure ($\rho = 0.22 \text{ g cm}^{-3}$) a fog forms above the miniscus. As the pressure is increased, the fog recedes and the liquid volume expands until at 70 ATM the liquid volume has increased three-

fold (we can see that this expansion of the liquid phase could nullify the common approximation that the "gas" phase is negligibly soluble in the liquid phase). Condensation of the olefin in the supercritical phase can be brought about by contact with a 35°C "hot" finger inserted in the top of the column. The retrograde condensate formed at the tip of the finger falls back through the supercritical phase giving a vigorous refluxing action.

Zosel [258] has proceeded with exploration of this retrograde refluxing to effect a fractionation. Figure 3 diagrams the apparatus which consists of a 25 liter still, a reflux column packed with copper rings, a "hot" finger, a flash vessel, a recycle pump, and valves for sampling and control. The still was charged with a mixture of α -olefins (traces C_{14} , 2% C_{16} , 2% C_{18} , and 7% C_{20}) and fractionated with supercritical ethane ($T_c = 32^\circ\text{C}$, $P_c = 48 \text{ ATM}$).

Fractionation was carried out at a temperature of 75°C and an initial pressure of 60 ATM ($\rho = 0.2 \text{ g cm}^{-3}$) with a finger temperature of 85°C ($\rho = 0.08 \text{ g cm}^{-3}$). The supercritical ethane-olefin phase passes through the copper ring packing where it is rectified by the retrograde condensate falling from the condenser finger. The tops are then flashed to 30 ATM, which precipitates the

FIGURE 3. BATCHWISE FRACTIONATION OF C_{14} - C_{20} α -OLEFINS. Supercritical ethylene solvent can be used to fractionate a mixture of C_{14} , C_{16} , and C_{20} α -olefins. The apparatus described by Zosel [258] operates as a batch still with a reflux column packed with copper rings located above the still. A "hot" finger (retrograde condenser) provides reflux for the column. The column operates at 75°C with a solvent density of 0.2 g cm^{-3} (at 60 ATM); the "hot" finger operates at 85°C such the solvent density has been reduced to 0.08 g cm^{-3} . The product and solvent exit the "hot" finger and are flashed to 30 ATM for solvent recovery. As the pressure is increased from 60 ATM to 110 ATM, higher carbon number α -olefins are collected in the flash tank. The fraction containing 25% of the C_{16} -olefin had a purity of 95.5%.



α -olefin fraction. The regenerated solvent is recompressed and recycled to the still. Ethane pressure is slowly increased to from 60 to 110 ATM ($\rho = 0.35 \text{ g cm}^{-3}$). A GC-analysis of the various fractions showed that a successful separation was accomplished; e.g., the fraction containing 25% of the C_{16} -olefin had a purity of 95.5%.

Increasing the pressure in this type of process is analogous to increasing the temperature in a distillation process. The components move into the supercritical ethane phase in order of their increasing boiling points. Zosel's conclusion was that this vaporization regime demonstrated that the separation is based primarily on the differences in vapor pressure of the components and thus resembles a distillation. If the α -olefin phase had contained a component which had little affinity for the ethane, then extraction characteristics would have been combined with distillation to achieve the process Zosel has designated as "destraction".

Peter and Brunner [171] have added a third component to a high boiling point and supercritical solvent mixture. Discussion proceeds to the next section.

Nonvolatile Glyceride Separation

Peter and Brunner [171] discuss the separation of mixtures of nonvolatile and heat-sensitive substances by means of compressed gases. The general process design

operates at a temperature lower than vacuum distillation. Addition of an entrainer enhanced the separation by altering the relative volatilities of the glyceride mixture. Peter and Brunner [171] obtained some interesting results with an oleic acid/ethylene system. The concentration of oleic acid in the supercritical fluid stage was increased 10 orders over that predicted by the vapor pressure alone. This very dramatic enhancement was attributed to intermolecular forces between oleic acid and ethylene. The authors continue by underscoring the importance of solvent density to solute solubility, and state that solute behavior can be understood, "if the density of the compressed gas is considered as decisive for the solubility of the nonvolatile component in the gaseous phase."

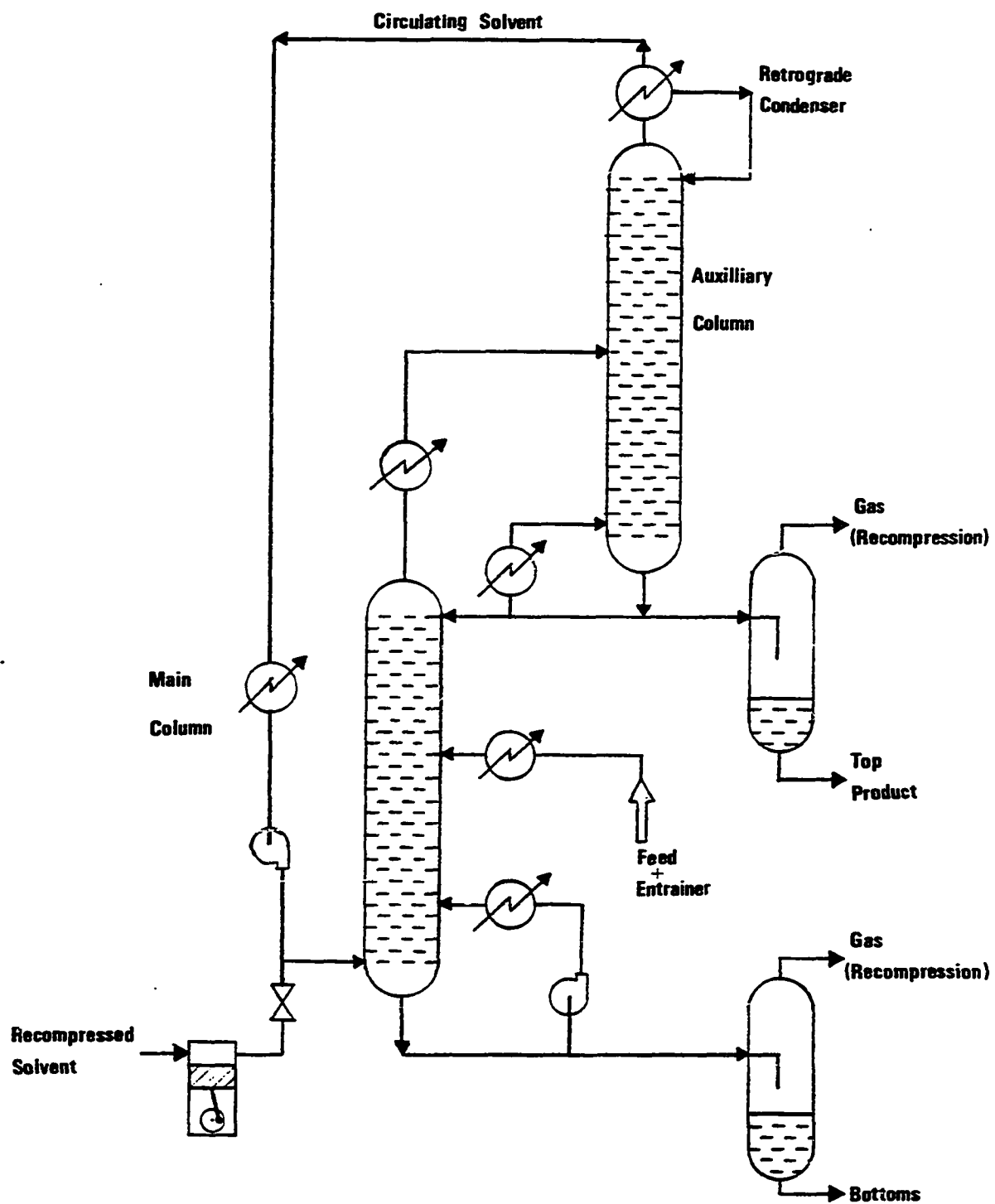
Peter and Brunner [171] appear to be saying that intermolecular forces between solute and solvent is a criterion for choosing the process solvent and that solvent density is used as a process variable to manipulate the solute solubility in the solvent phase. This approach only neglects one aspect. While intermolecular forces at one density favors a particular solvent, another density may favor a different solvent, i.e. higher order virial coefficients become involved.

Peter and Brunner [171] have compensated for the lack of theoretical basis by adding several degrees of sophistication to the supercritical solvent extraction process.

An entrainer and a column configuration with stripping sections, rectifying sections, and multiple feeds are used in glyceride processing. The process flow diagram is seen in Figure 4. The function of the entrainer is to increase the solubility of the low volatility solute in the solvent phase. The entrainer must further be chosen on the basis: 1) that the entrainer becomes only partially miscible with the solvent at a temperature not far above the extraction temperature and, 2) that the entrainer has a normal boiling point lower than the boiling point (or degradation temperature) of the solute. The first criterion enables a separation of the solvent and top products without a depressurizing step. The second criterion enables a separation of the top products stream into entrainer and final product.

This process resembles distillation to such an extent that the apparatus in Figure 4 can only be distinguished from a distillation process because the centroid of heat added to the system is toward the top instead of toward the bottom. (Instead of a condenser at the top of the column, a retrograde condenser is used, i.e. heat is added at the top, instead of being removed.)

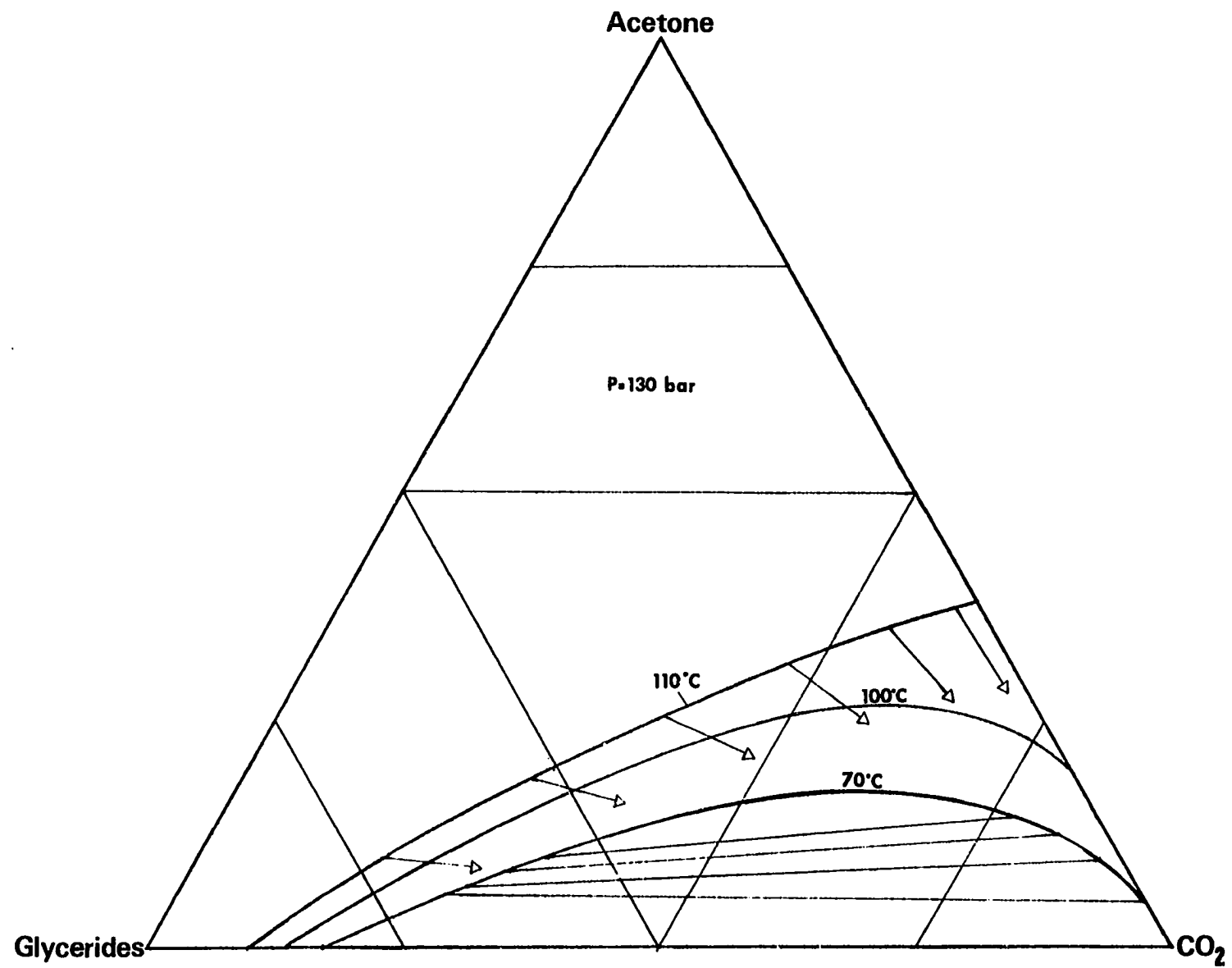
FIGURE 4. SUPERCRITICAL SOLVENTS APPLIED IN AN EXTRACTIVE DISTILLATION PROCESS CONFIGURATION. This process configuration resembles extractive distillation in all respects except for the substitution of a retrograde condenser (heat input) for the normal condenser (heat removal) at the top of the auxillary column. Peter and Brunner [171] used this plant to separate mono-glycerides from higher order glycerides. A mixture of mono-, di-, and tri-glycerides, along with 5 wt% acetone as entrainer, enter the main column. The main column operates at 70°C to 80°C ($P = 130\text{bar}$) and serves to separate mono-glycerides from the higher order glycerides. The supercritical solvent, entrainer, and mono-glycerides are then fed to an auxillary column for solvent recovery. The retrograde condenser at the top of the auxilliary column operates at 110°C which causes a retrograde condensation of mono-glyceride and acetone, which serves as a reflux. Recovered solvent from the top of the auxilliary column is then piped to the bottom of the main column via a recirculation pump. The retrograde condenser thus saves a solvent recompression step. The two flash tanks bring the product and bottoms streams down to atmospheric pressure. The entrainer (acetone) is easily recovered by simple distillation of the liquid streams.



The apparatus was used to separate a mixture of non-volatile mono-, di-, and tri-glycerides of oleic acid and glycerol. The supercritical solvent used was carbon dioxide; the entrainer used was acetone. The column was maintained at 135 bar with a bottom temperature of 80°C in the main column and 110°C in the top of the auxiliary column. The main column has 51 plates and the auxiliary column has 34 plates (bubble cap type). When a reflux ratio of 1.5 was used, 95% of the glyceride content of the top product was monoglyceride (selectivity mono/total = 95%). The monoglyceride weight yield was 50%. As the reflux ratio reached 2 the product concentration approached 100% monoglyceride. A major advantage of this process design is the absence of a need for expansion and recompression of the circulating gas. This savings in capital and operating expense is realized through the use of an entrainer.

Design of column characteristics relies on quasi-ternary phase diagrams of the type seen in Figure 5. The function of the entrainer can be seen in the 70°C envelope. At 5 wt. % entrainer, glyceride solubility in the solvent phase is enhanced. At high concentrations of entrainer the overall glyceride solubility in CO₂ is further enhanced; however, this is due to the movement of di- and tri-glycerides into the CO₂ phase. The optimum monoglyceride/diglyceride separation factor is thus

FIGURE 5. QUASITERNARY DIAGRAM OF THE ACETONE - CARBON DIOXIDE - GLYCERIDE SYSTEM. The acetone-glyceride-CO₂ system was used by Peter and Brunner [171] in fluid extraction analog to extractive distillation. When CO₂ and acetone are added to a mixture of mono-, di-, and tri-glycerides, the CO₂ rich phase contains mono-glycerides and the glyceride rich phase contains the higher order glycerides. The tie lines on the 70°C isotherm show that the addition of acetone as an entrainer increases the solubility of mono-glycerides in the CO₂ rich phase. At acetone concentrations greater than 5wt% the di- and tri-glycerides begin to move into the CO₂ rich phase. Complete miscibility of mono-, di-, and tri-glycerides with CO₂ occurs at an acetone concentration of slightly less than 10%. At higher temperatures (110°C) the solubility of glycerides in the CO₂ rich phase is negligible (the tie lines point to a pure CO₂ phase). The retrograde condensation of the heavy components at higher temperatures is utilized for solvent recovery, thus the solvent can be regenerated without a recompression step.



at about 5% entrainer concentration ($\alpha_{\text{mono/di}} > 100$ at 5% acetone; $\alpha_{\text{mono/di}} = 1.4$ at 12.5% acetone). The 110°C envelope demonstrates how the CO₂ solvent can be regenerated by temperature to save the cost of a recompression step. The tie lines for the 110°C envelope all point to relatively pure CO₂ [0.008 wt % non-volatiles]. Increasing the temperature causes a retrograde condensation of an acetone glycerine phase. The entrainer is thus responsible for reduction in column height due to increased separation factor and the savings of a compressor due to the retrograde condensation at increased temperature.

In a previous section, Katz's [109] definition of retrograde condensation was repeated for clarification. The need for specific description of multifluid-multicomponent phase behavior can be illustrated by Peter and Brunner's description of phase behavior. Peter and Brunner [171] have used the following terminology:

1. CO₂ and acetone are completely miscible at 70°C and 130 bar so the mixture is supercritical.
2. CO₂ and acetone just begin to phase split at 130 bar and some temperature between 100°C and 110°C; this temperature is called the critical temperature.

3. CO_2 and acetone form a fluid phase and a liquid phase at 130 bar and 110°C so the mixture is subcritical.

These might be useful definitions; however, as we discussed earlier, the Katz nomenclature will be followed. The process will thus be considered as an isobaric retrograde condensation.

Other Applications

Supercritical solvents have also been applied to processing of residuum oil and coal. An early patented supercritical solvent process was for deasphalting of oil (Messore, Phillips Petroleum Co., U.S. - Pat. 2420185 (1943)). Williams [253] has extensively reviewed the use of supercritical solvents. The most notable deasphalting and coal processes are:

1. USSR - propane/propylene mixtures for deasphalting;
2. Federal Germany - propane processing of top residuum;
3. U.K. National Coal Board - aromatics, paraffins, and water for coal liquifaction;
4. U.S. Kerr-McGee Refining Corp. - pentane, propane, or other proprietary solvents for deasphalting (Residual Oil Supercritical Extraction); and

5. U.S. Kerr-McGee Refining Corp. - toluene deashing of coal (Critical Solvent Deashing).

Zosel's [258] use of propane for top-resids processing brings to light one important feature of supercritical deasphalting: the yield of (V_2O_5).

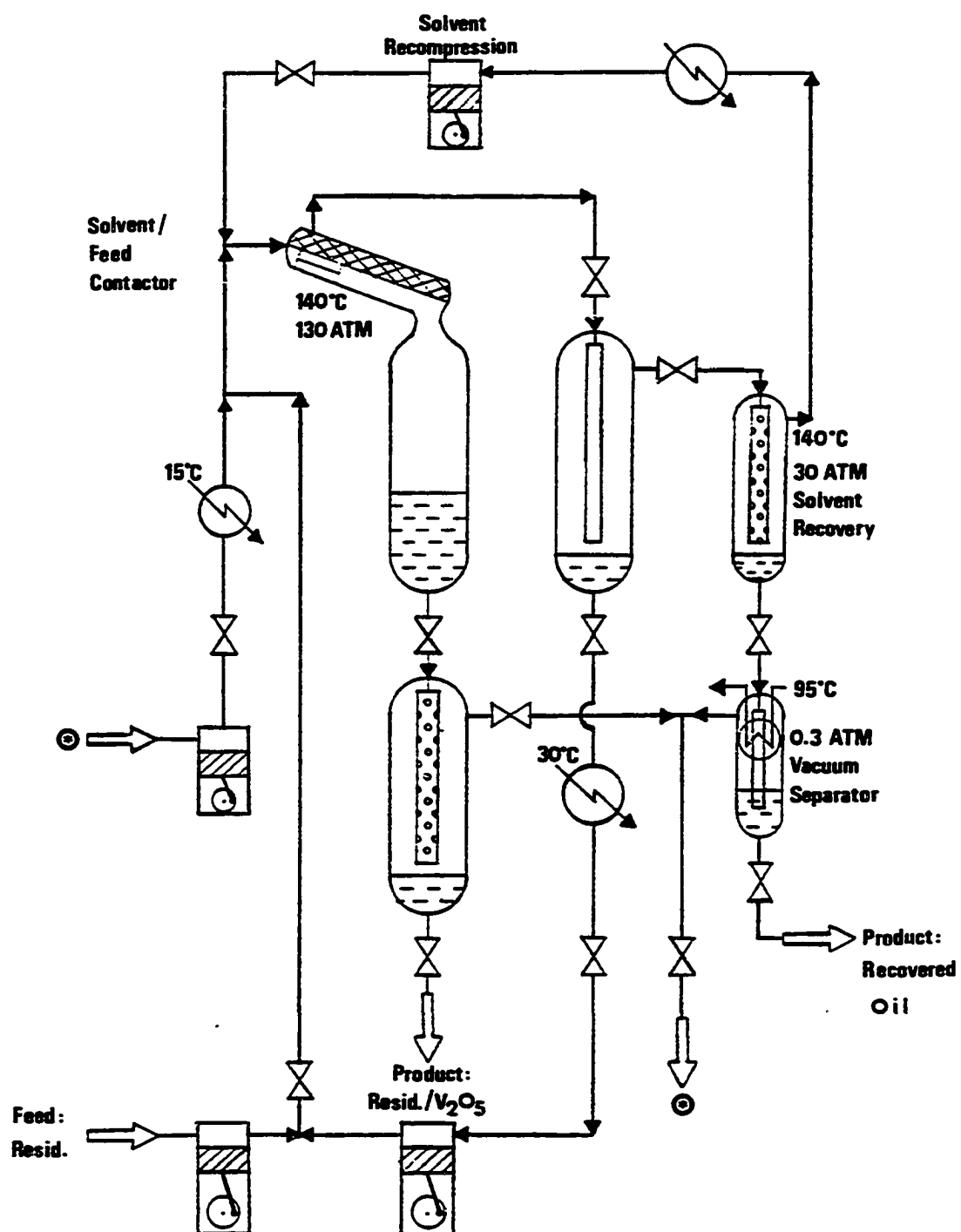
Zosel operated his deasphalting pilot plant at 140°C and at 70°C (T_c propane = 97°C (see Figure 6). The weight % product split was the same for both temperatures; 75% of the feed returned as recovered oil, and 25% of the feed remained as asphalt. The compositional difference of the two streams is dramatic. Supercritical propane extraction reduced the vanadium content in the recovered oil to 0.15 ppm, while subcritical propane left 2.4 ppm in the recovered oil. The Conradson number was also more favorable (1.3 compared to 2.0); the Conradson number refers to involatile materials.

Summary

This chapter has dealt mainly with the process variables and designs used in full scale and pilot plant operations. Supercritical solvent extraction processes can be applied to the food industry and the oil industry with equal success.

The food industry was extensively reviewed in order to demonstrate supercritical solvent extraction

FIGURE 6. PROCESS CONFIGURATION OF DEASPHALTING PILOT PLANT USING SUPERCRITICAL PROPANE SOLVENT. Supercritical propane solvent has been patented since 1934 as a solvent for fractionating heavy oils [Pilot and Shell Development Company U.S. pat. 2,315,131 (1943)]. The pilot plant shown in this figure was used by Zosel [258] in 1978 to fractionate top residual oil into recovered oil and resid. The yield of vanadium (V_2O_5) in the recovered oil was 0.15 ppm with supercritical propane at 140°C and 2.4 ppm with subcritical propane at 70°C.



in its most basic terms. These examples serve to demonstrate the solvation power of supercritical solvents. The coffee and spice processes illustrate how solutes can be extracted from solid inerts. Solvent regeneration was seen as a pressure let down or as a temperature step up. The tobacco process first hinted at the use of an entrainer. The entrainer was then used in a more sophisticated manner for glyceride fractionation. Glyceride processing also introduced refluxing by retrograde condensation. These are the building blocks of design strategy.

CHAPTER III

TWO PHASE EQUILIBRIUM: A SOLUBILITY EQUATION

The solubility of a heavy (liquid) component in a light phase (fluid or gas) can be determined by Raoult's Law. This Law gives good predictions for low and moderate pressures, however, at higher pressures, non-idealities must be described by addition terms. This chapter presents a derivation of the complete solubility relation. Prausnitz [181] and many others [44, 47, 48, 54, 91, 98, 122, 123] have used this solubility relation; however, the roots of the equation are not discussed. Arbitrary use of this equation in the highly unpredictable critical region was deemed unjustified. This chapter serves as a definition of the solubility equation and a clarification of inherent limitations.

The mixture fugacity coefficient of the heavy component in the light phase is the only mixture term in the solubility equation derived in this chapter. The necessary fugacity coefficient may be predicted by an appropriate equation of state or determined from

experimental data. The virial equation of state truncated after the second coefficient is to predict the fugacity coefficient.

The second virial EOS is not expected to be an appropriate equation of state for the high pressure conditions displayed in supercritical solvent extraction. However, many authors have determined the second virial cross coefficient for a variety of mixtures containing prospective supercritical solvents, notably the same authors as those above, using the solubility equation. Another result of this chapter is a concise review of the thermodynamics of phase equilibrium. A more appropriate equation can be introduced for the fugacity term, using the framework developed in this chapter.

ESTABLISHING CRITERION FOR TWO PHASE EQUILIBRIUM IN A MIXTURE

One of the major jobs of thermodynamics is to predict the mass and energy balances for multicomponent, multiphase processes. Fugacity as defined by Gibb's free energy is a most effective means of setting the equilibrium conditions, so that all phases can be related and the mass and energy balances between phases can be predicted. In the same sense, once the overall process balances are known, the fugacity term sets the balance for each component between the individual phases of a process unit. Conversely, determining the fugacity of the components in each phase will set the overall process energy and mass balance requirements.

The basic definition of fugacity says that a change in Gibb's free energy, divided by the temperature and gas constant, is equal to a logarithmic change in fugacity, where all changes occur at constant temperature:

$$d\bar{G} \big|_T = RT \, d \ln f \big|_T$$

In partial molar terms:

$$d\bar{G}_i|_T = d\mu_i|_T = RT d \ln \hat{f}_i|_T$$

where μ_i is the chemical potential. Since a differential change in free energy is equal to the product of specific volume and a differential pressure change at constant temperature, a boundary condition for fugacity is established, i.e., fugacity equals pressure as the system approaches the ideal gas state. The following boundary conditions and nomenclature will be observed:

$$d\bar{G}_i^O = RT(d \ln f_i^O)$$

$$\lim_{p \rightarrow 0} [f_i^O/P] = 1 \quad \text{Pure Component}$$

$$\phi_i^O = f_i^O/P$$

Const. Temp.

$$d\bar{G}_m = RT (d \ln f_m)$$

$$\lim_{p \rightarrow 0} [f_m/P] = 1 \quad \text{Mixture}$$

$$\phi_m = f_m/P$$

Const. Temp.

$$d\bar{G}_i = RT (d \ln \hat{f}_i)$$

$$\lim_{p \rightarrow 0} [\hat{f}_i/P] = 1$$

Component i in a Mixture

$$\hat{\phi}_i = \hat{f}_i / y_i P$$

Const. Temp.

Equilibrium between Phase I and Phase II is established and maintained when

$$\hat{f}_i^I = \hat{f}_i^{II}$$

$$T^I = T^{II}$$

$$P^I = P^{II}$$

(also:

$$x_i \gamma_i^{OI} \hat{f}_i^{OI} = y_i \gamma_i^{OII} \hat{f}_i^{OII} = \hat{f}_i^I = \hat{f}_i^{II}$$

$$= x_i \gamma_i^{OI} \phi_i^{OI} P = y_i \gamma_i^{OII} \phi_i^{OII} P = \hat{f}_i^I = \hat{f}_i^{II}$$

$$= \hat{\phi}_i^I x_i P = \hat{\phi}_i^{II} y_i P = \hat{f}_i^I = \hat{f}_i^{II}$$

all of which are equivalent). Other useful relations can also be derived from the above equations, in combination with the Gibbs-Helmholtz equation, to give

$$\left. \frac{\partial \ln \hat{f}}{\partial T} \right|_{P,X} = \frac{H^{I.G.} - H}{RT^2}$$

and

$$\left. \frac{\partial \ln f}{\partial P} \right|_{T,X} = \frac{V}{RT}$$

In derivation fashion:

$$\underline{H} = \underline{G} + T\underline{S}$$

$$\underline{S} = -\partial \underline{G} / \partial T \big|_P$$

Gibbs-Helmholtz
Maxwell

$$\frac{d}{dx} \left(\frac{u}{v} \right) = \frac{v \frac{du}{dx} - u \frac{dv}{dx}}{v^2}$$

Math tables

for $u = \underline{G}$; $v = T$; $x = T$

$$\frac{d(\underline{G}/T)}{dT} = \left[T \frac{d\underline{G}}{dT} - \underline{G} \frac{dT}{dT} \right] * \frac{1}{T^2}$$

$$\underline{G} - T \frac{d\underline{G}}{dT} \big|_P = -T^2 \frac{d(\underline{G}/T)}{dT} \big|_P$$

$$\underline{H} = -T^2 \frac{d(\underline{G}/T)}{dT} \big|_P$$

$$d(\underline{G}/T) \big|_T = R d \ln f \big|_T$$

$$\frac{-H}{RT^2} = \frac{d \ln f}{dT} \big|_P$$

Further useful relations are:

$$G - G^{IG} = RT \ln f - RT \ln P$$

where the mixture has changed from an ideal gas mixture to a real mixture at the same temperature, pressure, and composition, i.e., the only change is real to ideal. This change will be useful for using the ideal state as a reference point.

$$\underline{G} - \underline{G}^{IG} = RT \ln \frac{f}{P}$$

$$\left. \frac{\partial \underline{G}}{\partial N_i} \right|_{N_j, T, P} - \left. \frac{\partial \underline{G}^{IG}}{\partial N_i} \right|_{N_j, T, P} = \left. \frac{\partial}{\partial N_i} \right|_{N_j, T, P} [NRT \ln f - NRT \ln P]$$

$$\bar{G}_i - \bar{G}_i^{IG} = RT \left. \frac{\partial (N \ln f)}{\partial N_i} \right|_{N_j, T, P} - RT \ln P = RT \ln [\hat{f}_i / X_i P]$$

$$\text{where } \ln [\hat{f}_i / X_i] = \left. \frac{\partial}{\partial N_i} \right|_{N_j, T, P} [N \ln f]$$

Now Gibb's Free Energy can be quantitatively determined using the ideal gas as a reference state; for pure components we have:

$$\underline{G} = RT \ln \frac{f}{P} - \underline{G}^{IG}$$

and for component i in a mixture,

$$\bar{G}_i = RT \ln \frac{\hat{f}_i}{X_i P} - \bar{G}_i^{IG}$$

These equations are particularly useful when fugacity is calculated from an equation of state. The above relations can be obtained from Balzhiser [11] or Abbott and Van Ness [1].

COMBINING PHASE DEFINING RELATIONS
INTO ONE EQUATION

Our goal in this section is to combine the fugacities of a component, i , into a single equation. Since fugacities in each phase must be equal at equilibrium; we have:

$$\hat{f}_i^L = \hat{f}_i^V$$

THE V PHASE will be set as

$$\hat{f}_2^V = y_2 \gamma_2^{OL} f_2^{OV}$$

but also as,

$$\hat{f}_2 = \phi_2^V y_2 P$$

THE L PHASE will be set as

$$\hat{f}_2^L = x_2 \gamma_2^{OL} f_2^{OL} = x_2 \gamma_2^{OL} \phi_2^{OL} P$$

Before equating the fugacities in the V and L phases; a computational form of ϕ for the pure component in the liquid phase, will be developed.

$$dG_2^{\circ} = RT \, d \ln f_2^{\circ} = \underline{V}_2^{\circ} \, dP \text{ @ constant } T$$

$$RT \, d \ln f_2^{\circ} = RT \, d \ln \phi_2^{\circ} P$$

$$= RT \, d \ln \phi_2^{\circ} + RT \, d \ln P$$

$$d \ln \phi_2^{\circ} = \frac{\underline{V}_2^{\circ}}{RT} \, dP - d \ln P$$

$$d \ln \phi_2^{\circ} = \frac{\underline{V}_2^{\circ}}{RT} \, dP - \frac{dP}{P} = \left(\frac{\underline{V}_2^{\circ}}{RT} - \frac{1}{P} \right) \, dP$$

$$\text{or } \frac{d \ln \phi_2^{\circ}}{d \ln P} = (Z-1)$$

So far these equations hold for any component in any phase. The integration step will set boundaries on the implementations. In this particular case we are dealing with a liquid in equilibrium with a vapor. A useful and commonly used reference state for this case is the component at the temperature of the system and at the vapor pressure of the pure component. A common assumption used with this reference state is that the volume of the liquid will remain constant from the saturation pressure to the system pressure given that temperature is held constant; that is

$$\underline{V}_2^{\circ} = \underline{V}_2^{\circ \text{Sat}}$$

for any P Sat to P at constant temperature. By integration,

$$\int_{\phi_2^{\text{oSat}}}^{\phi_2^{\text{oPsys}}} d \ln \phi_2^{\text{o}} = \frac{1}{RT} \int_{P_{\text{sat}}}^{P_{\text{sys}}} \frac{V}{P} dP - \int_{P_{\text{sat}}}^{P_{\text{sys}}} d \ln P$$

$$\ln \phi_2^{\text{oL}} = \ln \phi_2^{\text{oSat}} - \ln P/P_2^{\text{oSat}} + V_2^{\text{oSat}} [P - P_2^{\text{oSat}}]/RT_{\text{sys}}$$

$$\phi_2^{\text{oL}} = \frac{[\phi_2^{\text{oSat}} P_2^{\text{oSat}}]}{P} \text{Exp} \left[\frac{V_2^{\text{oSat}} (P - P_2^{\text{oSat}})}{RT} \right]$$

The exponential term is referred to as the Poynting correction factor.

These equations form the framework for the thermodynamic equations generally used by researchers in the supercritical solvent field. On combining we have

$$\hat{f}_2^{\text{V}} = \hat{f}_2^{\text{L}}$$

$$\hat{\phi}_2^{\text{V}} y_2^{\text{P}} = x_2 \gamma_2^{\text{oL}} P \left[\frac{\phi_2^{\text{oSat}} P_2^{\text{oSat}}}{P} \right] \text{Exp} \left[\frac{V_2^{\text{oSat}} (P - P_2^{\text{oSat}})}{RT} \right]$$

$$\text{or } y_2 = \frac{x_2 P_2^{\text{oSat}}}{P} \left[\frac{\phi_2^{\text{oSat}} \gamma_2^{\text{oL}}}{\hat{\phi}_2^{\text{V}}} \right] \text{Exp} \left[\frac{V_2^{\text{oSat}} (P - P_2^{\text{oSat}})}{RT} \right]$$

Assumptions required for use: $V_2^{\text{oL}} = V_2^{\text{oSat}}$ at any P greater than the saturation pressure as determined at the temperature of the system.

Other simplifying assumptions:

$x_2 = 1$ and $\gamma_2^{\text{OL}} = 1$ when comp. 2 is a solid,

$x_2 = 1$ $\gamma_2^{\text{OL}} = 1$ when comp. 1 is negligibly soluble
in liquid comp. 2,

$\gamma_2^{\text{OL}} = 1$ for some liquids; and

$\phi_2^{\text{OSat}} = 1$ is also used as a reference state
by some authors, especially when
comp. 2 is a solid.

VIRIAL FUGACITY

The virial equation of state is a summation of single, binary, and multi-body interactions in Taylor series form. The virial equation is most often truncated after the two-body interaction coefficient. This gives several forms:

$$Z = 1 + B^* P$$

$$Z = 1 + B/\underline{V}$$

$$Z = 1 + BP/RT$$

where $B^* = B/RT$, B is the second virial coefficient given by:
in general,

$$B = \sum_{i=1}^m \sum_{j=1}^m y_i y_j B_{ij}$$

for binary mixtures,

$$B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

and for a pure component,

$$B = B_{11}$$

B_{12} is the second virial cross coefficient; this term represents the result of an interaction between a molecule of component 1 and a molecule of component 2. The interaction is best determined by experiment, but it can be predicted for hydrocarbon mixtures by Pitzer's method [177] or by Tsonopolis' method [237] with a reasonable degree of confidence. The real interaction may deviate a great deal from the value predicted by Pitzer's accentric method for a non-hydrocarbon mixture. It is this deviation which is of interest when considering non-ideal mixing, solubility, and separation. When interactions greater than London forces are anticipated, the second virial cross coefficient can be expected to deviate from Pitzer's predicted value.

The fugacity coefficient predicted from the virial equation may be useful in representing the effects of body interactions on the equilibrium mass and energy balances. Balzhiser [11, eq. 6-107] gives a relation suited for evaluating fugacity coefficients from an equation of state:

$$\ln \phi_2^o = \frac{1}{RT} \int_{\infty}^V \left(\frac{RT}{\underline{V}} - P \right) d\underline{V} + \frac{PV}{RT} - 1 - \ln \frac{PV}{RT}$$

The equation of state must be explicit in pressure for substitution into the integral equation. For the virial equation,

$$Z = \frac{PV}{RT} = 1 + \frac{B}{\underline{V}}$$

or,
$$P = \frac{RT}{\underline{V}} + \frac{BRT}{\underline{V}^2}$$

After substitution, the equations reduce to:

$$\ln \phi_2^o = B \int_{\infty}^{\underline{V}} - \frac{1}{\underline{V}^2} d\underline{V} + \frac{B}{\underline{V}} - \ln Z$$

which integrates to

$$\ln \phi_2^o = \frac{2B_{22}}{\underline{V}_2^o} - \ln Z_2$$

If the saturation temperature and pressure are being considered, then

$$\ln \phi_2^{oSat} = \frac{2B_{22}}{\underline{V}_2^{oSat}} - \ln \frac{P_2^{oSat} \underline{V}_2^{oSat}}{R T_2^{oSat}}$$

or,

$$\phi_2^{oSat} = \frac{R T_2^{oSat}}{P_2^{oSat} \underline{V}_2^{oSat}} \text{Exp} \left[\frac{2B_{22}}{\underline{V}_2^{oSat}} \right]$$

where B_{22} is evaluated at the saturation temperature.

The fugacity of component k in a mixture can be determined in a similar manner. The virial equation for a mixture, truncated after the second coefficient is:

$$Z_{\text{Mix}} = \frac{P \underline{V}_{\text{Mix}}}{N_{\text{Mix}} RT} = 1 + \frac{B_{\text{Mix}} N_{\text{Mix}}}{\underline{V}_{\text{Mix}}},$$

$$P = \frac{NRT}{\underline{V}} + \frac{N^2 RT}{\underline{V}^2} B_m$$

where,

$$B_m = \sum_{k=1}^c \sum_{i=1}^c y_k y_i B_{ki}$$

c is the number of components and N_k is the number of moles of component k . The partial derivative of pressure with respect to a change in moles of k , keeping the number of moles of all other components, temperature and volume constant is needed for the integration step; the partial is given by:

$$\begin{aligned} \left. \frac{dP}{dN_k} \right|_{T, V, N_i \neq N_k} &= \frac{RT}{V} \left. \frac{d}{dN_k} \right|_{T, V, N_i \neq N_k} \left\{ \sum_{i=1}^c N_i + \left[\sum_{i=1}^c N_i \right]^2 \frac{B_m}{V} \right\} \\ &= \frac{RT}{V} + \frac{d}{dN_k} \left[\sum_{i=1}^c N_i \right]^2 \frac{B_m}{V} \end{aligned}$$

Since
$$\left[\sum_{i=1}^c N_i \right]^2 = \sum_{i=1}^c \sum_{k=1}^c N_i N_k$$

and
$$B_m = \frac{\sum_{i=1}^c \sum_{k=1}^c N_i N_k B_{ik}}{\sum_{i=1}^c \sum_{k=1}^c N_i N_k}$$

then,

$$\left. \frac{dP}{dN_k} \right|_{T, V, N_i \neq N_k} = \frac{RT}{V} + \frac{RT}{V^2} \left\{ 2 \sum_{i=1}^c N_i B_{ik} \right\}$$

Modell and Reid [1974] have given a suitable form of the fugacity coefficient:

$$RT \ln \phi_k = \int_V^\infty \left[\left(\frac{dP}{dN_k} \right)_{T,V,N_i \neq N_k} - \frac{RT}{V} \right] dV - RT \ln Z$$

which can be combined with the previous equation to give upon integration:

$$\ln \hat{\phi}_k = \frac{2}{V} \sum_{i=1}^C N_i B_{ik} - \ln Z$$

or,

$$\ln \hat{\phi}_k = \frac{2}{V} \sum_{i=1}^C y_i B_{ik} - \ln Z$$

For a binary mixture, the fugacity coefficient of component 2 is given by

$$\ln \hat{\phi}_2 = \frac{2}{V_{\text{Mix}}} [y_2 B_{22} + y_1 B_{12}] - \ln Z_{\text{Mix}}$$

This equation can be used as a correction to the ideal case.

APPROXIMATION OF THE SECOND VIRIAL FUGACITY
COEFFICIENT ASSUMING IDEAL VOLUME MIXING
AND SMALL SOLUBILITIES

The second virial fugacity coefficient is given by

$$\ln \hat{\phi}_2 = \frac{2}{\bar{V}_m} [y_2 B_{22} + y_1 B_{12}] - \ln z_m$$

or
$$\hat{\phi}_2 = \frac{RT}{P\bar{V}_m} * \text{Exp} \left[\frac{2}{\bar{V}_m} \{y_2 B_{22} + y_1 B_{12}\} \right]$$

The volume of the mixture contains both the ideal summation of component volumes on a mole fraction basis, and the change in volume from mixing real components. The defining equations for volume, real and ideal are:

$$\bar{V}_m = \sum y_i \bar{V}_i \quad \text{Real Mixing}$$

$$\bar{V}_{\text{comps}}^o = \sum y_i \bar{V}_i \quad \text{Ideal Mixing}$$

$$\text{Real-Ideal} = \Delta \bar{V} \text{ of Mixing}$$

$$\bar{V}_m = \sum_{i=1}^C y_i \bar{V}_i + \Delta \bar{V}_{\text{mix}}$$

After much algebraic manipulation we have:

$$\hat{\phi}_2 = \frac{RT}{P} \left[(\text{Exp } 2B_m) / (V_m)^{(V_{\text{comp}})} \right]^{(1/(V_{\text{comp}} + \Delta V_m))} \\ * [V_m]^{(-\Delta V_m / (V_{\text{comp}} + \Delta V_m))}$$

In the limit as ΔV_m approaches zero,

$$\hat{\phi}_2 = \frac{RT}{P} \left[(\text{Exp } 2B) / (V_{\text{comp}})^{(V_{\text{comp}})} \right]^{(1/V_{\text{comp}})}$$

$$\text{or } \hat{\phi}_2 = [\text{Exp } 2B]^{1/V_{\text{comp}}} * \left[\frac{RT}{PV_{\text{comp}}} \right]$$

where $B = y_2 B_{22} + y_1 B_{12}$. Thus the second virial fugacity coefficient assuming small ΔV_{mix} is:

$$\hat{\phi}_2^{\text{virial}} = \left[\frac{RT}{PV_{\text{comp}}} \right] * [\text{Exp}(2y_{22}B_{22} + 2y_1B_{12})]^{(1/V_{\text{comp}})}$$

For small y_2 and small ΔV_{mixing} , the coefficient reduces to:

$$\hat{\phi}_2^{\text{virial}} = \left[\frac{RT}{PV_1} \right] * [\text{Exp}(2B_{12})]^{(1/V_1)}$$

or,

$$\ln \hat{\phi}_2^{\text{virial}} = \frac{2B_{12}}{V_1} - \ln z_1$$

or,

$$\hat{\phi}_2^{\text{virial}} = \frac{RT}{PV_1} \text{Exp} \frac{2B_{12}}{V_1}$$

The ratio of fugacity at saturation to fugacity in a mixture is important in determining the solubilities of components. The solubility of component 2 in a mixture can be expressed as:

$$y_2 = \left[\frac{x_2 p_2^{\text{oSat}}}{P} \right] \left[\frac{\phi_2^{\text{oSat}} \gamma_2^{\text{oL}}}{\hat{\phi}_2^V} \right] \text{Exp} \left[\frac{V_2^{\text{oSatL}} (P - p_2^{\text{oSat}})}{RT} \right]$$

The fugacity effects in the second term on the right, must hold the mixing properties, i.e. solvent/solute interactions. If the fugacities are represented by the virial equation truncated after second coefficient (and the following assumptions are met: 1) the change of volume upon mixing is small, 2) the mole fraction of component 2 in the light phase is small, 3) the activity coefficient of component 2 in the heavy phase is unity, and 4) the second virial fugacity applies) then the fugacity term reduces to:

$$\left[\frac{\phi_2^{\text{oSat}} \gamma_2^{\text{oL}}}{\hat{\phi}_2^V} \right] = \frac{RT_2^{\text{oSat}}}{p_2^{\text{oSat}} V_2^{\text{oSatV}}} \text{Exp} \left[\frac{2 B_{22}}{V_2^{\text{oSatV}}} \right] * \\ \frac{PV_1}{RT} \text{Exp} \left[- \frac{2 B_{12}}{V_1} \right]$$

But the saturation temperature is taken at the temperature of the system so:

$$\left[\frac{\phi_2^{\text{oSat}} \gamma_2^{\text{oL}}}{\hat{\phi}_2^V} \right] = \frac{PV_1}{p_2^{\text{oSat}} V_2^{\text{oSat}} V_1} \text{Exp} \left[\frac{2 B_{22}}{V_2^{\text{oSatV}}} - \frac{2 B_{12}}{V_1} \right]$$

When this last term is substituted into the solubility relation, we have:

$$y_2 = x_2 \left[\frac{\underline{V}_1}{\underline{V}_2^{\text{oSat}}} \text{Exp} \left\{ \frac{2 B_{22}}{\underline{V}_2^{\text{oSat}}} - \frac{2 B_{12}}{\underline{V}_1} \right\} \right] \text{Exp} \left[\frac{\underline{V}_2^{\text{oSat}} L (P - P_2^{\text{oSat}})}{RT} \right]$$

$$y_2 = x_2 \left[\text{Exp} \left\{ \ln \frac{\underline{V}_1}{\underline{V}_2^{\text{oSat}}} + \frac{2 B_{22}}{\underline{V}_2^{\text{oSat}}} - \frac{2 B_{12}}{\underline{V}_1} + \frac{\underline{V}_2^{\text{oSat}} L (P - P_2^{\text{oSat}})}{RT} \right\} \right]$$

and for $k_2 = y_2/x_2$,

$$\ln k_2 = \ln \frac{\underline{V}_1}{\underline{V}_2^{\text{oSat}}} + \frac{2 B_{22}}{\underline{V}_2^{\text{oSat}}} - \frac{2 B_{12}}{\underline{V}_1} + \frac{\underline{V}_2^{\text{oSat}} L (P - P_2^{\text{oSat}})}{RT}$$

The equilibrium distribution, k_2 , is a convenient grouping. The effects of volume differences on k may provide interesting insights,

$$\lim_{\underline{V}_2^{\text{oSat}} \rightarrow \underline{V}_1} \ln k_2 = \left[2RT \frac{(B_{22} - B_{12})}{[\underline{V}_1 RT]} + \underline{V}_1^2 (P - P_2^{\text{oSat}}) \right]$$

$$\lim_{\underline{V}_2^{\text{oSat}} \rightarrow 2\underline{V}_1} \ln k_2 = \ln 0.5 + \frac{[RT(B_{22} - 2 B_{12}) + 2 \underline{V}_1^2 (P - P_2^{\text{oSat}})]}{\underline{V}_1 RT}$$

$$\lim_{2\underline{V}_2^{\text{oSat}} \rightarrow \underline{V}_1} \ln k_2 = \ln 2.0 + \frac{[RT(4 B_{22} - 2 B_{12}) + 0.5 \underline{V}_1^2 (P - P_2^{\text{oSat}})]}{\underline{V}_1 RT}$$

Separation processes require a third component. The effects of a third component can only enter into the mixture fugacity

terms, as seen before, i.e. all other terms are for the pure component 2. The second virial fugacity coefficient of component 2 in a three component system is given by:

$$\ln \hat{\phi}_2 = \frac{2}{\bar{V}_m} \sum_{i=1}^c y_i B_{i2} - \ln \frac{P\bar{V}_m}{RT}$$

$$\text{or, } \hat{\phi}_2 = \frac{RT}{P\bar{V}_m} \text{Exp} \left[\frac{2}{\bar{V}_m} (y_1 B_{12} + y_2 B_{22} + y_3 B_{32}) \right]$$

Since the virial equation has been truncated after the second coefficient, the interaction of component 2 with component 3 is related in the equation, but the interaction of the third component with the solvent does not appear. The previous statement holds a slight misnomer. since the solvent-solute (comp 3) interaction is algebraically hidden in the y_3 term. By assuming small concentrations of solutes 2 and 3 in the solvent 1 rich phase, the $\hat{\phi}_2$ and k_2 terms reduce to the binary forms. Thus the solubility of any solute is independent of the solubility of all other solutes when the virial fugacity holds, ideal mixing is assumed, small mole fractions are considered, and the activity coefficient of each solute in the liquid phase is unity.

DISSECTION OF A SOLUBILITY EQUATION INTO IDEAL
AND NON-IDEAL GROUPS

The solubility relation developed earlier can be dissected into an ideal term and two non-ideal terms. The general solubility equation assumes only that the volume of pure component 2 in the heavy phase (component 2 rich phase) remains constant over the range from its saturation pressure at the temperature of the system, up to the pressure of the system. This assumption amounts to assuming an incompressible liquid or solid phase. The general equation is given by:

$$y_2 = \left[\frac{x_2 P_2^{\text{oSat}}}{P} \right] \left[\frac{\phi_2^{\text{oSat}} \gamma_2^{\text{OL}}}{\phi_2 V} \right] \text{Exp} \left[\frac{V_2^{\text{oSat}} (P - P_2^{\text{oSat}})}{RT} \right]$$

where: $T = T$ (of system) = T_2^{oSat} = CONSTANT. The first term in brackets is the ideal case. The second term is the fugacity correction term. The third term, including the Exp functionality, is the Poynting correction factor. The ideal and the Poynting terms can be calculated on a basis of the pure component, and the mole fraction of component 2 in the heavy phase. The fugacity term is a

function of the overall mixture, and so. includes the effects of the solvent and the effects of other solutes.

Since the literature so often contains the second virial cross coefficient as a reference point, the separation of virial prediction from the non-ideal case would be a worthy endeavor. The fugacity coefficients can be given by:

$$\phi_2^{\text{oSat}} = f_2^{\text{oSat}} / p_2^{\text{oSat}} = f_2^{\text{oSat virial}} / p_2^{\text{oSat}} *$$

$$f_2^{\text{oSat real}} / f_2^{\text{oSat virial}}$$

$$\text{or, } \phi_2^{\text{oSat}} = \phi_2^{\text{oSat virial}} * (\phi_2^{\text{oSat real}} / \phi_2^{\text{oSat virial}})$$

and, for the mixture

$$\hat{\phi}_2^V = \hat{f}_2^V / y_2 P = \hat{f}_2^{\text{virial}} / y_2 P * \hat{f}_2^{V \text{ real}} / \hat{f}_2^{\text{virial}}$$

$$\text{or, } \hat{\phi}_2^V = \hat{\phi}_2^{\text{virial}} * (\hat{\phi}_2^V / \hat{\phi}_2^{\text{virial}})$$

The solubility relation then becomes:

$$y_2 = \left[\frac{x_2 p_2^{\text{oSat}}}{P} \right] \left[\frac{\phi_2^{\text{oSat virial}}}{\hat{\phi}_2^{\text{virial}}} \right] \text{Exp} \left[\frac{v_2^{\text{oSat}} (P - p_2^{\text{oSat}})}{RT} \right] \\ * \left[\frac{\hat{\phi}_2^{\text{virial}} * \phi_2^{\text{oSat}}}{\phi_2^{\text{oSat virial}} * \hat{\phi}_2^V} * \gamma_2^{\text{OL}} \right]$$

or, in logarithmic terms,

$$\ln y_2 = \ln \text{Ideal} + \ln \text{virial fugacity} + \text{Polynting} \\ + \ln [\text{virial to real fugacity}]$$

The difference between real and virial fugacity can be found by comparing the predicted and experimental data. This relation is:

$$(y_2^{\text{EXPER}}/y_2^{\text{PRED}}) = \left[\frac{\hat{\phi}_2^{\text{virial}} * \phi_2^{\text{oSat}} * \gamma_2^{\text{oL}}}{\phi_2^{\text{oSat virial}} * \hat{\phi}_2^{\text{V}}} \right]$$

or,

$$y_2^{\text{EXPER}} = y_2^{\text{PRED}} * \left[\frac{\hat{\phi}_2^{\text{virial}}}{\phi_2^{\text{oSat virial}}} \right] * \left[\frac{\phi_2^{\text{oSat}} \gamma_2^{\text{oL}}}{\hat{\phi}_2^{\text{V}}} \right]$$

or,

$$\left[\frac{\phi_2^{\text{oSat}} \gamma_2^{\text{oL}}}{\hat{\phi}_2^{\text{V}}} \right] = \left[\frac{y_2^{\text{EXPER}}}{y_2^{\text{PRED}}} \right] \left[\frac{\phi_2^{\text{oSat virial}}}{\hat{\phi}_2^{\text{virial}}} \right]$$

For the case of pure component activity coefficient in the heavy phase assumed equal to one, and the virial saturated fugacity assumed equal to the real saturated fugacity, the relation reduces to

$$\phi_2^{\text{V}} = \left[\frac{y_2^{\text{PRED}}}{y_2^{\text{EXPER}}} \right] [\hat{\phi}_2^{\text{virial}}]$$

Obviously, if the prediction of solubilities is good, then $\hat{\phi}_2^V$ equals $\hat{\phi}_2^{\text{virial}}$. This series of equations can lead to a basis of better prediction of the actual solubilities by differentiating the underlying causes. Notice that if the virial fugacities are assumed valid, then γ_2^{OL} is $y^{\text{EXPER}}/y^{\text{PRED}}$.

VIRIAL AND REAL FUGACITIES OF A CO₂

AND WATER MIXTURE

The solubility equation, assuming the virial equation holds and an incompressible liquid phase 2 with an activity coefficient of unity ($\gamma_2^{\text{OL}} = 1$), and small y_2 , is given by:

$$y_2 = \left[\frac{x_2 p_2^{\text{OSat}}}{P} \right] \left[\frac{p \underline{v}_1}{p_2^{\text{OSat}} \underline{v}_2^{\text{OSatV}}} \text{Exp} \left[\frac{2 B_{22}}{\underline{v}_2^{\text{OSatV}}} - \frac{2 B_{12}}{\underline{v}_1} \right] \right] \\ * \text{Exp} \left[\frac{\underline{v}_2^{\text{OSatL}} (P - p_2^{\text{OSat}})}{RT} \right]$$

Once the system is defined by choosing a solute (comp 2) and a solvent (comp 1), setting the temperature of the system sets p_2^{OSat} , $\underline{v}_2^{\text{OSat}}$, B_{22} , and B_{12} . After thus setting the system, a change in pressure affects only y_2 , x_2 , P , and $\underline{v}_1$. Terms which will remain constant at constant temperature can be separated from the pressure variable terms.

$$y_2 = C_1 x_2 \underline{v}_1 \text{Exp} \left[C_2 + \frac{C_3}{\underline{v}_1} \right] \text{Exp} [C_4 P + C_5]$$

where
$$C_1 = \frac{P_2^{\text{oSAT}} P}{P P_2^{\text{oSAT}} \underline{V}_2^{\text{oSAT}}} = \frac{1}{\underline{V}_2^{\text{oSATV}}}$$

$$C_2 = 2 B_{22}/\underline{V}_2^{\text{oSATV}}$$

$$C_3 = - 2 B_{12}$$

$$C_4 = \underline{V}_2^{\text{oSATL}}/RT$$

$$C_5 = - P_2^{\text{OSAT}} \underline{V}_2^{\text{oSATL}}/RT$$

A slightly modified form will be used for calculation so that the fugacity terms can be pulled out for later comparisons. This modified but equivalent form is:

$$y_2 = \left[\frac{x_2 C_1}{P} \right] \left[\frac{\text{Exp } C_3}{C_2} \right] [z_1 \text{ Exp } (P C_4/z_1)] * \text{Exp } [P C_5 + C_6]$$

where,

$$C_1 = P_2^{\text{oSAT}}$$

$$C_2 = P_2^{\text{oSAT}} \underline{V}_2^{\text{oSATV}}/RT$$

$$C_3 = 2 B_{22}/\underline{V}_2^{\text{oSATV}}$$

$$C_4 = - 2 B_{12}/RT$$

$$C_5 = \underline{V}_2^{\text{oSATL}}/RT$$

$$C_6 = - P_2^{\text{oSAT}} \underline{V}_2^{\text{oSATL}}/RT$$

and where

$$\phi_2^{\text{oSat}} = \left[\frac{\text{Exp } C_3}{C_2} \right]$$

$$\hat{\phi}_2^{\text{virial}} = [Z_1 \text{Exp } (P C_4/Z_1)]^{-1}$$

Poynting Correction Factor

$$= \text{Exp } [P C_5 + C_6]$$

Ideal Solubility

$$= \left[\frac{X_2 C_1}{P} \right]$$

Ideal Solubility (assuming "light" component is negligibly soluble in the "heavy" phase)

$$= \frac{C_1}{P} \text{ (or, } P_2^{\text{oSat}}/P)$$

The separation of the constant terms from the variable terms enables our calculations to run at a faster pace, which is especially important for hand calculators and large jobs such as reservoir studies.

The Enhancement Factor

The virial equation of state (EOS) has been applied to supercritical solvents by many authors. Williams [251] gives an excellent review of the rele-

vant references. Williams cites and explains an approximate relationship for the enhancement of the solubility of a solid in the gas phase:

$$y_2 = E * (P_2^{\text{oSolid}}/P)$$

where $E = \text{Exp} ((V_2^{\text{oSolid}} - 2B_{12})/V_m)$

= the enhancement factor

y_2 = the mole fraction of the solid
solute (2) in the gas phase (1).

V_2^{oSolid} = the volume of pure solid solute.

V_m = the specific volume of the gas
phase mixture.

P_2^{oSolid} = the vapor pressure of the solid
at the temperature of the system.

B_{12} = the second virial cross coefficient.

This equation appears simple and straight forward in use; however, it is clear from the simplicity that a great number of approximations and assumptions have been made. Without elucidation upon these assumptions, the equations provide little predictive utility. This chapter was developed so that equations, of the type seen above, could be applied with better confidence. The derivations in this chapter demonstrate that:

$$\ln \hat{\phi}_2^{\text{virial}} = \frac{2 B_{12}}{V_1} - \ln z_1,$$

$$\ln \phi_2^{\text{oSatV}} = \frac{2 B_{22}}{V_2^{\text{oSatV}}} - \ln z_2^{\text{oSatV}},$$

and

$$\text{Poynting} = \exp [V^{\text{oSatL}}(P - P_2^{\text{oSat}})/RT],$$

with the assumptions:

1. y_2 is small
2. ΔV_{mixing} of 1 and 2 in the vapor phase is small
3. The virial equation truncated after the second coefficient yields a valid fugacity coefficient
4. The specific volume of pure liquid 2 remains constant at pressures well above the saturation pressure.

Comparing these equations to the enhancement factor cited by Williams [258], we have

$$E = [\phi_2^{\text{oSatV}} / \hat{\phi}_2^{\text{virial}}] * \text{Poynting}$$

or,

$$E = \left[\exp \left[\frac{V_2^{\text{oSatL}}}{RT} (P - P_2^{\text{oSat}}) + \frac{2 B_{22}}{V_2^{\text{oSatV}}} - \frac{2 B_{12}}{V_1} \right] \right] * \frac{z_1}{z_2^{\text{oSatV}}}$$

This equation reduces to William's equation when the following assumptions are also included:

1. $\phi_2^{\text{oSatV}} = 1$
2. $P - P_2^{\text{oSat}} = P$
3. The pressure of the system is high enough such that $Z_1 = 1$ ($P_R = 5-15$; $T_R = 1-15$)

These approximations and assumptions yield the relation:

$$E = \text{Exp} [(\underline{V}_2^{\text{oSatL}} - 2 B_{12})/\underline{V}_1]$$

This method of analysis proves very successful. The enhancement factor presented by Williams was easily derived from the fugacity and Poynting terms developed in this chapter. The seven assumptions need to comply with theoretical and practical supercritical solvent separation. Two of the assumptions do, however, give problems. The assumption that the virial equation second coefficient yields a valid fugacity equation will be discussed in a later chapter. The assumption that the compressibility factor is approximately equal to one is a serious problem.

The majority of supercritical solvent processes operate in the range $T_R = 0.96$ to 1.1 , and $P_R = 2$ to 5 . In this range, a normal hydrocarbon has a compressibility factor ranging from 0.3 to 0.7 . The assumption that

$Z \approx 1$ would be more valid in the range $T_R = 1.0$ to 15 and $P_R = 5$ to 15 ($Z = 0.7$ to 1.3). Most supercritical solvent processes have demonstrated that this extreme range is not necessary.

CHAPTER IV

THE CARBON DIOXIDE AND WATER BINARY SYSTEM

Mixtures of carbon dioxide and water enter into most realms of science and engineering. Respiration in zoological systems, supercritical carbon dioxide solvent, separation of ethanol and water, tertiary oil recovery in petroleum reservoirs, and methanol production all require knowledge of the $\text{CO}_2\text{-H}_2\text{O}$ binary. This chapter provides a review of the literature on the $\text{CO}_2\text{-H}_2\text{O}$ binary, followed by an analysis of the data relevant to the supercritical solvent phenomena.

A Review of Literature on the

$\text{CO}_2\text{-H}_2\text{O}$ Binary

Literature on the $\text{CO}_2\text{-H}_2\text{O}$ binary is not overwhelming in volume; however, some very good works do exist. Plinius Secundus, in his Natural History, 79AD, speaks of exhalations from a silver mine in Spain which are particularly harmful to dogs. The gas especially harmful to dogs and more concentrated near the floors

of the drifts is evidently carbon dioxide [222]. A.L. Lavoisier was the first author (with LaPlace) to give the atomic composition of carbon dioxide. It was common in Lavoisier's day (circa 1782) to absorb carbon dioxide with water. More recently, Wiebe, 1941 [250], published data on the $\text{CO}_2\text{-H}_2\text{O}$ binary system under pressure. This publication is the backbone of today's data on the $\text{CO}_2\text{-H}_2\text{O}$ system and is referred to by many authors.

Wiebe presents data on both the water rich phase and the CO_2 rich phase. The temperature range is 12°C to 100°C and the pressure range is 1 ATM to 800 ATM. This range completely covers the range of interest for supercritical solvent extraction processes, and tertiary oil recovery. These data form the main body of experimental solubilities used in the numerical analysis in the later half of this chapter. The most interesting aspect of this data comes from taking the supercritical solvent viewpoint.

In this system, $\text{CO}_2\text{-H}_2\text{O}$, CO_2 is considered as the supercritical solvent; however, this system does not behave in the same manner as more typical supercritical solvent systems such as $\text{CO}_2\text{-benzoic acid}$ [123]. The $\text{CO}_2\text{-benzoic acid}$ system displays increased solubility of benzoic acid in CO_2 when the temperature is decreased (for pressures greater than the critical of CO_2 and a temperature range centering around the

critical). In contrast, the $\text{CO}_2\text{-H}_2\text{O}$ system displays a consistantly increasing solubility with temperature and pressure. At still higher pressures (2.2 Pr CO_2) the temperature response of the CO_2 -benzoic acid system reverses such that an increase in temperature increases solubility. Individual $\text{CO}_2\text{-H}_2\text{O}$ isotherms show a typical pressure response. The solubility of H_2O in the CO_2 rich phase increases with an increase in pressure (when the pressure is greater than the critical pressure of CO_2).

Tödheide, 1963, gives a more complete coverage of $\text{CO}_2\text{-H}_2\text{O}$ binary [233] The system is too complex to do justice in describing it in its entirety; for this, the original publication must be the authority. One of the significant features of the system is that the solubility of H_2O in the CO_2 rich phase does not appear to change in the pressure range from 250 bar to 3500 bar at a constant temperature; this is accurate for temperatures of 50°C , 100°C , and 150°C . The same nil pressure response is approximately accurate for the water rich phase. At temperatures above 266°C the system has divergent upper and lower critical solution temperatures. These are divergent in the sense that isotherms on a P-X diagram are hyperbolic as opposed to the more commonly occurring (closed) ellipse. [The two phases become more alike, as pressure is increased, and a region of complete miscibility

then occurs. If pressure is further increased, two phases will again form; the composition of these two phase diverges as pressure is increased. For discussion purposes only, a crude extrapolation at a temperature of 267°C gives a pure CO₂ and pure H₂O phase in equilibrium at approximately 10,000 bar.]

Tödheide's data explains some of the questions posed by Wiebe. Wiebe found that a phase inversion takes place at temperatures below 12°C. Wiebe also states that a large increase in H₂O solubility in CO₂ appeared to take place at "much higher pressures" (i.e. over 800 ATM), which Wiebe attributes to "some critical mixing" phenomena. This increase is not supported by Tödheide's data; however, Tödheide did find a high pressure phase inversion at 50°C: 800 bar, 100°C: 1250 bar, and 250°C: 2000 bar. The high pressure phase inversion is evidently what Wiebe was finding.

The next important work on the CO₂-H₂O binary came from A.D. King [48], in 1971. King remeasured Wiebe's data in the range 25°C to 75°C and 1 ATM to 120 ATM. The second virial cross coefficients were determined from the revised data. King also measured the N₂O-H₂O, C₂H₆-H₂O, and Ar-H₂O binaries. From a comparison of the data, aided by a statistical mechanical development, King separates the B₁₂ into contribution from dispersion forces, dipole-quadrupole interactions, and physical interactions.

King deduces that the reaction of water and CO_2 in the gas phase forms the same compound as in the liquid phase [H_2CO_3]. Contributions to the second virial cross coefficient from dispersion and dipole interaction were used to calculate the equilibrium constant for the reaction. Lambert [125] gave the relation as:

$$B_{12}(T) = B_{12}(T)_{\text{phys}} - RT/2K_p$$

where $K_p = P_{\text{H}_2\text{O}} P_{\text{gas}} / P_{\text{complex}}$

King's equilibrium constant yields a partial pressure for the complex which approximately equals the partial pressure of the water. This is not too surprising since the B_{12} physical is approximately half the B_{12} apparent [the distribution of interaction forces is evenly split between physical interactions and "complex" interactions].

The numerical analysis in the second half of this chapter uses the B_{12} apparent from King as the complete B_{12} , thus the physical and complexing contributions are retained in one overall coefficient.

The Virial Equation of State Applied to the Carbon Dioxide and Water Binary System

The numerical formulations derived in the preceding chapter are used to predict the behavior of the $\text{CO}_2\text{-H}_2\text{O}$ binary system. The derived equations provide an easy and effective means of calculation.

Virial EOS equations in general require more parameters than equations such as the Peng-Robinson EOS. The required parameters for the calculations were obtained from a variety of sources:

1. Saturation pressures and specific volumes of pure water from Balzhiser [11]
2. Pure component second virial from Dymond [65]
3. Second virial cross coefficients from King [48]
4. Compressibility of pure carbon dioxide from Weeter [248] and from Van Huff [239].

The experimentally determined solubilities are from the extensive work of Wiebe [250]. Table 1 compiles the temperature dependent parameters and the calculated coefficients used in the solubility equation. The constants C1 through C6 are the same as previously derived. An additional constant, C4a has been added; C4a is used to check the assumption that the mole fraction of H_2O in the CO_2 phase is negligible in the mixture fugacity equation.

Table 2 demonstrates how the calculations were used to establish a 33 x 15 matrix as a work space on a mini-computer. Each investigated pressure function was written in a vector of the matrix for

TABLE 1

Temperature Dependent Parameters of the
Carbon Dioxide -- Water System, for use
with the Virial Equation of State.

TEMPERATURE K	298.15	304.19	323.15
TEMP DEPENDENCE			
PsatH2O ATM	.03134	.04455	.1224
Vsat(H2O-LIQ) cc/gmol	18.07	18.087	18.236
Vsat(H2O-VAP) cc/gmol	782497	561032	217039
B11 CO2 cc/gmol	-124.5	-119	-103.5
B12 CO2-H2O	-214	-197	-151
B22 H2O	-1162.4	-1060.2	-812.2
FUG-CO-VIR-PURE-H2OsatVAP	.99466877770	.99491006936	.99071828284
C1 Psat	.03134	.04455	.1224
C2 PsatVsat(H2O-VAP)/RT	1.0023773035	1.0013243411	1.0018423866
C3 2*B22/Vsat(H2O-VAP)	-.0029710018	-.0037794636	-.0074843692
C4 -2*B12/RT	.01749416910	.01578467534	.01138904077
C4a -2*B22/RT	.09502440264	.08494879593	.06125946299
C5 Vsat(H2O-LIQ)/RT	.00073859728	.00072461275	.00068771704
C6 -PsatVsat(H2O-LIQ)/RT	.00002314764	.00003228150	.00008417657
R cc*ATM/gmol*K	82.057	82.057	82.057

* Computed parameters are represented as truncated values and
are not intended as significant digits.

	A		B		C	
			TABLE 2-a		Dissection of the Solubility Equation.	
1						
2						
3						
4						
5						
6			PRESSURE		ATM	
7			TEMP		K	
8			X H2O EXPER		$1-(C32/(C32+(1350.8861)))$	
9			Y H2O EXPER		$1-((1/(C33*1E-6))/((1/(C33*1E-6))+1350.8861))$	
10			Y H2O PREDICTED		$C15*C14$	
11			Psat/P		$B29/C29$	
12			X H2O * Psat/P		$C8*C11$	
13			(XPsat/P)*(POYNTING)		$C12*C15$	
14			(XPsat/P)*(FCsat/FCVIR)		$C12*C21/C18$	
15			POYNTING		$EXP(C29*B34+B35)$	
16			1/FUG-CO-W/O-Z(CO2)		$(EXP(C29*((B32*(1)+(0)))))$	
17			1/FUG-CO-VIRIAL-H2O-MIX		$(EXP(C29*((B32*(1)+(0))/C31)))*C31$	
18			FUG-CO-VIRIAL-H2O-MIX(V)		$1/(C31*EXP(C29*((B32*(1)+(0))/C31)))$	
19			FUG-CO-EXPER--H2O-MIX(V)		$(C10/C9)*C18$	
20			FUG-CO/FUG-CO-VIRIAL H2O		$C19/C18$	
21			FUG-CO-VIR-PURE-H2O _{sat} VAP		$(EXP(B31))/B30$	
22			ACTIV-CO-H2O-LIQ-W/VIR		$1/C20$	
23			DELVIRIAL GIBB (J/GMOL)		$8.3144*C30*(LN(C19/C18))$	
24			DEL--Psat GIBB (J/GMOL)		$8.3144*C30*(LN(C19/C21))$	
25			DELVRPsat GIBB (J/GMOL)		$8.3144*C30*(LN(C18/C21))$	
26			DELVIRIAL GIBB (BTU/lbm)		$0.110262*((C30*9/5))*(LN(C20))$	
27			DEL--Psat GIBB (BTU/lbm)		$0.110262*((C30*9/5))*(LN(C19/C21))$	
28						
29			.03134		1	
30			1.002377303485193		298.15	
31			-.002971001805757722		.9948	
32			.01749416910249298		1.5	
33			.09502440263896189		23	
34			.0007385972796309538			
35			.00002314763874363409			

C.

TABLE 2-b

Dissection of the Solubility Equation:

PRESSURE ATM	1	70	75	80	400
TEMP K	298.15	298.15	298.15	298.15	298.15
X H2O EXPER	.998891	.978105	.977885	.977659	.972206
Y H2O EXPER	.030134	.002237	.002587	.002883	.004371
Y H2O PREDICTED	.031550	.007567	.053868	.057021	1.25667
Psat/P	.03134	.000448	.000418	.000392	.000078
X H2O * Psat/P	.031305	.000438	.000409	.000383	.000076
(XPsat/P)*(POYNTING)	.031329	.000461	.000432	.000406	.000102
(XPsat/P)*(FCsat/FCVIR)	.031526	.007185	.050964	.053748	.935202
POYNTING	1.00076	1.05309	1.05698	1.06089	1.34375
1/FUG-CO-W/O-Z(CO2)	1.01765	3.40278	3.71383	4.05331	1094.08
1/FUG-CO-VIRIAL-H2O-MIX	1.01245	53.6463	613.447	653.487	17203.1
FUG-CO-VIRIAL-H2O-MIX(V)	.987704	.060620	.007975	.007088	.000081
FUG-CO-EXPER--H2O-MIX(V)	1.03411	.205010	.166065	.140206	.023291
FUG-CO/FUG-CO-VIRIAL H2O	1.04699	3.38189	20.8226	19.7814	287.490
FUG-CO-VIR-PURE-H2OsatVAP	.994669	.994669	.994669	.994669	.994669
ACTIV-CO-H2O-LIQ-W/VIR	.955122	.295693	.048025	.050553	.003478
DELVIRIAL GIBB (J/GMOL)	113.824	3020.43	7526.15	7398.99	14033.7
DEL--Psat GIBB (J/GMOL)	96.4052	-3915.1	-4437.4	-4857.0	-9306.8
DELVRPsat GIBB (J/GMOL)	-17.418	-6935.5	-11964.	-12256.	-23340.
DELVIRIAL GIBB (BTU/lbm)	2.71706	72.1000	179.655	176.620	334.997
DEL--Psat GIBB (BTU/lbm)	2.30127	-93.457	-105.92	-115.94	-222.16
	.03134	1	70	75	80
1.002377303485193	298.15	298.15	298.15	298.15	298.15
-.002971001805757722	.9948	.3075	.2044	.2159	.7175
.01749416910249298	1.5	30.24	30.55	30.87	30.62
.09502440263896189	23	1.66	1.92	2.14	3.25
.0007385972796309538					
.00002314763874363409					

* Computered parameters are represented as truncated values and are not intended as significant digits.

TABLE 2-c

Dissection of the Solubility Equation:
using .5 of the B12

PRESSURE ATM	1	70	75	80	400
TEMP K	298.15	298.15	298.15	298.15	298.15
X H2O EXPER	.998891	.978105	.977885	.977659	.972206
Y H2O EXPER	.030134	.002237	.002587	.002883	.004371
Y H2O PREDICTED	.031274	.001033	.002175	.002231	.009581
Psat/P	.03134	.000448	.000418	.000392	.000078
X H2O * Psat/P	.031305	.000438	.000409	.000383	.000076
(XPsat/P)*(POYNTING)	.031329	.000461	.000432	.000406	.000102
(XPsat/P)*(FCsat/FCVIR)	.031250	.000981	.002058	.002103	.007130
POYNTING	1.00076	1.05309	1.05698	1.06089	1.34375
1/FUG-CO-W/O-Z(CO2)	1.00879	1.84466	1.92713	2.01328	33.0769
1/FUG-CO-VIRIAL-H2O-MIX	1.00359	7.32436	24.7679	25.5634	131.161
FUG-CO-VIRIAL-H2O-MIX(V)	.996427	.444002	.197529	.181188	.010626
FUG-CO-EXPER--H2O-MIX(V)	1.03411	.205010	.166065	.140206	.023291
FUG-CO/FUG-CO-VIRIAL H2O	1.03782	.461732	.840710	.773818	2.19189
FUG-CO-VIR-PURE-H2OsatVAP	.994669	.994669	.994669	.994669	.994669
ACTIV-CO-H2O-LIQ-W/VIR	.963557	2.16576	1.18947	1.29229	.456227
DELVIRIAL GIBB (J/GMOL)	92.0268	-1915.7	-430.12	-635.65	1945.39
DEL--Psat GIBB (J/GMOL)	96.4052	-3915.1	-4437.4	-4857.0	-9306.8
DELVRPsat GIBB (J/GMOL)	4.37841	-1999.5	-4007.3	-4221.3	-11252.
DELVIRIAL GIBB (BTU/lbm)	2.19676	-45.728	-10.267	-15.173	46.4380
DEL--Psat GIBB (BTU/lbm)	2.30127	-93.457	-105.92	-115.94	-222.16
	.03134	1	70	75	80
1.002377303485193	298.15	298.15	298.15	298.15	298.15
-.002971001805757722	.9948	.3075	.2044	.2159	.7175
.00874708455124649	1.5	30.24	30.55	30.87	38.62
.09502440263896189	23	1.66	1.92	2.14	3.25
.0007385972796309538					
.00002314763874363409					

* Computered parameters are truncated values and are not intended as significant digits.

the calculations. Column C contains the defining equations for the parameters of interest, column B. As an example, in column C: row 6 the alphanumeric C29 is found. C29 refers to column C: row 29 to find the pressure of interest, P (in ATM). A column corresponds to a pressure and each table of calculations corresponds to one temperature; the constants from Table AA are seen in column B: rows 29 to 35. The equations in column C are "replicated" through column P ($P = 400$ ATM). Super Calc^R represents the beginning of vectorization; it is not the complete vectorization such as used in the CRAY-2 ultra-high speed computer; however, it represents the basics of this form of programming.

Rows 1 through 15 are self explanatory. The "Y H₂O Predicted" in row 10 is the mole fraction solubility of water in the CO₂ rich phase, as predicted by the solubility equation previously derived (this equation uses the second virial fugacity coefficient for H₂O in the mixture). The assumptions are: 1) negligible Y_{H_2O} in the fugacity equation, 2) an ideal volume mixing, 3) the activity coefficient of pure water in the liquid phase is unity, 4) the specific volume of pure liquid water is constant (held at the saturation value) for any pressure greater than the saturation pressure, and 5) the virial equation truncated after the second coefficient yields a valid fugacity coefficient.

Tables 2 (a-c) show the dissection of the solubility equation into its contributing effects. Row 11 is Y_{H_2O} predicted by the ideal case, assuming the solubility of CO_2 in the H_2O phase is negligible. Row 12 is the ideal case, or Raoult's Law. Row 13 is Raoult's Law with the Poynting correction factor. Row 14 is Raoult's Law with the virial fugacity effect. Row 10, Y_{H_2O} predicted, combines Raoult's Law, the fugacity effects, and the Poynting correction factor. Row 18 is the fugacity coefficient of H_2O in the mixture predicted by the second virial EOS. Row 19 is the experimental fugacity coefficient of H_2O in the mixture assuming the activity coefficient of water in the liquid phase is unity. Row 22 is the activity coefficient of water in the liquid phase, assuming that the virial fugacity is correct. The fugacity coefficient of pure water at the temperature of the system and the saturation pressure of pure water is given in Row 21. The remainder of the Table BB series will be discussed after a look at the complete set of data in tabular and graphical form.

Tables 3, 4, and 5 characterize the CO_2 - H_2O binary system from 1 ATM to 400 ATM at constant temperatures of 25°C, 31°C, and 50°C. The data are more easily viewed in graphical form. Figure 7 shows each of the Y_{H_2O} predicted cases from the dissection of the solubility

TABLE 3

The Carbon Dioxide and Water
Binary System at 298.15 K .

PRESSURE ATM	1	30	50	60	70	75
TEMP K	298.2	298.2	298.2	298.2	298.2	298.2
X H2O EXPER	.9989	.9866	.9802	.9788	.9781	.9779
Y H2O EXPER	.0301	.0016	.0014	.0015	.0022	.0026
Y H2O PREDICTED	.0316	.0016	.0016	.0020	.0076	.0539
Psat/P	.0313	.0010	.0006	.0005	.0004	.0004
X H2O * Psat/P	.0313	.0010	.0006	.0005	.0004	.0004
(XPsat/P)*(POYNTING)	.0313	.0011	.0006	.0005	.0005	.0004
(XPsat/P)*(FCsat/FCVIR)	.0315	.0016	.0015	.0019	.0072	.0510
POYNTING	1.001	1.022	1.038	1.045	1.053	1.057
FUG-CO-VIRIAL-H2O-MIX(V)	.9877	.6419	.4007	.2650	.0606	.0080
FUG-CO-EXPER--H2O-MIX(V)	1.034	.6476	.4520	.3649	.2050	.1661
FUG-CO/FUG-CO-VIRIAL H2O	1.047	1.009	1.128	1.377	3.382	20.82
FUG-CO-VIR-PURE-H2OsatVAP	.9947	.9947	.9947	.9947	.9947	.9947
ACTIV-CO-H2O-LIQ-W/VIR	.9551	.9911	.8864	.7263	.2957	.0480
DELVIRIAL GIBB (J/GMOL)	113.8	22.25	299.0	792.7	3020.	7526.
DEL--Psat GIBB (J/GMOL)	96.41	-1064	-1955	-2486	-3915	-4437
DELVRPsat GIBB (J/GMOL)	-17.4	-1086	-2254	-3279	-6936	-1e4
DELVIRIAL GIBB (BTU/lbm)	2.717	.5312	7.137	18.92	72.10	179.7
DEL--Psat GIBB (BTU/lbm)	2.301	-25.4	-46.7	-59.3	-93.5	-106.

PRESSURE	80	85	100	120	130	150	200	300	400
TEMP	298.2	298.2	298.2	298.2	298.2	298.2	298.2	298.2	298.2
X H2O EXPE	.9777	.9774	.9770	.9766	.9764	.9761	.9751	.9735	.9722
Y H2O EXPE	.0029	.0032	.0036	.0037	.0038	.0039	.0041	.0043	.0044
Y H2O PRED	.0570	.0728	.1123	.1725	.2266	.3613	.4990	.8680	1.257
Psat/P	.0004	.0004	.0003	.0003	.0002	.0002	.0002	.0001	.0001
X H2O * Ps	.0004	.0004	.0003	.0003	.0002	.0002	.0002	.0001	.0001
(XPsat/P)*	.0004	.0004	.0003	.0003	.0003	.0002	.0002	.0001	.0001
(XPsat/P)*	.0537	.0683	.1043	.1579	.2058	.3234	.4305	.6955	.9352
POYNTING	1.061	1.065	1.077	1.093	1.101	1.117	1.159	1.248	1.344
FUG-CO-VIR	.0071	.0052	.0029	.0016	.0011	.0006	.0004	.0001	.0001
FUG-CO-EXP	.1402	.1206	.0912	.0741	.0677	.0583	.0432	.0294	.0233
FUG-CO/FUG	19.78	22.99	31.24	46.11	59.49	92.90	122.4	202.3	287.5
FUG-CO-VIR	.9947	.9947	.9947	.9947	.9947	.9947	.9947	.9947	.9947
ACTIV-CO-H	.0506	.0435	.0320	.0217	.0168	.0108	.0082	.0049	.0035
DELVIRIAL	7399.	7772.	8532.	9497.	10129	11233	11917	13162	14034
DEL--Psat	-4857	-5230	-5922	-6438	-6663	-7033	-7774	-8727	-9307
DELVRPsat	-1e4	-1e4	-1e4	-2e4	-2e4	-2e4	-2e4	-2e4	-2e4
DELVIRIAL	176.6	185.5	203.7	226.7	241.8	268.1	284.5	314.2	335.0
DEL--Psat	-116.	-125.	-141.	-154.	-159.	-168.	-186.	-208.	-222.

* Computed parameters are represented as truncated values and
are not intended as significant digits.

TABLE 4

The Carbon Dioxide and Water
Binary System at 304.19 K

PRESSURE ATM	1	30	50	60	70	75
TEMP K	304.2	304.2	304.2	304.2	304.2	304.2
X H2O EXPER	.9990	.9879	.9824	.9808	.9794	.9787
Y H2O EXPER	.0414	.0022	.0017	.0018	.0027	.0030
Y H2O PREDICTED	.0448	.0022	.0020	.0022	.0029	.0060
Psat/P	.0446	.0015	.0009	.0007	.0006	.0006
X H2O * Psat/P	.0445	.0015	.0009	.0007	.0006	.0006
(XPsat/P)*(POYNTING)	.0445	.0015	.0009	.0008	.0007	.0006
(XPsat/P)*(FCsat/FCVIR)	.0448	.0022	.0019	.0021	.0028	.0056
POYNTING	1.001	1.022	1.037	1.044	1.052	1.056
FUG-CO-VIRIAL-H2O-MIX(V)	.9890	.6770	.4630	.3470	.2225	.1026
FUG-CO-EXPER--H2O-MIX(V)	1.069	.6874	.5191	.4188	.2458	.2024
FUG-CO/FUG-CO-VIRIAL H2O	1.081	1.015	1.121	1.207	1.105	1.973
FUG-CO-VIR-PURE-H2OsatVAP	.9949	.9949	.9949	.9949	.9949	.9949
ACTIV-CO-H2O-LIQ-W/VIR	.9248	.9850	.8920	.8284	.9053	.5067
DELVIRIAL GIBB (J/GMOL)	197.7	38.34	289.2	476.0	251.6	1719.
DEL--Psat GIBB (J/GMOL)	182.7	-935.	-1645	-2188	-3536	-4027
DELVRPsat GIBB (J/GMOL)	-15.0	-974.	-1934	-2664	-3788	-5746
DELVIRIAL GIBB (BTU/lbm)	4.720	.9152	6.903	11.36	6.007	41.04
DEL--Psat GIBB (BTU/lbm)	4.361	-22.3	-39.3	-52.2	-84.4	-96.1

C.

PRESSURE	80	85	100	120	130	150	200	300	400
TEMP	304.2	304.2	304.2	304.2	304.2	304.2	304.2	304.2	304.2
X H2O EXPE	.9787	.9785	.9782	.9777	.9774	.9771	.9763	.9747	.9735
Y H2O EXPE	.0032	.0036	.0039	.0041	.0042	.0043	.0045	.0050	.0051
Y H2O PRED	.0151	.0331	.0653	.0900	.1230	.1677	.2831	.4901	.6860
Psat/P	.0006	.0005	.0004	.0004	.0003	.0003	.0002	.0001	.0001
X H2O * Ps	.0005	.0005	.0004	.0004	.0003	.0003	.0002	.0001	.0001
(XPsat/P)*	.0006	.0005	.0005	.0004	.0004	.0003	.0003	.0002	.0001
(XPsat/P)*	.0142	.0312	.0607	.0825	.1120	.1504	.2449	.3943	.5134
POYNTING	1.060	1.064	1.075	1.091	1.099	1.115	1.156	1.243	1.336
FUG-CO-VIR	.0382	.0164	.0071	.0044	.0030	.0019	.0009	.0004	.0002
FUG-CO-EXP	.1808	.1527	.1182	.0966	.0875	.0748	.0550	.0358	.0280
FUG-CO/FUG	4.739	9.328	16.57	22.07	29.41	38.96	62.29	98.02	133.3
FUG-CO-VIR	.9949	.9949	.9949	.9949	.9949	.9949	.9949	.9949	.9949
ACTIV-CO-H	.2110	.1072	.0604	.0453	.0340	.0257	.0161	.0102	.0075
DELVIRIAL	3935.	5648.	7100.	7825.	8552.	9263.	10450	11597	12374
DEL--Psat	-4313	-4740	-5387	-5897	-6148	-6545	-7321	-8409	-9030
DELVRPsat	-8247	-1e4	-1e4	-1e4	-1e4	-2e4	-2e4	-2e4	-2e4
DELVIRIAL	93.92	134.8	169.5	186.8	204.1	221.1	249.4	276.8	295.4
DEL--Psat	-103.	-113.	-129.	-141.	-147.	-156.	-175.	-201.	-216.

* Computed parameters are represented as truncated values and are not intended as significant digits.

TABLE 5

The Carbon Dioxide and Water
Binary System at 323.15 K .

PRESSURE ATM	1	30	50	60	70	75
TEMP K	323.2	323.2	323.2	323.2	323.2	323.2
X H2O EXPER	.9996	.9918	.9874	.9856	.9845	.9836
Y H2O EXPER	.1116	.0054	.0041	.0039	.0038	.0038
Y H2O PREDICTED	.1222	.0053	.0040	.0039	.0040	.0041
Psat/P	.1224	.0041	.0024	.0020	.0017	.0016
X H2O * Psat/P	.1224	.0040	.0024	.0020	.0017	.0016
(XPsat/P)*(POYNTING)	.1224	.0041	.0025	.0021	.0018	.0017
(XPsat/P)*(FCsat/FCVIR)	.1221	.0052	.0039	.0037	.0038	.0039
POYNTING	1.001	1.021	1.035	1.042	1.049	1.053
FUG-CO-VIRIAL-H2O-MIX(V)	.9925	.7736	.6185	.5376	.4529	.4083
FUG-CO-EXPER--H2O-MIX(V)	1.087	.7596	.5982	.5376	.4733	.4413
FUG-CO/FUG-CO-VIRIAL H2O	1.095	.9820	.9672	.9999	1.045	1.081
FUG-CO-VIR-PURE-H2OsatVAP	.9907	.9907	.9907	.9907	.9907	.9907
ACTIV-CO-H2O-LIQ-W/VIR	.9131	1.018	1.034	1.000	.9571	.9253
DELVIRIAL GIBB (J/GMOL)	244.2	-48.9	-89.6	-.283	117.9	208.5
DEL--Psat GIBB (J/GMOL)	249.0	-714.	-1355	-1643	-1985	-2173
DELVRPsat GIBB (J/GMOL)	4.834	-665.	-1266	-1642	-2103	-2381
DELVIRIAL GIBB (BTU/lbm)	5.829	-1.17	-2.14	-.007	2.814	4.977
DEL--Psat GIBB (BTU/lbm)	5.944	-17.0	-32.4	-39.2	-47.4	-51.9

PRESSURE	80	85	100	120	130	150	200	300	400
TEMP	323.2	323.2	323.2	323.2	323.2	323.2	323.2	323.2	323.2
X H2O EXPE	.9835	.9826	.9814	.9807	.9804	.9799	.9789	.9773	.9759
Y H2O EXPE	.0038	.0041	.0049	.0057	.0061	.0066	.0073	.0081	.0082
Y H2O PRED	.0043	.0046	.0079	.0212	.0274	.0399	.0629	.1247	.1599
Psat/P	.0015	.0014	.0012	.0010	.0009	.0008	.0006	.0004	.0003
X H2O * Ps	.0015	.0014	.0012	.0010	.0009	.0008	.0006	.0004	.0003
(XPsat/P)*	.0016	.0015	.0013	.0011	.0010	.0009	.0007	.0005	.0004
(XPsat/P)*	.0041	.0044	.0074	.0195	.0250	.0360	.0548	.1014	.1214
POYNTING	1.057	1.060	1.071	1.086	1.094	1.109	1.148	1.229	1.317
FUG-CO-VIR	.3645	.3202	.1607	.0509	.0365	.0220	.0108	.0039	.0024
FUG-CO-EXP	.4093	.3646	.2627	.1890	.1652	.1336	.0934	.0597	.0477
FUG-CO/FUG	1.123	1.139	1.635	3.716	4.522	6.072	8.622	15.33	19.57
FUG-CO-VIR	.9907	.9907	.9907	.9907	.9907	.9907	.9907	.9907	.9907
ACTIV-CO-H	.8905	.8781	.6116	.2691	.2211	.1647	.1160	.0652	.0511
DELVIRIAL	311.7	349.1	1321.	3527.	4054.	4846.	5788.	7334.	7990.
DEL--Psat	-2375	-2686	-3567	-4451	-4813	-5384	-6346	-7547	-8152
DELVRPsat	-2687	-3035	-4888	-7978	-8868	-1e4	-1e4	-1e4	-2e4
DELVIRIAL	7.440	8.334	31.54	84.19	96.78	115.7	138.2	175.1	190.7
DEL--Psat	-56.7	-64.1	-85.1	-106.	-115.	-129.	-151.	-180.	-195.

* Computed parameters are represented as truncated values and are not intended as significant digits.

FIGURE 7. PREDICTED SOLUBILITY OF WATER IN A CARBON DIOXIDE PHASE AT A TEMPERATURE OF 298K AND A PRESSURE RANGE OF 1 TO 300 ATM. The solubility of water in a carbon dioxide rich phase is predicted by several forms of the solubility equation. The solubility equation derived in this dissertation is broken down into its familiar components and plotted as curves a through e which were formulated as follows: 1) Curve "a" is the ideal case assuming the solubility of CO_2 in the H_2O phase is negligible; 2) Curve "b" is Raoult's law; 3) Curve "c" is Raoult's law with the Poynting correction factor; 4) Curve "d" is Raoult's law with the fugacity effect from the second virial EOS; 5) Curve "e" is the complete solubility equation which included Raoult's law, the Poynting correction, and the fugacity effect. The most important feature of this illustration is the effect displayed by the fugacity term. Fugacity must be included so that the enhancement of solubility above the critical pressure of CO_2 can be predicted.

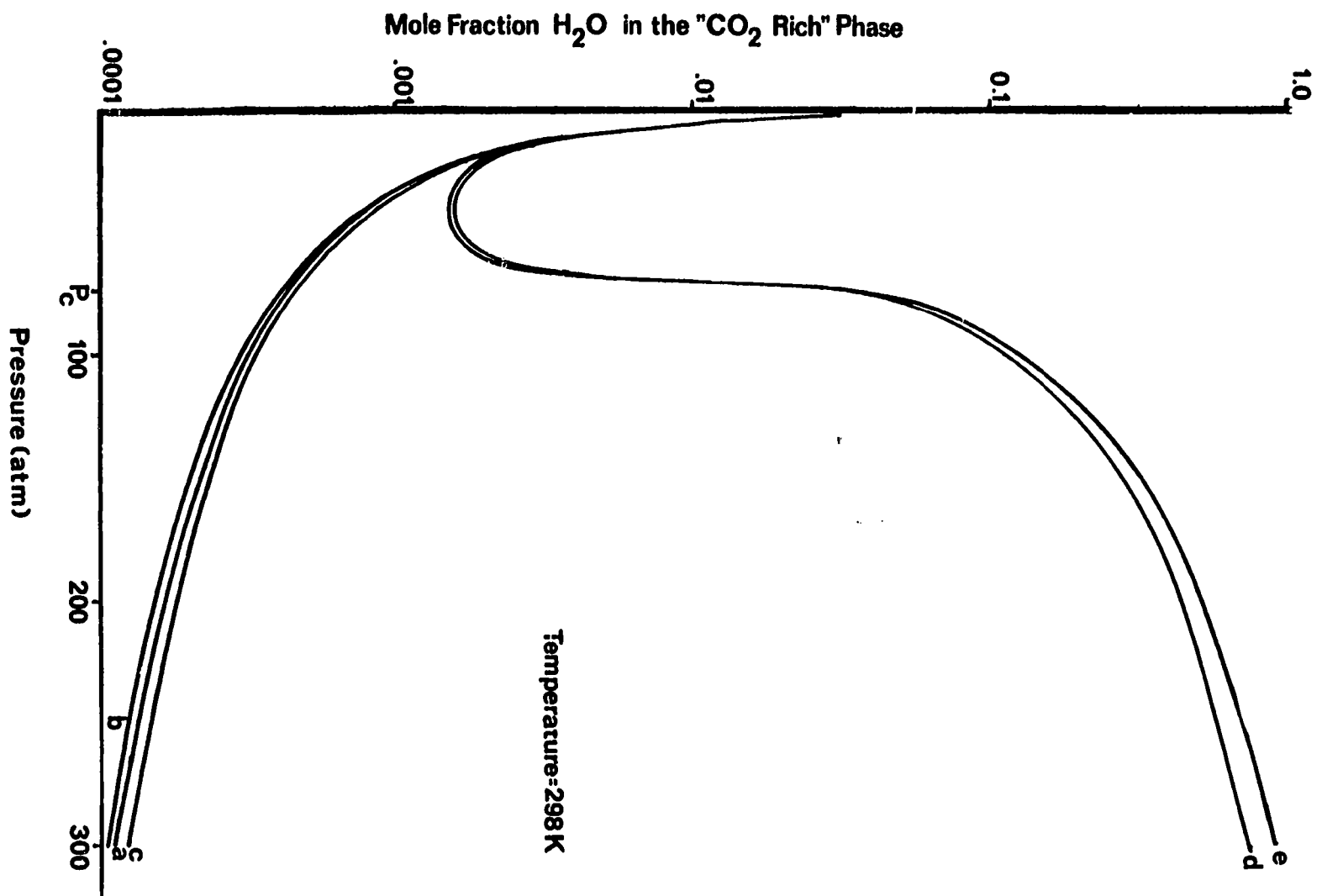


FIGURE 8. PREDICTED SOLUBILITY OF WATER IN A CARBON DIOXIDE PHASE AT A TEMPERATURE OF 304K AND A PRESSURE RANGE OF 1 TO 300 ATM. The solubility of water in a carbon dioxide rich phase is predicted by several forms of the solubility equation. The solubility equation derived in this dissertation is broken down into its familiar components and plotted as curves a through e which were formulated as follows: 1) Curve "a" is the ideal case assuming the solubility of CO_2 in the H_2O phase is negligible; 2) Curve "b" is Raoult's law; 3) Curve "c" is Raoult's law with the Poynting correction factor; 4) Curve "d" is Raoult's law with the fugacity effect from the second virial EOS; 5) Curve "e" is the complete solubility equation which included Raoult's law, the Poynting correction, and the fugacity effect. The most important feature of this illustration is the effect displayed by the fugacity term. Fugacity must be included so that the enhancement of solubility above the critical pressure of CO_2 can be predicted.

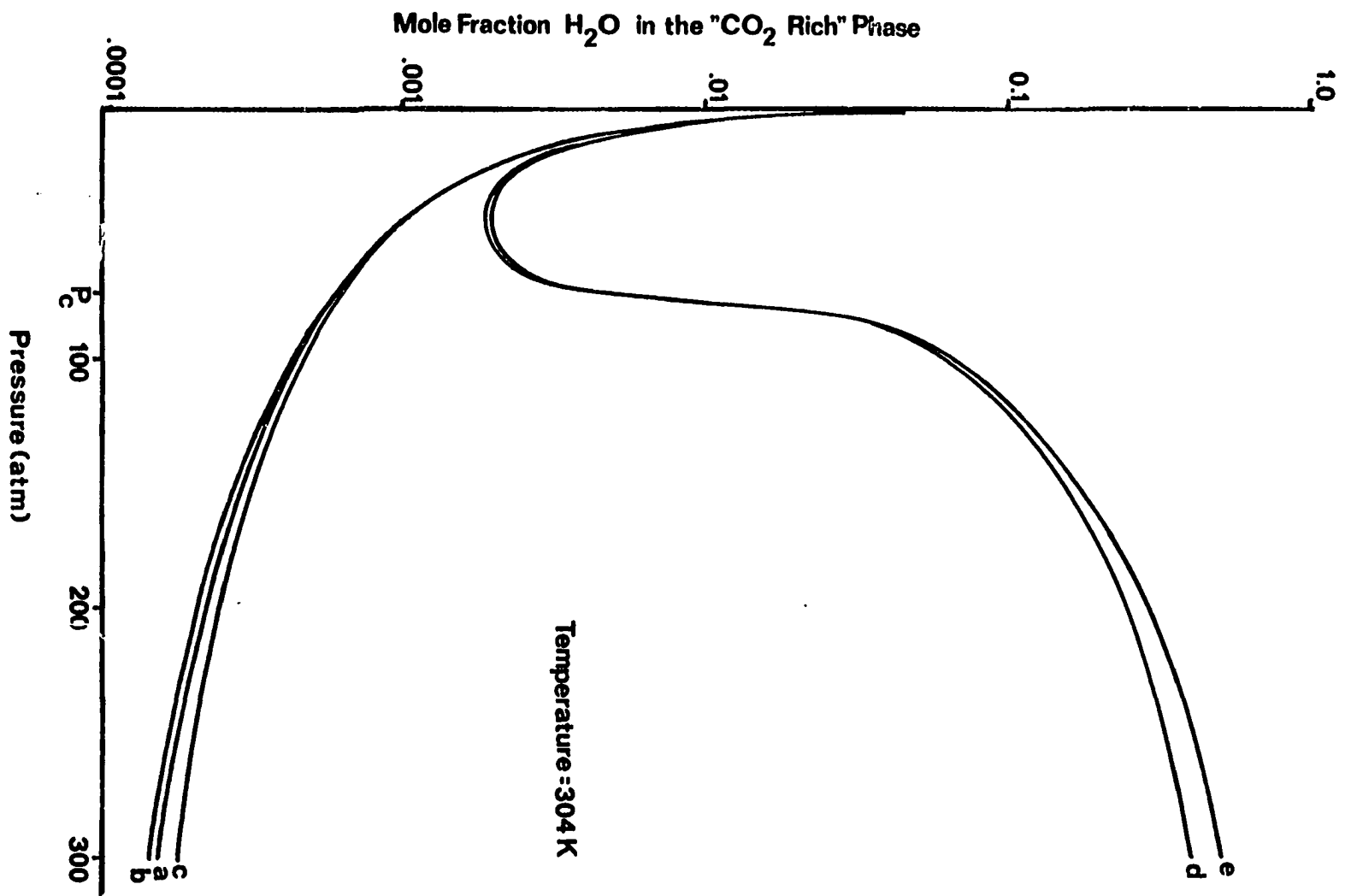
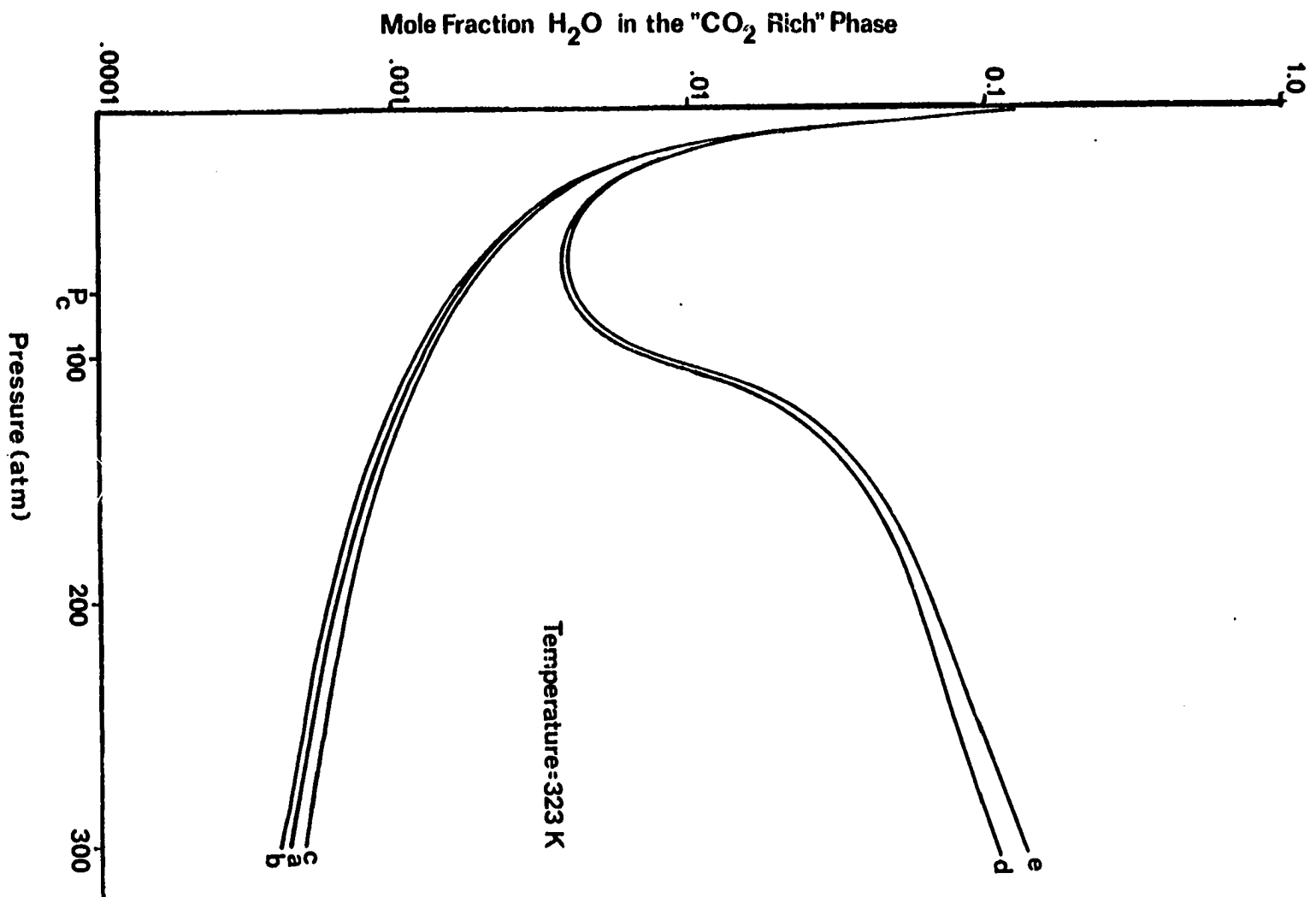


FIGURE 9. PREDICTED SOLUBILITY OF WATER IN A CARBON DIOXIDE PHASE AT A TEMPERATURE OF 323K AND A PRESSURE RANGE OF 1 TO 300 ATM. The solubility of water in a carbon dioxide rich phase is predicted by several forms of the solubility equation. The solubility equation derived in this dissertation is broken down into its familiar components and plotted as curves a through e which were formulated as follows: 1) Curve "a" is the ideal case assuming the solubility of CO_2 in the H_2O phase is negligible; 2) Curve "b" is Raoult's law; 3) Curve "c" is Raoult's law with the Poynting correction factor; 4) Curve "d" is Raoult's law with the fugacity effect from the second virial EOS; 5) Curve "e" is the complete solubility equation which included Raoult's law, the Poynting correction, and the fugacity effect. The most important feature of this illustration is the effect displayed by the fugacity term. Fugacity must be included so that the enhancement of solubility above the critical pressure of CO_2 can be predicted.



quation; curves a through d denote rows 11 through 14, and curve e is the total predicted Y_{H_2O} . The lower curves are the ideal cases and the upper curves are the fugacity cases with and without the Poynting term. The similarity between this figure and the well published CO_2 -Naphthalene binary is striking. Figure 8 and 9 are the comparable cases for $31^\circ C$ and $50^\circ C$. Figure 10 is a compilation of Figures 7, 8, and 9.

Figure 10 represents the supercritical solvent case between the critical pressure and 110 ATM (beyond this pressure the prediction breaks down). An increase in temperatures gives decreased solubility by the ideal computation, and gives decreased solubility for the virial case. Figure 10, however, does not correspond to the experimental data, as seen in Figure 11 (the notation E-298K in Figure 11 denotes the experimental data at 298K). The experimental data curves demonstrate an enhanced solubility with a temperature increase above the critical pressure of CO_2 . The predicted data curves demonstrate an enhanced solubility with a temperature decrease in the same pressure region. The increase in solubility with an increase of pressure, at constant temperature is seen in both the experimental and predicted data. Thus the prediction is qualitatively accurate for the pressure response but not for the temperature response. Both the simplicity of the model and the complexity of the CO_2 - H_2O binary lead to diminished predictive capabilities.

FIGURE 10. COMPARISON OF PREDICTED SOLUBILITIES OF WATER IN CARBON DIOXIDE AT TEMPERATURE OF 25°C, 31°C and 50°C WITH A PRESSURE RANGE OF 1 TO 300 ATM. The curves of predicted solubility from Figure 7, 8, and 9 have been overlayed in this figure for comparison. The convex downward curves represent ideal cases which contain only vapor pressures, Raoult's law, and the Poynting correction factor. The curves in the top half of the figure also contain the fugacity effect. These upper curves illustrate the enhanced solubility at the critical pressure of CO₂. The region between the critical pressure of CO₂ and 100 ATM show this enhance solubility. A noteworthy aspect of this region is the temperature response. Higher temperatures in this region are predicted to have reduced solubilities. Similar behavior is also found in this region for systems such as the CO₂ and naphthalene binary. The region beyond approximately 100 ATM displays the breakdown of the predictive capabilities of the solubility equation. The near linear segments of the curves beyond 110 ATM have a qualitatively correct slope; however, higher temperature curves would be expected to display higher solubilities.

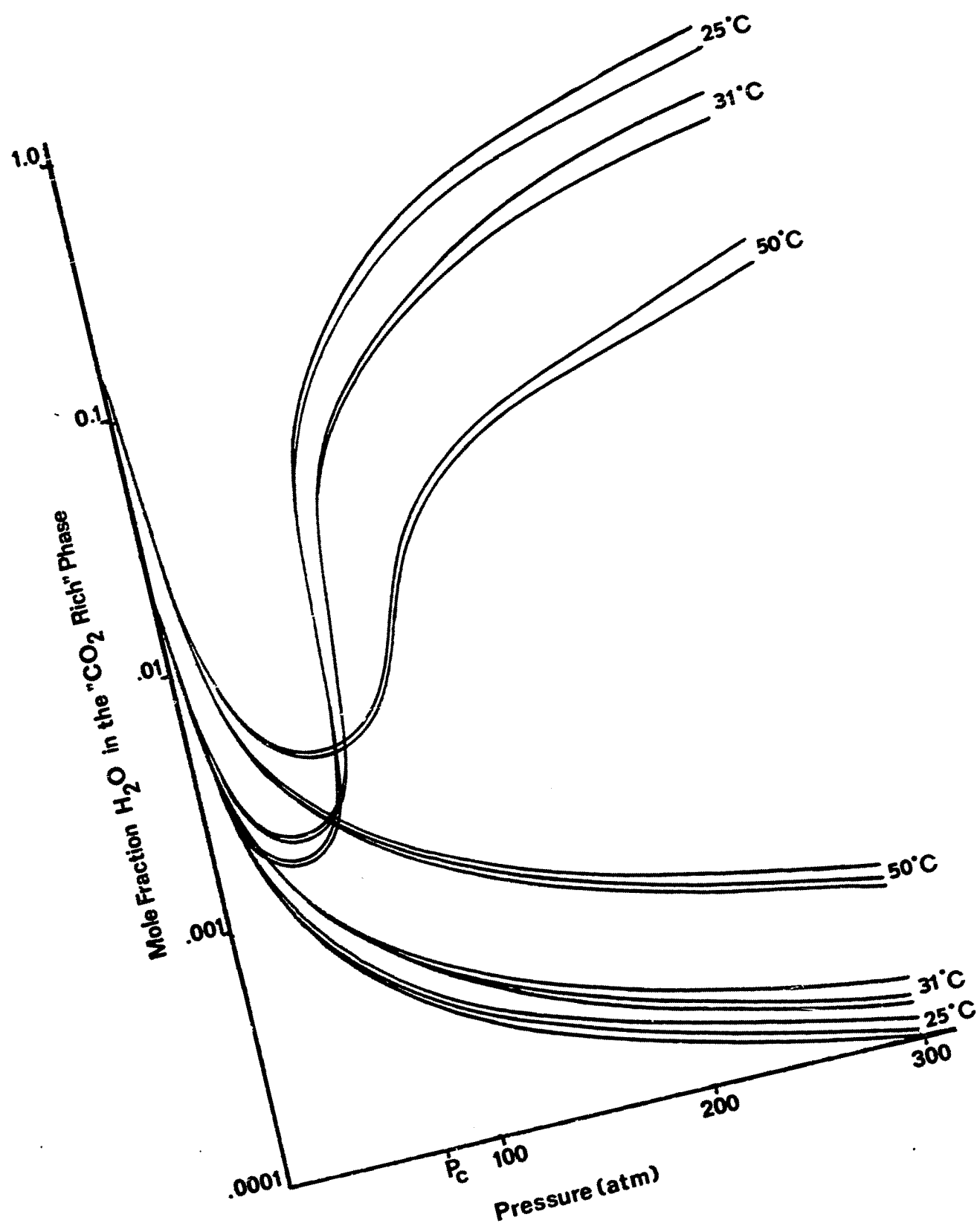
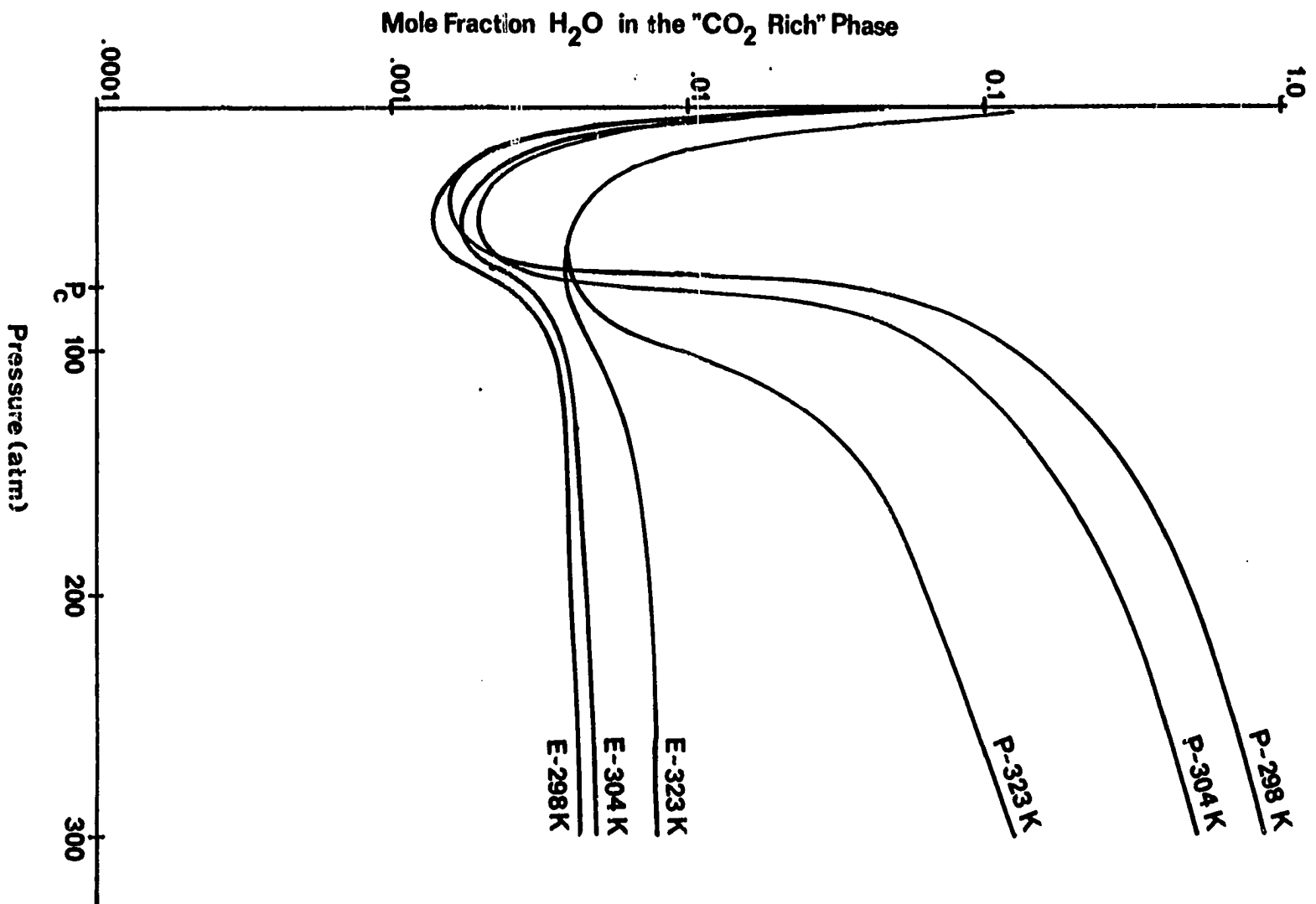


FIGURE 11. COMPARISON OF PREDICTED AND EXPERIMENTAL SOLUBILITIES OF WATER IN A CARBON DIOXIDE RICH PHASE IN THE RANGE 25°C TO 50°C AND 1 ATM TO 300 ATM. The solubility of water in a carbon dioxide rich phase was predicted by a solubility equation incorporating the virial equation of state truncated after the second coefficient. Predicted solubility is compared to the experimental data of Wiebe¹. Predicted data is denoted by P-298K, P-304K, and P-323 K, where the number is temperature in degrees Kelvin. Experimental data is denoted by E-298K, E-304K, and E-323. A noteworthy aspect of the experimental system is the temperature response of solubility between the critical pressure of CO₂ and 110 ATM. The solubility of H₂O in CO₂ increases with an increase in temperature in this pressure range. This solubility response is contrary to the type displayed by systems such as the CO₂-naphthalene binary.

¹ Wiebe, R., Chem. Rev. 29: pp. 475-481 (1941).



Gibb's free energy values are displayed in Figure GG. The general equation for relating Gibb's free energy to fugacity is

$$\Delta \hat{G}_i = \int_1^2 \bar{V}_i dP = RT \ln \frac{f_1}{f_2} = R \ln \phi * T$$

The curves in Figure 12 display the partial molar Gibb's free energy of H₂O in the CO₂ rich phase at various reference states and with various assumptions. Curve "Ideal" has a $\phi = P/P_2^{\text{OSat}}$. Using partial pressure (XH₂O P) in this equation instead of using total pressure (P) may have been more exact; however, this method (P) better illustrates the effects of the fugacity term. The P/PSat term is multiplied by a $\phi_{\text{EXPER}}/\phi_{\text{Sat}}$ term to yield a ϕ value for the curve "Exper". This is the experimental Gibb's free energy. The Gibb's free energy predicted by the virial EOS is shown in curve "virial". For this curve, $\phi = \phi_{\text{virial}} * P/\phi_{\text{Sat}}/P_{\text{Sat}}$. The remaining curves have ϕ values of:

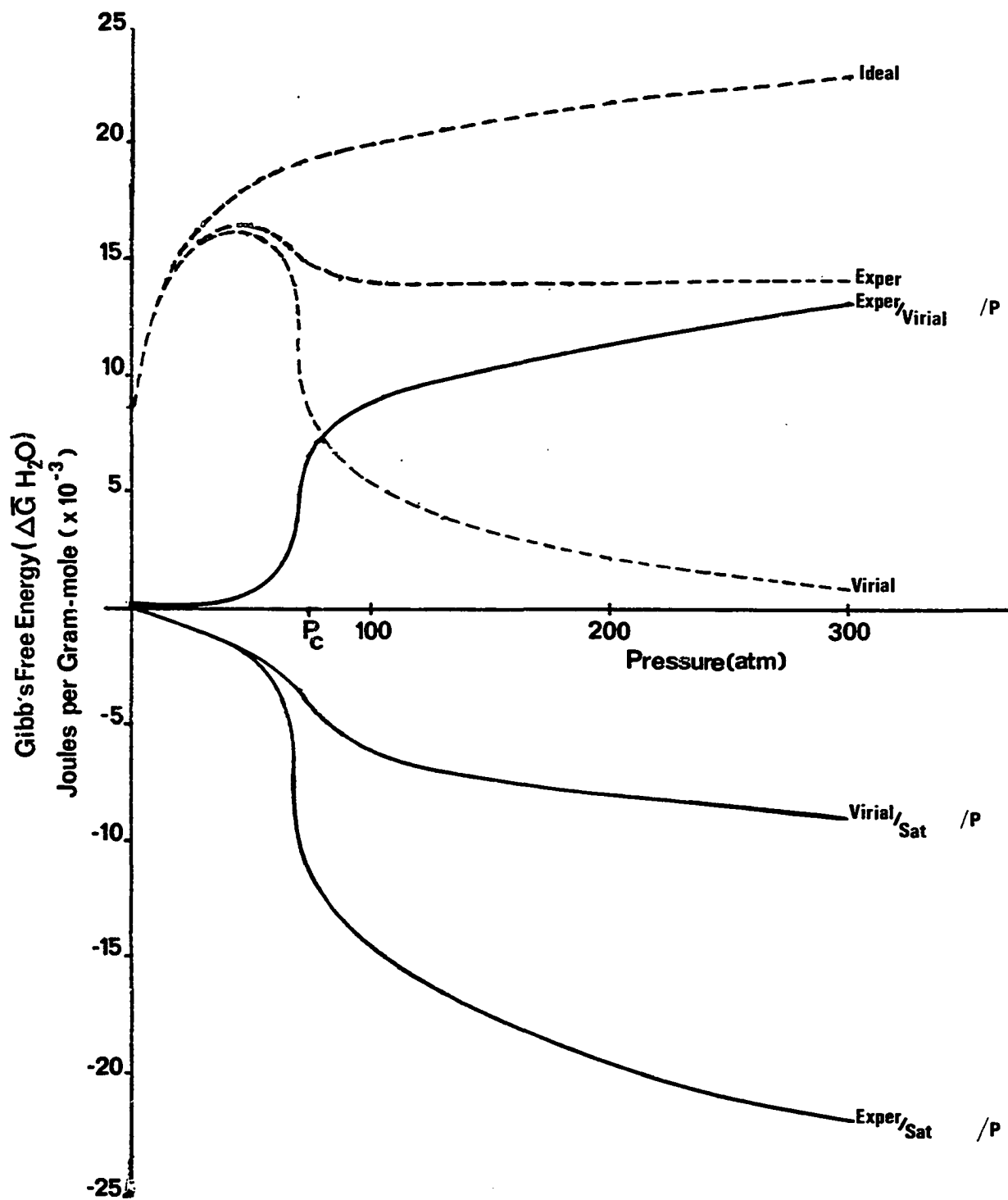
$$\phi = \hat{\phi}_2^{\text{Exper}} / \hat{\phi}_2^{\text{virial}} \quad \text{Exper/Virial/P}$$

$$\phi = \hat{\phi}_2^{\text{virial}} / \hat{\phi}_2^{\text{OSat}} \quad \text{Virial/Sat/P}$$

$$\phi = \hat{\phi}_2^{\text{Exper}} / \hat{\phi}_2^{\text{OSat}} \quad \text{Exper/Sat/P}$$

FIGURE 12. PARITAL MOLAR GIBB'S FREE ENERGY OF WATER IN A CARBON DIOXIDE RICH PHASE AT SATURATION CONDITIONS OF 25°C WITH A PRESSURE RANGE OF 1 TO 300 ATM. Partial molar Gibb's free energy of water in a carbon dioxide rich phase is displayed. The curve labeled "ideal" is the Bigg's free energy assuming that Raoult's law is valid. The "Exper" curve is the Gibb's free energy calculated from the experimental data of Wiebe¹, and the "virial" curve is calculated from the solubility equation utilizing the virial EOS truncated after the second coefficient. The remaining curves are the difference in Gibb's free energy calculated from each of the previous methods. As would be expected from the solubility of H₂O in CO₂, the partial molar free energy of water decreases above the critical region as the solubility is enhanced.

¹Wiebe, R., Chem. Rev. 29: pp. 475-481 (1941).



The "Exper/Virial/P" curve shows the logarithmic difference of Gibb's free energy from the virial prediction and the experimental values (assuming: $\gamma_{\text{H}_2\text{O}}^{\text{Liquid}} = 1$).

Returning to the analysis of the solubility equation, let us look again at Tables 2(b) and 2(c); these tables include two derived parameters not seen in the other tables. The effect we are dealing with is the jump in solubility at the critical point. The two tables demonstrate that the occurrence of the jump is dictated by the compressibility factor of the supercritical solvent. The magnitude of the increase in solubility is dictated by the magnitude of the second virial cross efficient.

The derived parameter "1/FUG-CO-W/O-Z(CO₂)" is the inverse of the fugacity coefficient predicted by the virial equation in which the compressibility factor (Z) has been set equal to a constant value of one (which is the ideal gas case; Z = 1 at any pressure). The parameter increases steadily without a "jump" in solubility at the critical pressure. The derived parameter "1/FUG-CO-VIRIAL-H₂O-MIX" is the inverse of the predicted fugacity coefficient. This term includes the real case compressibility factor and is seen to make a "jump" increase in solubility at the critical pressure (P_CCO₂ = 72.8 ATM). The value of this parameter at 70 ATM is 53.6 and the value at 75 ATM is 613.4. The

values of this parameter are 7.3 at 70 ATM and 24.7 at 75 ATM when the second virial cross coefficient is reduced by one-half. Table 2 (c) shows the calculated values when $B_{H_2O-CO_2}$ is 0.5 of the reported literature value. The reduction in B_{21} also improves the prediction of the water solubility in the CO_2 rich phase. A further research effort on these aspects of the solubility equations could prove beneficial to the pool of basic knowledge on high pressure phase equilibria.

The mole fraction of water in the CO_2 rich phase was assumed to be negligible in calculating the fugacity of H_2O in the mixture. Table HZ tests the validity of assuming that y_{H_2O} is negligible. The y_{H_2O} term had been removed from the mixture fugacity term during the analysis of the solubility equation. The y_{H_2O} term was inserted back into the fugacity term. Both the experimentally determined y_{H_2O} and the y_{H_2O} predicted for an ideal solution, constructing this table. The value of y_{H_2O} thus predicted by the solubility equation did not change dramatically in any case except at very high pressures. The collapse of the equation was expected at high pressures and high densities from the character of the virial equation truncated after the second virial coefficient. The second virial equation does not give

a good prediction of the quantitative effects of pressure on systems containing supercritical solvents. Improvements could be made in the prediction by including more sophisticated equations in the mixture fugacity term; this must be done before the solubility equation can be used for design purposes. The virial equation does, however, serve to give a first look at the $\text{CO}_2\text{-H}_2\text{O}$ binary system.

FIGURE 13. THE EFFECT OF REDUCING THE SECOND VIRIAL CROSS COEFFICIENT ON THE PREDICTION OF THE SOLUBILITY OF WATER IN A CARBON DIOXIDE RICH PHASE. The second virial cross coefficient used in the solubility equation was reduced by a factor of 0.5 to note the change in predictive capability. The curve drawn in this figure on experimental data and the data points indicate selected values of predicted solubilities. The reduction of the virial coefficient yields a better prediction. Further effort in this area may produce a more meaningful prediction.

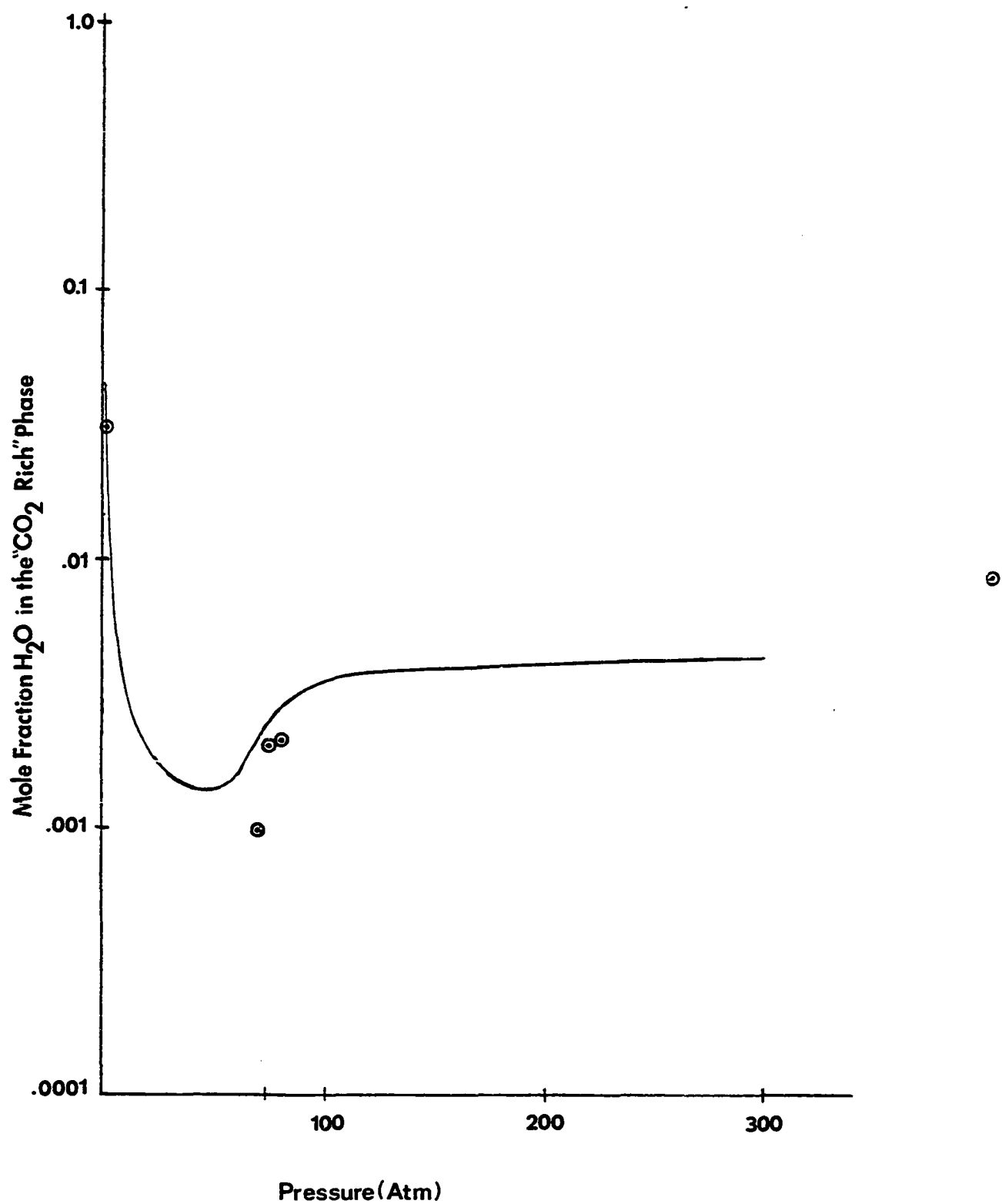


TABLE 6 Effect of Assuming that the
 Solubility of H₂O in the CO₂
 Rich Phase is not Negligible

PRESSURE	ATM	1	30	400
TEMP	K	323.15	323.15	323.15
X H ₂ O	EXPER	.9996300	.9917555	.9759496

If Y H₂O = 0 is used in fugacity equation

Y H ₂ O	EXPER	.1116105	.0053879	.0081731
Y H ₂ O	PREDICTED	.1222291	.0052907	.1599146

If Y H₂O = Y_{EXPER} is used in fugacity equation

Y H ₂ O	EXPER	.1116105	.0053879	.0081731
Y H ₂ O	PREDICTED	.1229140	.0053397	.2007118

If Y H₂O = P_{sat}/P is used in the fugacity equation

Y H ₂ O	EXPER	.1116105	.0053879	.0081731
Y H ₂ O	PREDICTED	.1229804	.0053277	.1612809

* Computed parameters are represented as truncated values and are not intended as significant digits.

CHAPTER V

EQUIPMENT

The significance and quantity of phase equilibrium data produced in the laboratory relies heavily on the equipment for success. Handling of the fluid or material under investigation must be kept to a minimum, while external automated controls, measurement devices, and recorders handle the bulk of the data being produced. This is the ideal function of a piece of research equipment. The ideal case must, however, be adjusted for considerations of time period of construction, capital budget, and technical expertise.

The criterion of minimum fluid handling indicates a batch process. The simplicity of the batch system necessitates few process controls. Once the fluid is contained in an equilibrium cell for study, only the temperature of the cell must be controlled. Accurate temperature control can be achieved by total immersion of the fluid handling equipment in a bath, jacket, oven, room, or cryostat. Volume, mass, and pressure in a batch system are set, not controlled.

The volume is set by the physical constraint of the system, and the material constraints of construction. Canfield's "Burnett Cell" is an excellent example of constraining volume[32]. Pressure is set with sample inlet pressure and may be reset with a displacement volume, usually mercury. Pressure will adjust with temperature.

The overall ease of controlling a batch process is its major advantage over a continuous process. The batch process has another feature which can be a major advantage or disadvantage, i.e. equilibrium is reached over a period of time. Equilibrium data are obtained when process variables of the equipment and the fluid have reached constant values. When all time transients have disappeared, the system is in equilibrium. This equilibrium data can then be applied to the system, under any processing conditions. The transient responses must, however, be added back into the data before this data can be used in process design. These transients, along with fluid flow effects, are best determined in a continuously flowing process. The advantage of equilibrium data, then, is the applicability to any system; the drawback is that the transients and fluid flow characteristics must be evaluated before final process design can be completed.

The ideal piece of research equipment would give three completely independent sets of data: 1) equilibrium mass and energy balance, 2) temperature transients and pressure perturbation, and 3) fluid flow characteristics. This piece of equipment would be unrealistic due to a high degree of complexity of design. Complexity in fluid handling is the major cause of error in experimental data. The fluid handling system must be "simple", leaving the mechanical, electromechanical, and electronic system the chore of data conversion and analysis.

The equipment used for this dissertation research was of the continuous flow class. The space requirement of 500 cubic feet and the ethanol and water mixture feed rate serve to designate the apparatus as being bench scale.

Batch equipment was initially considered for construction; however, budget limitations prevented the use of this configuration. The batch system originally proposed for use in this dissertation is outlined in the "Batch Equipment" section. The continuously fed system which was the equipment constructed for this dissertation research is outlined in the "Continuous Processing" section.

If new capital budget restrictions had been less rigorous, the batch equipment would have been chosen over the continuous flow equipment.

Batch Equipment

Closed systems have been used by many authors to investigate thermodynamic properties. A few of the many authors who have constructed and operated batchwise equipment are J. Kohn [111], M.S. Haines [92], L. Grausø and A. Fredenslund [69], R. Jockers and G. Schneider [202], A. Blancett [32], and A. Francis [72]. The batch equilibrium unit is used extensively to determine P, V, T and phase relations along with caloric properties.

The equipment used in this dissertation is limited to a high degree by availability of parts (capital budget = \$500.00). The first proposed piece of equipment was a batch equilibrium system modeled after the system used by Kohn [111].

Kohn used an oil bath for controlling the temperature of a liquid level gauge. The level gauge employed, contained a sight glass for viewing the phase split. The ratio of phase heights gives a measure of the volume of each phase present. Pressure is transferred by a mercury pump. The availability of a comparable mercury pump proved to be the deciding factor in abandonment of this type of unit. The system required a mercury pump with a 250 ml displacement. The mercury would be used

to displace sample from the holding bomb to intensify pressure in the equilibrium cell. The only mercury pump available had a displacement of 10 ml. This pump would have necessitated 25 valve manipulations and 1000 hand turns during each experimental run. Therefore, this batch system was abandoned.

The next proposed system was a volumetric bank method. The purpose of the volumetric measurement bank is to control the volume of mercury removed from the equilibrium cell. A hand operated Ruska pump would be used to control volumes in the range 0.08 cm^3 to 10 cm^3 . Volumes of mercury in this range may be removed, or added, to the equilibrium cell. To create 10 cm^3 steps in the volume of mercury removed, four bombs in the range of ten milliliters were to be used to receive 10 cm^3 mercury from the equilibrium cells. These 10 cm^3 bombs would be initially at vacuum, then the appropriate valves are opened to allow mercury to flow from the cell to the volumetric bomb.

Since the equilibrium cell has a volume of 45 cm^3 , the 10 cm^3 capacity of the Ruska pump and the 40 cm^3 capacity of the volumetric bomb bank would accurately control the volume displacement for the equilibrium cell. Accuracy of system volume measurements would be considered as 1 decimal place $(0.1) [\text{cm}^3]$.

Two drawbacks are seen in this design. The bank requires an extensive number of valves (12 valves). Also, the volumetric bombs must be emptied by a combination of system pressure and gravity. Discharging mercury at 1500 psi from the bombs could prove to be delicate. It is also implicit in the design that the bomb would only be used once in a test run, thus putting a time constraint on the number of runs that could be performed in one day. The volumetric bank can be seen in Figure 14.

The equilibrium cell would be of the Jerguson type with a total volume of 45 cm^3 . The cell is supported on a yoke and shaken by hand or with mechanical agitation. A sample bomb is mounted on the yoke (see Figure V2). Vapor phase components could be sampled from the cell by opening the valve connecting the sample bomb and the cell. ETOH or other liquids could be injected into the cell via a three-way valve in the CO_2 /vacuum line. Liquid phase volume would be measured by graduations on the equilibrium cell. These graduations may be viewed through a sight tube via a prism system (see Figure 16).

The equilibrium cell is contained in a heater box made of wood and insulation. Temperature is controlled with an electrical resistance heater actuated by an external controller. Heat flux would be made uniform by a fan and baffle system (Figure 15).

FIGURE 14. BATCH SYSTEM FOR EQUILIBRIUM STUDIES; VOLUME MEASUREMENT AND VACUUM SOURCE. Batch system may easily be employed in the study of multi-phase equilibria. Although a continuous system was employed in the experimental phase of this dissertation research, a batch system of the type illustrated here may be replaced by a sufficiently large mercury pump. The overall purpose of the mercury pump is to control the volume of the fluid in the equilibrium cell. Mercury is a very useful working fluid in batch systems; however, great caution must be used because of the high toxicity of mercury.

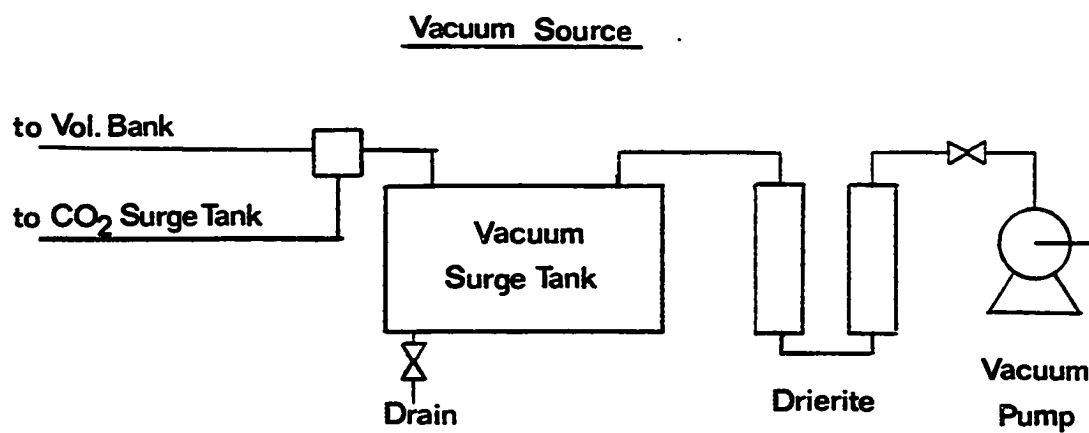
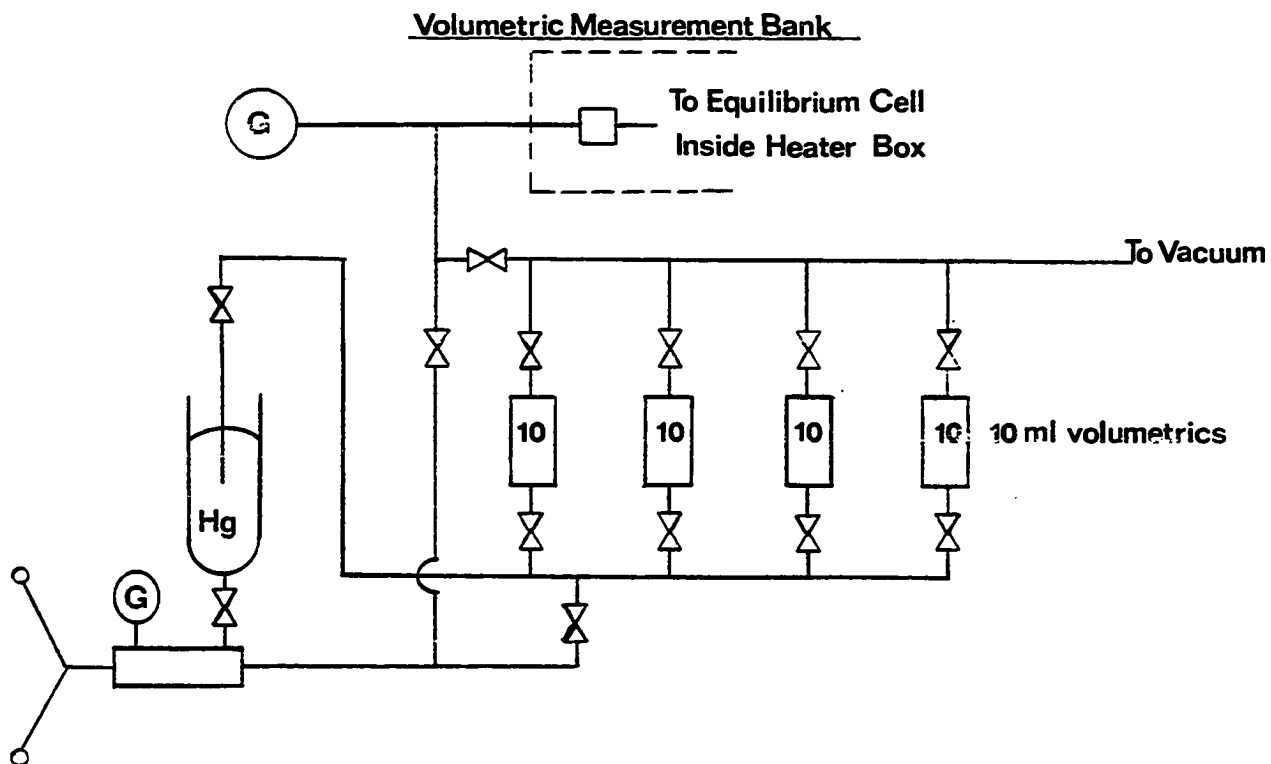
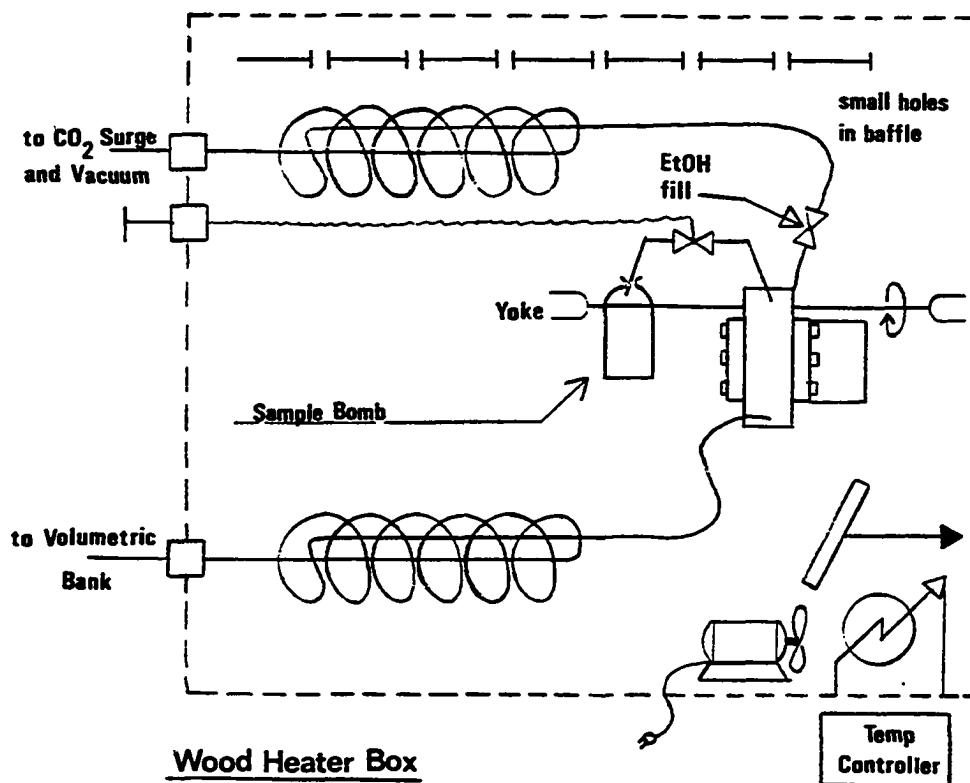
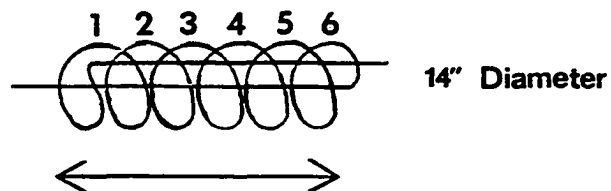


FIGURE 15. BATCH SYSTEM FOR EQUILIBRIUM STUDIES; EQUILIBRIUM CELL AND HEATER BOX. This illustration depicts a typical arrangement of equilibrium cell in a temperature controlled oven. The dashed lines at the top of the oven represent a baffle system for even heat distribution. The flexible line is used to facilitate agitation of the equilibrium cell.

Equilibrium Cell and Heater Box



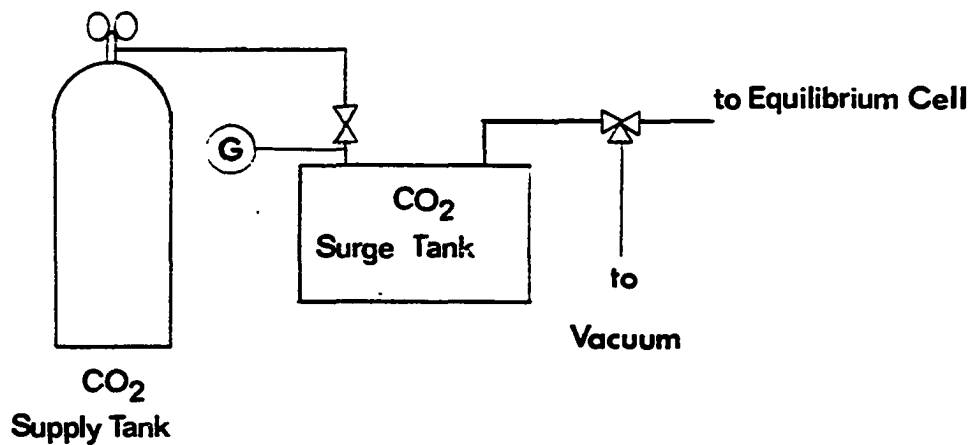
Wood Heater Box with Insulation



Flexible Line S.S. 1/8" QD.
0.035 wall thickness

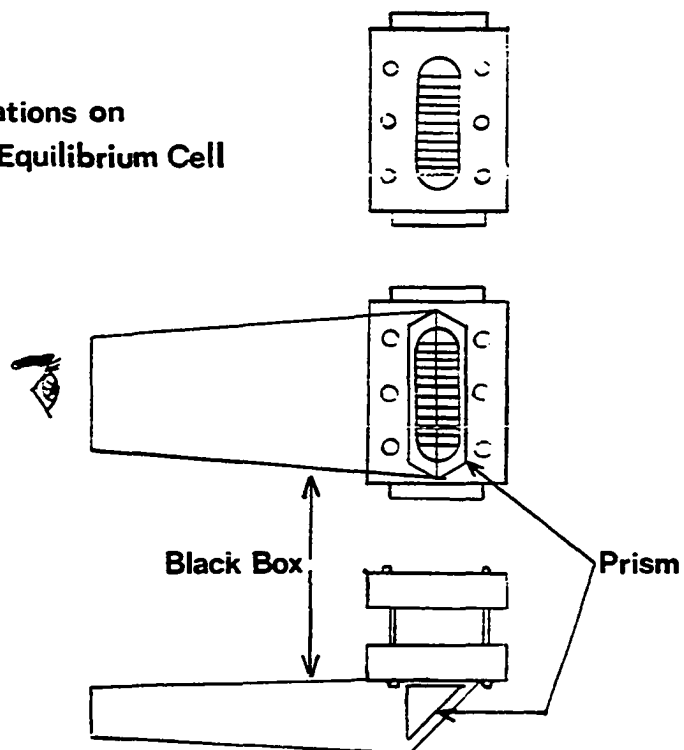
FIGURE 16. BATCH SYSTEM FOR EQUILIBRIUM STUDIES: CARBON DIOXIDE SUPPLY AND PHASE VOLUME FRACTION MEASUREMENT. Batch systems employing a visual window may be used for accurate measurement of the volume of each phase. The "eye" shown in the illustration may be replaced with a cathetometer for more accurate measurement.

Carbon Dioxide Supply



Liquid Phase Volume Measurement

Graduations on
Equilibrium Cell



The advantage of this system over the previous system is that a large mercury pump is not needed. Another advantage of this system is ease of construction. The major disadvantage of this system is complexity of mercury handling. Calibrating the volume bank would be difficult. The calibration routine does, at first, appear simple; however, the twelve valves would cause measureable volume change, i.e. a valve stem has a finite volume which could not be neglected in this system. Another disadvantage of this system is that it requires liquid CO_2 feed because a gas feed would again necessitate large volume changes from a mercury pump to intensify the pressure. The large number of valves required in this system would also be prohibitive because of the high cost of valves and high pressure tube fittings. This system was also abandoned.

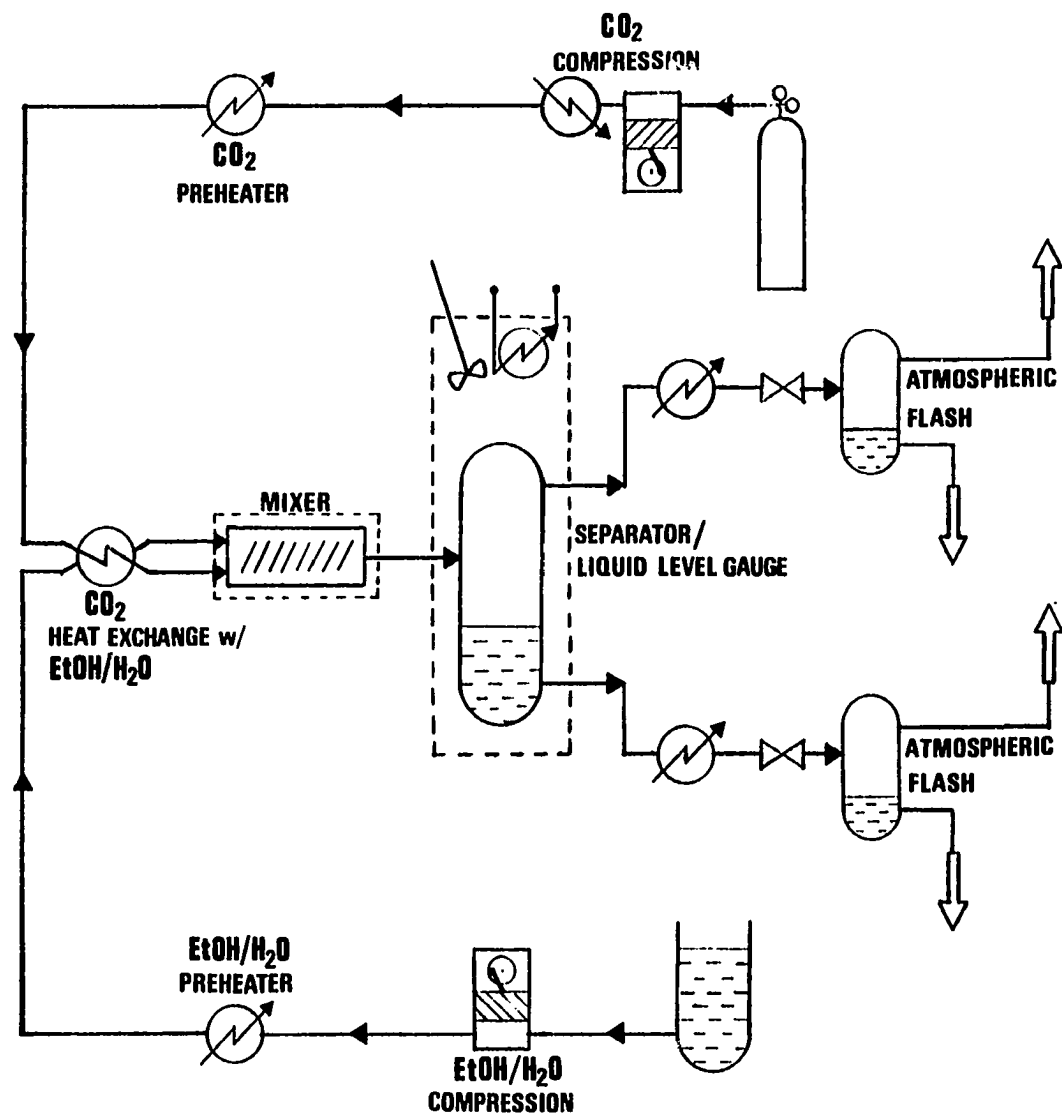
Continuous Processing

Continuous processing provides data on how well a particular system will perform in a full scale production mode. The equipment constructed to evaluate the CO_2 - ETOH - H_2O system was on the bench-pilot plant scale. The feed rate of the ethanol and water mixture could be varied from 0 to 460 ml/hr, and the CO_2 feed rate normally ran at 30 SCF/HR. This is a 200 gal/yr plant.

The process flow diagram of Figure P1 illustrates the continuous process plant constructed for this work. This is a single stage, one pass continuous unit. The CO_2 solvent feed is independently compressed and preheated. The $\text{ETOH-H}_2\text{O}$ mixture is also independently compressed and preheated. The CO_2 stream is then co-currently heat exchanged with $\text{ETOH-H}_2\text{O}$ stream to fine-tune any temperature differences between the two streams. The independent preheating is necessitated because the CO_2 stream requires an order of magnitude more heat input than the $\text{ETOH-H}_2\text{O}$ stream. After the two feed streams exchange heat, they are mixed in an adiabatic mixing coil. The mixed stream then flows to a liquid level guage for splitting of the two phases. Phase separation (one liquid bottoms and one fluid extract) can be viewed and measured through the liquid level guage. The "lights" and "heavies" then flow to independent heaters, throttling valves, and atmospheric flash tanks. Each flash tank may have one vapor and one liquid product stream.

The general process flow diagram follows standard high pressure fluid-liquid separation strategy. The specific design of the unit is based on the high pressure design considerations discussed by Haines [92], and by Blancett [32]. The specific design of a piece of equipment hinged as much on availability as on optimum design (see Figure 17).

FIGURE 17. THE CONTINUOUSLY FED APPARATUS FOR STUDY OF THE CARBON DIOXIDE - ETHANOL-WATER SYSTEM AT ELEVATED PRESSURE AND AMBIENT TEMPERATURE. The process flow diagram in this figure illustrates the continuously fed apparatus constructed for the study of the CO_2 - ETOH - H_2O system at elevated pressure and ambient temperature. The gas (CO_2) feed stream and the liquid ($\text{ETOH}/\text{H}_2\text{O}$ mixture) feed streams are independently compressed and preheated. Heat is exchanged between the two feed streams to assure uniform temperature of the two streams. Conditions of the two feed streams have now been established at an elevated pressure (2000 psia max) and a predetermined temperature near ambient. The feed streams are then mixed in an adiabatic mixing coil. The CO_2 - ETOH - H_2O mixture then flows to a Jerguson liquid level gauge for phase separation. The exit streams of the separator must be heated as the pressure is throttled to atmospheric. The most difficult aspect of operation of this apparatus is the control of the exit stream heat content and flow rate. Sufficient heat must be supplied to the throttling valves to prevent solid phase formation and the resulting valve sticking.



The ETOH/H₂O feed mixture is compressed by an axial type positive displacement pump. This pump was originally designed as a high pressure liquid chromatography pump. The controllability of this pump is very good. Flow can be metered between 46 ml/hr and 460 ml/hr in 0.1% increments of full scale. This pump and all other pieces of major equipment are summarized in a Major Equipment List (Table E-7).

The CO₂ feed compressor is of the diaphragm positive displacement type. The diaphragm is incorporated to separate the gas undergoing compression from the work fluids of the pump, thus avoiding contamination. The positive displacement design of the pump presents an additional process problem not encountered with centrifugal pumps, that is, pulsed flow. The positive displacement action moves a volume, pauses, for a time frame ($t=1/2$ RPM), and moves another volume, resulting in pulsed flow. The problems of pulsed flow can be overcome by several methods: 1) a diaphragm as a side arm, 2) a large surge tank, 3) or multi-sized tubing cross flow. None of these pulse dampening methods could be employed because of the minimal capital budget. The resulting phase flow did give a very interesting characteristic to the critical region. The critical region would pulse in and out of the opaque region with the cycling of the pump.

TABLE 7

MAJOR EQUIPMENT LIST

1. Compressors

Diaphragm Type:

Corblin (Paris) Type B20 1000
Serial No.: B. 2110 Year 1963
Flow Displacement 8.7 CuFt/Hr
Discharge 15,000 psig
Suction Variable
Speed 400 RPM
Brake Hp 6Hp

with 7.5 Hp electric drive, output cooler
(water), and skid mounting base

Axial Type:

Milton Roy Co.
196-9066-003 39/330 HM
46/460 ml/hr 0.2% divisions
Max. 5000 psig
Laboratory Data Control Division
Riviera Beach, Florida

with Pressure Controller

Helicoid^R ACCO
Model 240L 1DC
Dual: Min. = ON; Max = OFF
Range: 0-5000 psig
Solid State; 2 Amp, 120 VAC

2. Temperature Controllers

Thermotrol^R

Model 1053A

Hallikainen Instruments, Richmond, CA.

3. Pressure Guage

Heise Guage No. H44270
Range 0-5000 psig (5 psig div)
Temp Compensated -25 to +125°F
Newtown, Conn.

4. Cryostat-strip-Silvered Glass Dewar

No. 203200
600 mm long x 250 mm I.D.
H.S. Martin and Son
with 9 inch I.D. glass pipe flange and clamp
ring with pad

5. Liquid Level Gauge

Jerguson
Size No. 12, Series T-30
Rated @2900 psig @100°F

6. Chart Recorder

SPEEDOMAX TYPE G
Leeds & Northrup Co.
Philadelphia, Penn.

7. Pressure Regulator

Model GC-31 Serial No. I-352
TYPE LOAD-BLEED
Max. in 36000 psig Max. out 3600 psig
Victor Equipment Co.
San Francisco, CA.

8. Fan Motor

Model 5KH29G88
RPM 1725 HP1/12
115 VAC 2.1A
CODE S GAU
General Electric
Fort Wayne, Ind.

9. Valves

Metering: Needle valves
1/8" tube x 1/8" tube
25 graduations per 1/32" axial movement
Nupro " M " series
Nuclear Products Co.
Cleveland, Ohio

Standard: Needle Valves
3/16" Flare AN X 3/16" Flare AN
off-on type

10. Thermister

GB32P8
Fenwal Electronics
Framingham, Mass.

11. Oscillator

Transistorized oscillator circuit designed
and donated by John Noe U.S. Pat. 3,475,698
(1963)
Currently: University of Oklahoma, Norman, OK.

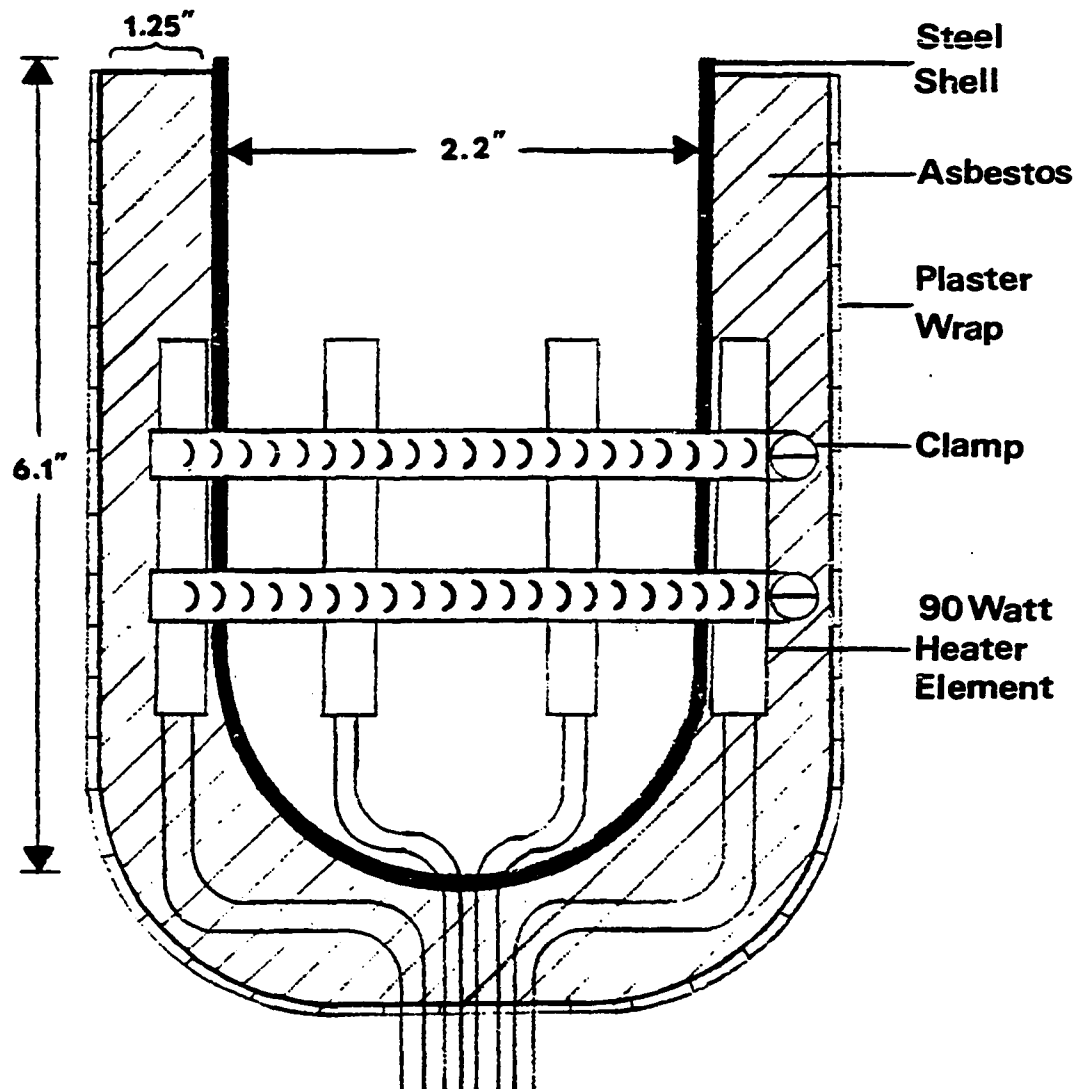
12. Constant Temperature Water Supply

Haake Instruments, Inc.
Control from 0 to 100°C (heater only)
Type 423 NR. 73040
Saddle Brook, N.J.
Berlin, Germany

The stream preheaters were constructed on site. Figure 18 shows one of these oil bath heaters. The end of a small bomb was removed to give a steel liner for the oil bath. Six 90 watt heaters were then uniformly placed around the shell and secured in place with clamps. Asbestos insulation supported by plaster wrap shields the outside of the heater from the ambient surroundings. Mineral oil is used as the heat transport medium inside the steel shell. Tubes conducting feed solution ran inside the oil medium. Using six individual heating elements results in an added advantage. The resistive heaters were connected to the power source through rotary switches. The selection of several resistance values (heating values) was possible. The CO₂ preheater had a selection of resistances at values: 1) 440Ω, 2) 220Ω, 3) 110Ω, 4) 40Ω, 5) 20Ω. The ETOH/H₂O preheater could be switched to either 440Ω or 110Ω.

Thermotrol^R temperature controllers were used to control the oil bath preheaters. Platinum resistance thermometers are normally used with these controllers; however, Pt elements were not available. The thermistor listed in the Major Parts List was substituted for the Pt resistor. The Thermotrols^R were rewired to accept either the Pt resistor or the thermistor. The rewiring consisted of adding a part in

FIGURE 18. FEED STREAM PREHEATER. Feed stream preheaters were constructed of six 90 watt heating elements clamped to a carbon steel liner and insulated with asbestos. The steel liner was filled with mineral oil to act as a heat transfer medium. A coiled length of the process flow line to be heated was then installed in the oil bath. Heater element network switching provides a range of overall resistance from 20 ohm to 440 ohm, while supplying necessary current to all heaters at a potential of 110 volts.



parallel to the opposite leg from the Pt resistor port on the Wheatstone bridge making up the temperature sensing and setting circuit. This addition provides two modes of operation: 1) a Pt resistor may be used according to original factory specification, or 2) a thermistor may be wired to the spare port (a fixed $100\Omega \times 100\Omega$ "Pseudo Pt resistor" must be connected in to the Pt resistor port in place of the original Pt resistor).

Preheated feed CO_2 and H_2O - ETOH mixture are cocurrent heat exchanged to bring both streams to a constant temperature.

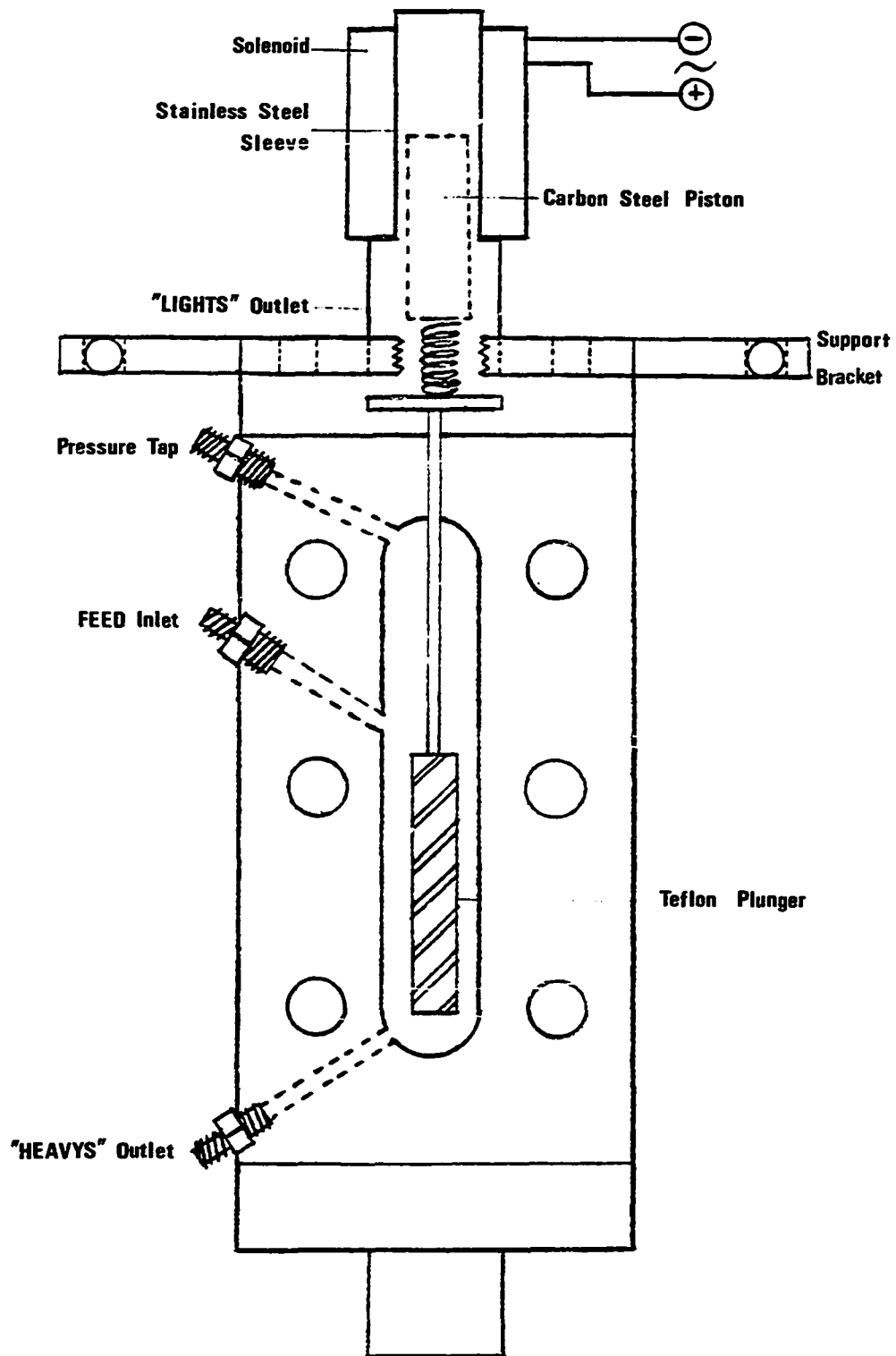
The two feed streams, now at a consistent temperature are adiabatically mixed. A Swagelok^R tee fitting joins the $\text{ETOH}/\text{H}_2\text{O}$ line, the CO_2 line, and the mixer line. The mixer is a 3/8 inch O.D. tube in a coil arrangement. The mixer is 6 inches long by 4 inches O.D. The coil makes 10 outside loops; inside the loops are six loops to form an inner coil. The fluid flow path is from the top of the mixer, through the inside set of loops, up the outside set of loops and out of the mixer. A dewar flask with 2 inches of foam as the lid, forms the thermal insulation to make this an adiabatic mixer.

The mixed fluid flows to the separator. Several possible designs exist for this separator and the

surrounding thermal environment (heater or cooler). The Figure 18 shows part of the separator used. This is the stainless steel chamber of a Jerguson liquid level meter.

This modified Jerguson cell was the key to the particular cell and bath arrangement finally employed. What appeared to be a standard Jerguson cell was checked out from the stockroom. It was desired to force some type of electrically actuated mixing action onto the cell. This is not an easily solved problem. The stainless steel chamber [the section shown in Figure 18] has a significant resistance to a changing magnetic field. The 20 pounds of cast iron surrounding the stainless steel cell would direct a magnetic field around and away from the chamber of interest. Thus, an external, changing magnetic field could not be used to actuate an internal magnet or iron bar for agitation and mixing. Therefore, a carbon steel piston must lie outside the main structure of the cell and move a mixer inside the cell. The mixer inside the cell is inert Teflon^R, which is connected to the carbon steel piston through a steel, brass, or plastic rod (brass was used in the final design, this connecting rod would have to be changed to a stainless steel rod if H₂S or other corrosive environments are to be used). A cylinder must house the carbon steel piston and form a pressure tight seal with

FIGURE 19. HIGH PRESSURE CELL. The high pressure cell is a modified Jerguson liquid level gauge. Modifications include side ports for feed and exit streams and an internal piston-plunger with external electromagnet for agitation and mixing.



the equilibrium cell. Outside this cylinder is a solenoid with an applied oscillating electric potential. The mixing action inside the cell is thus controlled by the frequency and power of the oscillating electric potential. Haines [92] had used just such a system for mixing in a Jerguson cell, therefore, his basic designs of cell and cryostat were used.

The volume of the equilibrium cell with stirrer is 62 milliliters. The rating is 2900 psig at 100°F. The frequency of the mixer could be set from 0 to 500 cycles per minute by varying the resistance of an RC timer. Although the resistor could be varied from 0 to 111,111 ohms the normal setting was 4772 ohms (with a 4 MF capacitor]. The RC timer sets the response for an oscillator designed by John Noe (see parts list).

A constant temperature air bath surrounded the equilibrium cell. Insulation was provided by a cryostat. Heat was added through a copper coil heat exchanger with water as a working fluid. Heat was distributed by a blower powered by an external electric motor. The working fluid of the heat exchanger was circulated, heated, and temperature controlled by a Haake^R constant temperature water bath.

The stainless steel plate shown schematically in Figure 18 shows the locations of the fluid and pressure transmitting ports. The feed port is directed

to the center level of the cell. The "bottoms" port leaves is not directly located on the bottom, thus leaving a 0.2 ml residual volume in the cell. The light phase leaves the cell through a fitting (not shown) on the cylinder housing the mixer piston. Fluid feed and outlets are valved through as short a distance as possible, just outside of the equilibrium cell, resulting in an additional residual volume of 1 milliliter total.

The two exit streams flow through a control panel. Here, the two streams are heated by heating tape. The fluids then flow through an off-on valve and heated again. The exit streams then flow through a needle valve for final throttling control.

After throttling, the light phase passes to an atmospheric flash tank. The tank has a volume of 2000 cubic inches and an overall height of 22 inches. The heavy phase flows to a 500 cubic inch (22 inch tall) flash tank, after throttling.

The twenty-five thermocouples used for temperature monitoring were built from standard #18 copper-constantine thermocouple wire. These thermocouples were lead soldered as opposed to arc welding.

The total new capital cost of the pilot plant was kept at under \$500 by using available equipment and fabricating all other necessary parts.

CHAPTER VI

METHODS

Operation of the continuous flow pilot plant demonstrates that processing in the critical region of a solvent is feasible on a production level. The particular methods running the pilot plant constructed for this dissertation research are not extendable to full scale production. The process control of this pilot plant was only successfully accomplished by a highly trained operator. This level of operator proficiency was necessitated by the absence of any flow controllers (other than throttling valves) in the system. Operator training consisted of operating the system with pure CO₂ for a period of one month. By the end of the one month period, the operator (this author) was able to operate the pilot plant such that the CO₂ in the Jerguson cell consistently displayed the critical opacity of the thermodynamic critical point.

Pilot Plant Operation

The critical point is not merely opaque, it is opalescent. The opalescence appears as a reddish-brown

irridescence when transmitted light is observed through the cell viewport. The temperature range in which this opalescence occurs is dependent on the molecular species (ether = $\Delta 2^{\circ}\text{C}$; sulfur dioxide = $\Delta 0.1^{\circ}\text{C}$) [235]. The temperature range in which critical opalescence occurs for CO_2 is smaller than the accuracy of the thermometer; i.e. no temperature range could be distinguished. A more accurate temperature measurement procedure would be required.

Since the critical point is a unique thermodynamic state, it is also a unique calibration point. Operation of the pilot plant so that the phenomena of critical opalescence is displayed defines the state of the system in the apparatus. Pressure and temperature gradients may now be checked as system variables around a well defined thermodynamic state.

The CO_2 preheater was set to oscillate between 67°C and 74°C in an 18 minute cycle. This was found to be the maximum stability of the oil bath temperature controller with a heater setting of 220 ohms and a CO_2 load of 0.44 SCF/MIN at $29.0 \pm 0.2^{\circ}\text{C}$ feed to the preheater and 1050 psig at the Jerguson cell. Critical opalescence is observed when in the separator the outlet of the CO_2 preheater is at $31.3 \pm 0.1^{\circ}\text{C}$ and the adiabatic mixing coil has a uniform temperature of $31.2 \pm 0.1^{\circ}\text{C}$. Drift in the temperature recorder base line

decreased the accuracy of the temperature measurements; this baseline drift must be continually adjusted. The 18 minute cyclic nature of the heater control caused an unsteady temperature response in the adiabatic mixer. During a cycle, the temperature of the mixer inlet would fall to 30.5°C, and then climb back to 31.3°C as the cycle continued. Although this 0.8°C change in temperature is not significant for most processes, 0.8°C change in temperature removes the critical opalescence phenomena.

Operation and calibration of the apparatus in the critical region of pure CO₂ feed shows that the temperature measurement is correct within ±0.2°C and the pressure recording must be adjusted upward by 5 psi and then given an accuracy rating of ±2.5 psia. A discussion of pilot plant operation with the addition of ETOH and H₂O follows.

Feed H₂O, ETOH, and CO₂ are compressed to working pressure, preheated, heat exchanged to the same temperature, then mixed, and fed into the separator. The intent of the preheater/adiabatic-mixer section of the overall unit is to provide a feed stream to the separator which has a specified stream flow rate, temperature, and pressure. Except for the final outlet expansion valves, all process controllers are located in this (pre-separator) subsystem.

H₂O and ETOH flow rates are controlled by a constant flow rate pump. The pumping capacity varies from 0 to 100% of 460 ml/hr in 0.46 ml increments. Because of this positive displacement pumping method employed, the flow rate of H₂O/ETOH feed is independent of CO₂ flow rate and pressure [to a maximum of 5000 psig].

CO₂ flow rate is controlled by feed conditions to the CO₂ pump. This pump has a boiler plate specification of 8.7 CuFt per hour displacement. Unlike the H₂O/ETOH feed conditions which are invariant, CO₂ feed varies in both temperature and pressure. Control of CO₂ flow rate is thus controlled by specifying compressor feed pressure and separator pressure while monitoring CO₂ outlet volumetric flow rate at atmospheric pressure.

System pressure is strongly dependent on two variables: 1) compressor feed pressure [CO₂ feed] and 2) expansion valve constriction [outlet]. Control of these two independent variables results in a specified CO₂ flow rate and separator fluid pressure.

Temperature of the CO₂ feed to the compressor is an indeterminate. Evaporative cooling in the CO₂ supply tank causes the vapor pressure of the supply CO₂ to decrease. Thus the load-bleed type regulator on the CO₂ supply tank requires constant monitoring and adjustment to give the desired CO₂ flow rate and system pressure.

Preheating BTU's are applied to the system by exchange with oil bath type preheaters. These preheaters run at a temperature gradient from 1°C to 20°C. Oil temperature is controlled by Thermotrol^R temperature controllers with the sensing thermister inserted into the oil. Oil temperature is cyclic with a period of ~15 to 20 min and an amplitude of 0 to 10°C. The cyclic nature of a temperature controller and the necessity of larger temperature gradients for heat exchange when CO₂ is at or above the critical point results in a cyclic system temperature with a forward "phasic" shift from the oil temperature; i.e. CO₂ temperature lags the changing oil temperature and is diminished in amplitude [magnitude]. Preheating of the H₂O-ETOH feed stream follows the same method as the CO₂ feed stream.

The design of the preheaters necessitates an exchange on heat between the two feed streams prior to mixing. Since the absolute temperatures of the two feed streams are always expected to differ, the two streams are forced to exchange heat in an adiabatic enclosure. The intent of the adiabatic heat exchange is to bring the two streams to the same temperature. Heat loss in the adiabatic heat exchanger is negligible; however, the heat capacity of the heat exchanger may not be neglected if a change in temperature is desired.

The temperature of the separator feed stream can be greatly influenced by this mixer unit. Study has shown that this mixer has a large heat capacity compared to the fluid mixture flowing through the mixture. The large heat capacity presents, at times, as large as a 30 minute transient in temperature stabilization. The large heat capacity may also effectively hide or mask the effects of ΔG mixing terms. At steady state the temperature gradient from inlet to outlet of the mixer is not detectable, as determined at the critical opalescence of pure CO_2 .

Temperature control of the high pressure separator and surrounding cryostat is attained by an external constant temperature Haake water bath. After a two hour startup period the temperature difference between the constant temperature bath and the first loop of the heat exchanger inside the cryostat was negligible. The temperature gradient across the separator (Jerguson liquid level gauge) was not negligible. The baffle system used to duct the heated air from the heat exchanger caused the cell to have a temperature gradient of up to 2°C .

The throttling valves used to control the flow rate and of the "Light" and "Heavy" phases exiting the separator required additional heat exchange. The heat was provided by heating tape, a 90-watt heater

cartridge on each throttle valve housing block. This heating method counter-balanced the expansion cooling effects in each case except that of the $\text{CO}_2\text{-H}_2\text{O}$ binary. The $\text{CO}_2\text{-H}_2\text{O}$ binary caused solidification of CO_2 and H_2O in the throttle body with the expansion of CO_2 from high pressure to atmospheric pressure. Pure CO_2 or $\text{CO}_2\text{-ETOH-H}_2\text{O}$ systems gave less freezing problems. Here, the voltage to the heaters was set at 50 volts to provide the heat taken in by expansion.

Gas Chromatograph Calibration

Compositional determination of gas and liquid samples was performed by gas chromatograph analysis. Thermal conductivities were monitored on a Hewlett-Packard 5840A gas chromatograph Model 18802B. The G.C. column was a six foot glass, 9 inch coil packed at the Supelco factory with Chromosorb^R - 102.

The thermal conductivity detector (TCD) response to absolute ethanol is shown in Figure M-1. The response is linear within the range of sample volumes used in analysis. Figure M-2 shows the linear response of the TCD to triple distilled water. The carbon dioxide TCD response was more difficult to determine. Figure M-3 shows moles CO_2 ($\times 10^{-6}$) per 0.1 ml of 20 mole per cent CO_2 in air. The conversion from volume to moles was based on the linear region found at a sample volume range of 0.1 ml to 0.4 ml. Larger sample volumes flood the column and thermoconductivity detector giving a non-linear response. The response of the TCD to each of the compounds, along with the retention time of each compound, was entered into the external calibration subroutine of the gas chromatograph microprocessor. This method did not give satisfactory results; a direct

readout of mole percent was anticipated; however, the results were not acceptable. The method finally employed was to convert the TCD area response to moles with a computer program based on the calibration curves of figures 19 through 21. The actual moles were then converted to the mole percent of each component in the sample.

FIGURE 20. GAS CHROMATROGRAPH CALIBRATION: ETHANOL. The response of the thermal conductivity detector a sample of ethanol is shown. The near linear response of the detector is advantageous in ethanol concentration determination. At high sample volumes the detector response becomes non-linear. Sample volumes were thus held to 2 or 5 microliters to avoid detector flooding.

TCD RESPONSE TO 3-DIS WATER: AREA VERSUS MICROLITERS

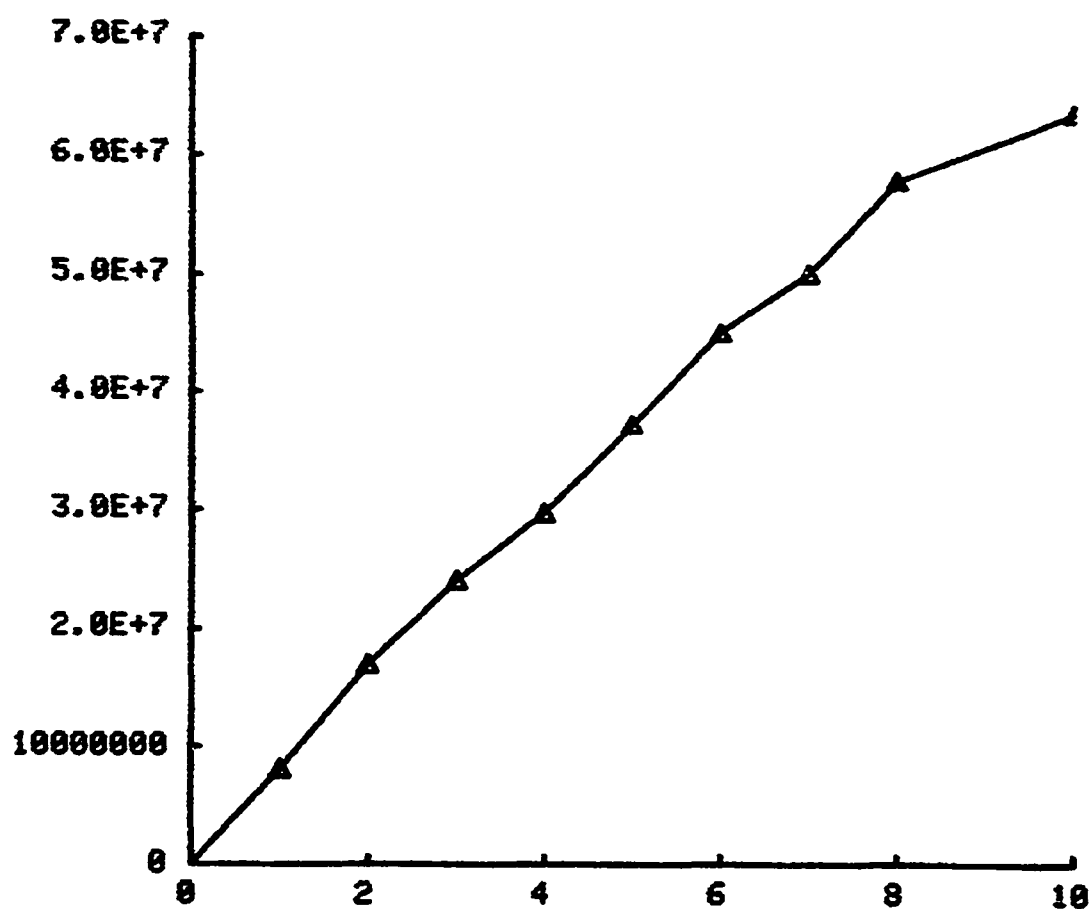


FIGURE 21. GAS CHROMATOGRAPH CALIBRATION: WATER. The response of the thermal conductivity detector to water is shown. Sample volumes were held to 2 or 5 microliters to maintain TCD response in the linear region.

TCD RESPONSE TO ABSOLUTE ETHANOL: AREA VERSUS MICROLITERS

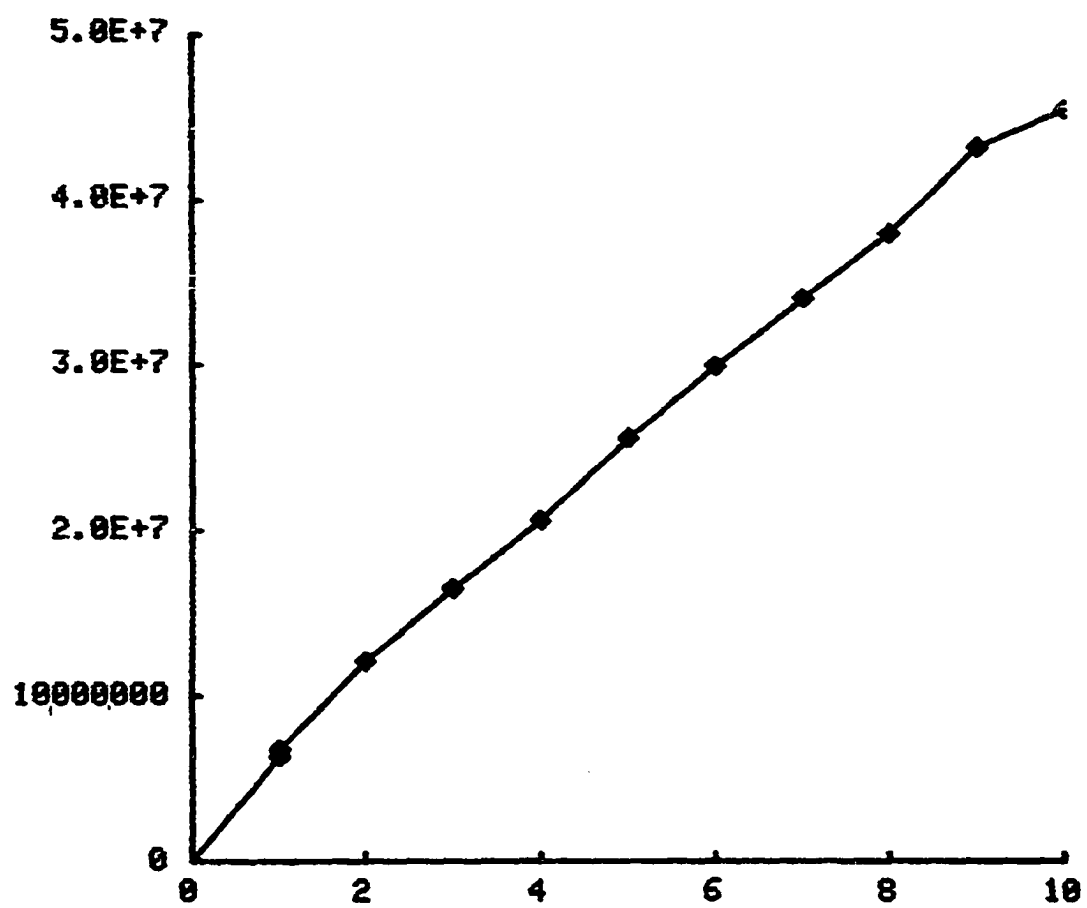
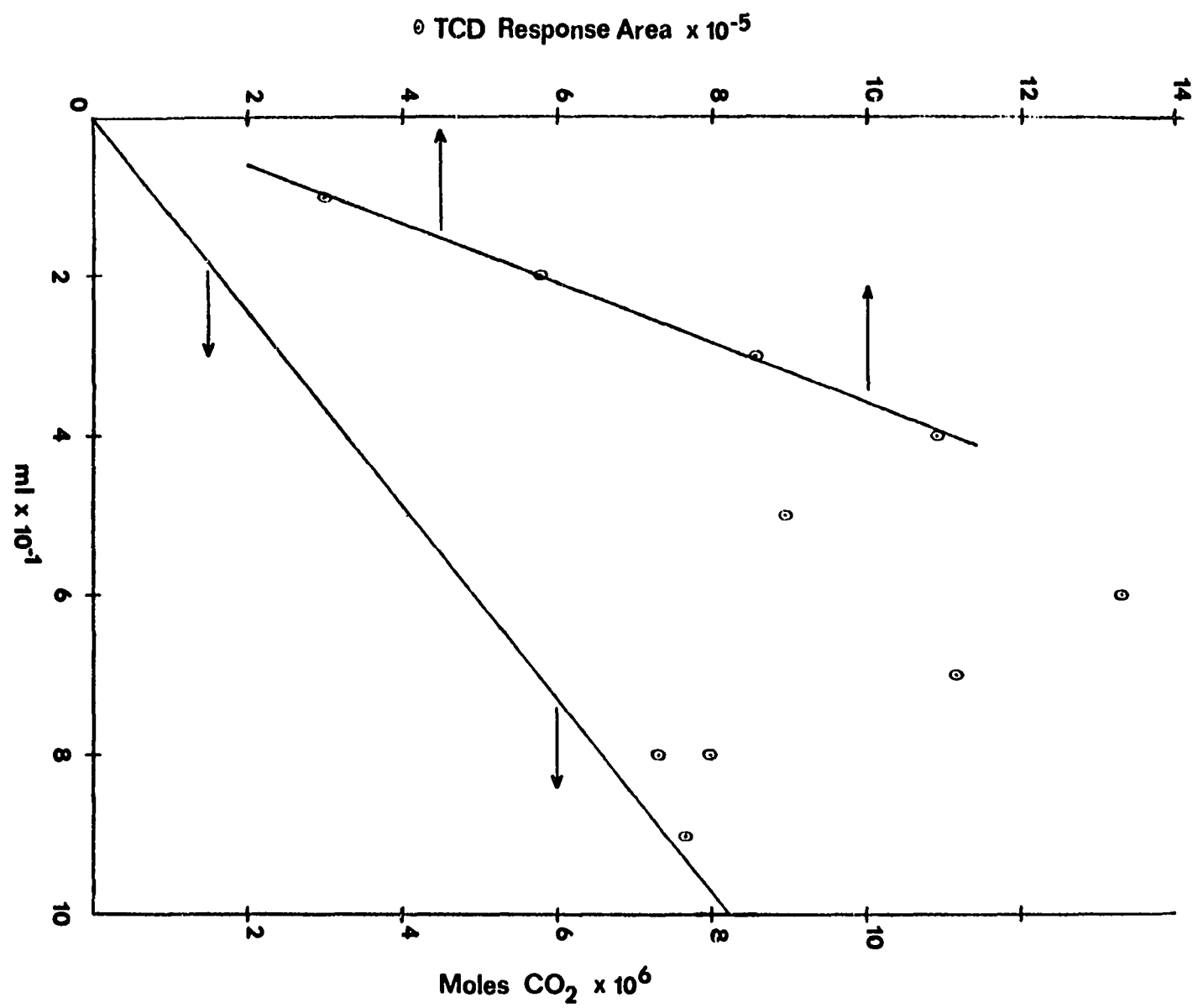


FIGURE 22. GAS CHROMATOGRAPH CALIBRATION: CARBON DIOXIDE. The response of the thermal conductivity detector to carbon dioxide is shown. Volumes of carbon dioxide at atmospheric pressure were injected into the gas chromatograph. As the figure illustrates, volumes greater than 0.4 ml of gas caused detector flooding and gave non-reproducible results. Volumes of CO₂ gas samples were thus held to under 0.4 ml to maintain a linear detector response.



CHAPTER VII

RESULTS AND DISCUSSION

The results of this dissertation research encompass the operation of a continuously fed apparatus in the critically opaque region of pure carbon dioxide, and the liquid-liquid two phase region of the carbon dioxide-ethanol-water system at elevated pressure and ambient temperature.

The Carbon Dioxide-Ethanol-Water System in Pilot Plant Operation

The carbon dioxide-ethanol-water system was investigated at a temperature of 25°C and 1000 psia to correspond with the ternary equilibrium data published by Francis [72] in 1954. The pilot plant was difficult to operate, as there were not any flow controllers. Regardless of operational difficulties, a consistent set of data was obtained. The equilibrium data of Francis [72] is shown in Figure 22. The diagram was retrieved from the published plot by tracing the enlargement of an opaque projector. Since the original

size of the published plot was 1" per side, the retrieved data does not have a high quantitative significance, but the trends are apparent.

A set of four operational tie lines is displayed in Figure 22. These tie lines are the experimental result of operating the apparatus with a continuous feed of 0.1 moles per minute ETOH, 0.1 moles per minute H₂O, and 0.62 moles per minute CO₂. The high pressure separator was maintained at a pressure of 1000 psia $\pm$ 2.5 psia and a temperature of 25°C $\pm$ 0.2°C. The resulting operational tie lines do not overwhelmingly match the Francis literature data. This result is not unexpected as the pilot plant is expected to be a steady state process, not an equilibrium process. Thermodynamic equilibrium, such as measured in batch systems, is approached as mass transfer limitations are removed. Although the unit may be operating in a steady state manner, batch equilibrium conditions are not necessarily reached. The degree of inconsistency in this data can be qualitatively observed by noting that the feed composition does not lie on a line connecting data points between two phases. The consistency of the data must be tested, and corrected if need be, so that errors in analysis of the data do not replicate

throughout process design calculations. The analysis of the consistency of the mass balance is presented in Appendix 2.

A test for the consistency of the mass balance was run. The results are displayed in Figure 23. The important benefit of performing the consistency test is that the feed location now falls on the tie line defined by the two outlet locations. Statistical averaging alone does not yield a consistent set of data in the sense that the feed and outlet locations will fall on the tie line. A more complete discussion of the consistency test may be found in Appendix 2.

A summary of the experimental data and the consistency test results are listed in Table 8. The fractional flow rates of the feed, heavy, and light streams are listed in Table 9. These flow rates were calculated from the results of the consistent data test. As these two tables describe, the two phase liquid-liquid CO_2 -ETOH- H_2O system at 25°C and 1000 psia yields a heavy phase rich in H_2O and a light phase rich in CO_2 . When the feed fractional flow rates (moles per minute) are 0.622 CO_2 :0.098 ETOH:0.100 H_2O , the heavy phase fractional flow rates are 0.0236 CO_2 :0.0684 ETOH:0.0961 H_2O , and the light phase fractional flow rates are 0.598 CO_2 :0.030 ETOH:0.004 H_2O . A comparison of these fractional

flow rates show that a 49.5 mole % ETOH stream may be split into a 41.6 mole % ETOH stream and an 88 mole % ETOH stream (the calculation is on a CO_2 free basis).

The overall results of this analysis can be summarized. A 23.4% conversion of a 49.5 mole % ETOH- H_2O feed stream to an 88 mole % ETOH- H_2O "light" stream may be accomplished with liquid CO_2 at 25°C and 1000 psia, and a solvent (CO_2) to feed (ETOH and H_2O) ratio of 3.12. The resulting heavy stream contains 41.5 mole % ETOH (where mole % is on a CO_2 free basis).

During the time of the writing of this dissertation, two authors, Panlaitis [169] and McHugh [144], presented papers on the separation of ethanol and water with supercritical solvents. The solvents used by Panlaitis are CO_2 and ethylene. McHugh used ethane as a supercritical solvent. Some of the results of the work by Paulaitis may be compared to the work in this dissertation. Paulaitis experimental data and smoothed curved of the CO_2 -ETOH- H_2O system at 35°C and 2000 psia are used for this comparison. A 31.3% conversion of a 49.5 mole % ETOH- H_2O feed stream to a 76 mole % ETOH- H_2O "light" stream may be accomplished with supercritical CO_2 at 35°C and 2000 psia, and a solvent (CO_2) to feed (ETOH and H_2O) ratio of 3.12. The resulting heavy stream

contains 36 mole % ETOH (where mole % is on a CO_2 free basis). The thermodynamic conditions for the example from Paulaitis are above the CO_2 critical point, where as the work in this dissertation is below the critical point with respect to temperature and pressure. A comparison of the two conditions show that the supercritical values reported by Paulaitis have a higher yield in conversion than the subcritical values reported in this dissertation. The selectivity of ETOH for H_2O , however, is higher for the subcritical values reported in this dissertation than the supercritical values reported by Paulaitis. Paulaitis performed calculations along the three phase line of CO_2 -ETOH- H_2O system. Paulaitis notes that his calculations suggest that although supercritical CO_2 appears to be a good solvent for separating ETOH and H_2O , CO_2 at sub-ambient temperatures and more moderate pressures may prove to be a better solvent. The improved selectivities demonstrated in this dissertation at subcritical conditions verify the prediction of Paulaitis that higher selectivities may be achieved at subcritical conditions.

Another important result may be seen from the comparison of this dissertation work at subcritical conditions and the work of Paulaitis at temperatures and pressures greater than the critical point. The elevation

of temperatures and pressures above the critical point does not necessarily bring about an enhancement of selectivities. Thus, supercritical temperature and supercritical pressure is not a sufficient criterion for enhanced selectivity with supercritical solvents.

Supercritical solvent behavior is a thermodynamic phenomenon which can only exist at high solvent concentrations. The phenomenological behavior of a supercritical solvent is such that when a mixture contains a high solvent concentration, and the mixture is maintained at a temperature above the critical temperature of the mixture, and the mixture is maintained at a pressure sufficiently higher than the critical pressure of the pure component solvent, the equilibrium distribution (the k value) of other components in the mixture may increase by several orders of magnitude. This supercritical behavior is a phenomena which occurs along side retrograde condensation; however, the observed occurrence of retrograde condensation is not always associated with the supercritical solvent behavior, notably at lower solvent concentrations. The occurrence of high solvent concentrations, temperatures greater than the critical temperature of the mixture, and pressures greater than the critical pressure of the pure component solvent is not a sufficient criterion for the existance of super-

critical solvent behavior; the nature of the mixture must be considered in the final analysis.

The results of this dissertation demonstrate higher selectivities ethanol in the CO_2 - ETOH - H_2O system at sub-critical conditions than those reported by Paulaitis in the phase fluid-liquid region at temperatures and pressures above the critical point or in the three phase region at temperatures above the critical and pressures slightly below the critical.

While the initial objective of the dissertation research was to operate experiments at supercritical conditions, this initial objective could not be met due to limitations of the experimental equipment; however, the following objectives were accomplished:

- 1) A continuously fed experimental apparatus for investigating the carbon dioxide-ethanol-water system at high pressures was built and the needs determined for future modifications.
- 2) A thermodynamic analysis was performed.
- 3) Calculations were performed conceptually for the process.

- 4) The continuously fed apparatus was operated in the critical region of pure CO_2 , while observing critical opalescence for an extended period of time.

This dissertation research lays a framework for further investigations in solvent behavior at elevated pressure. While the research began with an emphasis on supercritical behavior, the final results are for the subcritical case at elevated pressure and ambient temperatures. The subcritical case gave higher selectivity but lower conversion than the supercritical case presented by Paulaitis [169]. Paulaitis, however, predicted that these results might be found. Further efforts in the subcritical region at ambient temperatures and elevated pressures may yield a more economic process.

Further work should also continue in an effort to better characterize the supercritical region for the CO_2 - $\text{ETOH-H}_2\text{O}$ system. A more extensive search by both experiment and equation of state calculation may find a region of the CO_2 - $\text{ETOH-H}_2\text{O}$ system which displays the enhanced selectivities suggested by supercritical solvent behavior.

FIGURE 23. EXPERIMENTAL TIE LINES OF THE CO₂-ETOH-H₂O SYSTEM AT 25°C and 1000 PSIA. The experimental tie lines of the CO₂-ETOH-H₂O system at 25°C and 1000 psia determined in this research are presented. The batch equilibrium tie lines (solid) of Francis² are also shown, along with the smooth curve. The data sets 1-4 denote the experimental tie lines from the continuously fed apparatus. The data set 1 is connected with a dashed line. The slope of the operational tie line deviates from the batch equilibrium tie line. This deviation in slope may be due to mass transfer effects in the continuous apparatus. The flow rate of the ethanol/water mixture is 0.1 moles ethanol and 0.1 moles of water per minute. Note that the feed location, F, does not fall on any tie line; this feature necessitates a consistency of mass balance test.

² Francis, A.W., J. Phys. Chem., 58: pp. 1099-1144 (1954).

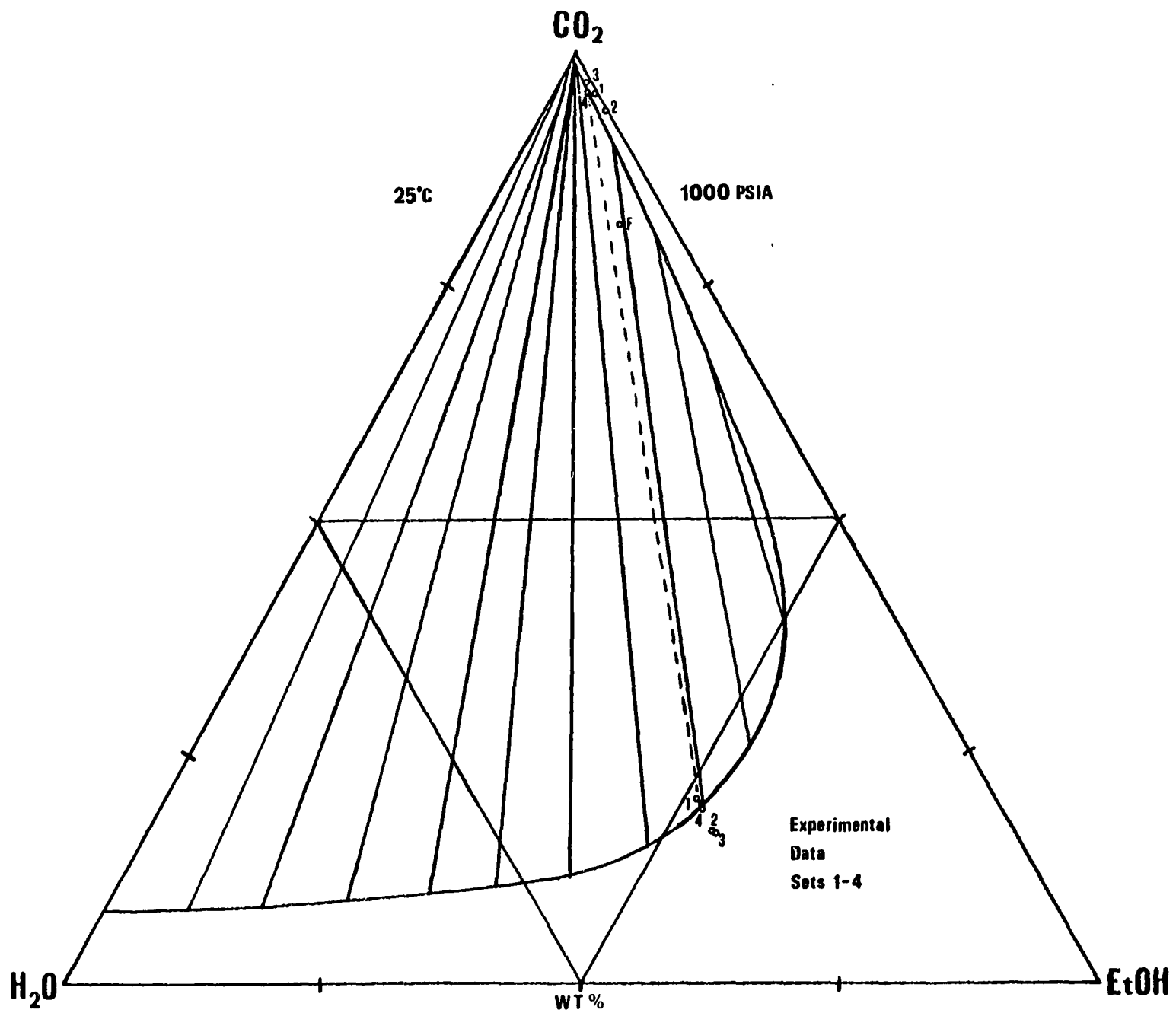


FIGURE 24, CONSISTENT TIE LINE OF THE CO₂-ETOH-H₂O SYSTEM AT 25°C and 1000 PSIA. A test for the consistency of the mass balance was run on the experimental data. The consistency test gives a tie line with feed and exit stream which are consistent with the tie line. For the consistent tie line, all components fall on the tie line. The compositions on this line in mole fraction are: 1) a feed of 0.757 CO₂:0.120 ETOH:0.123 H₂O, 2) a heavy stream of 0.124 CO₂:0.360 ETOH: 0.509 H₂O, and 3) a light stream of 0.941 CO₂:0.47 ETOH:0.006 H₂O. This tie line represents the steady state condition at feed flow rates in moles per minute of 0.622 CO₂:0.098 ETOH:0.100 H₂O.

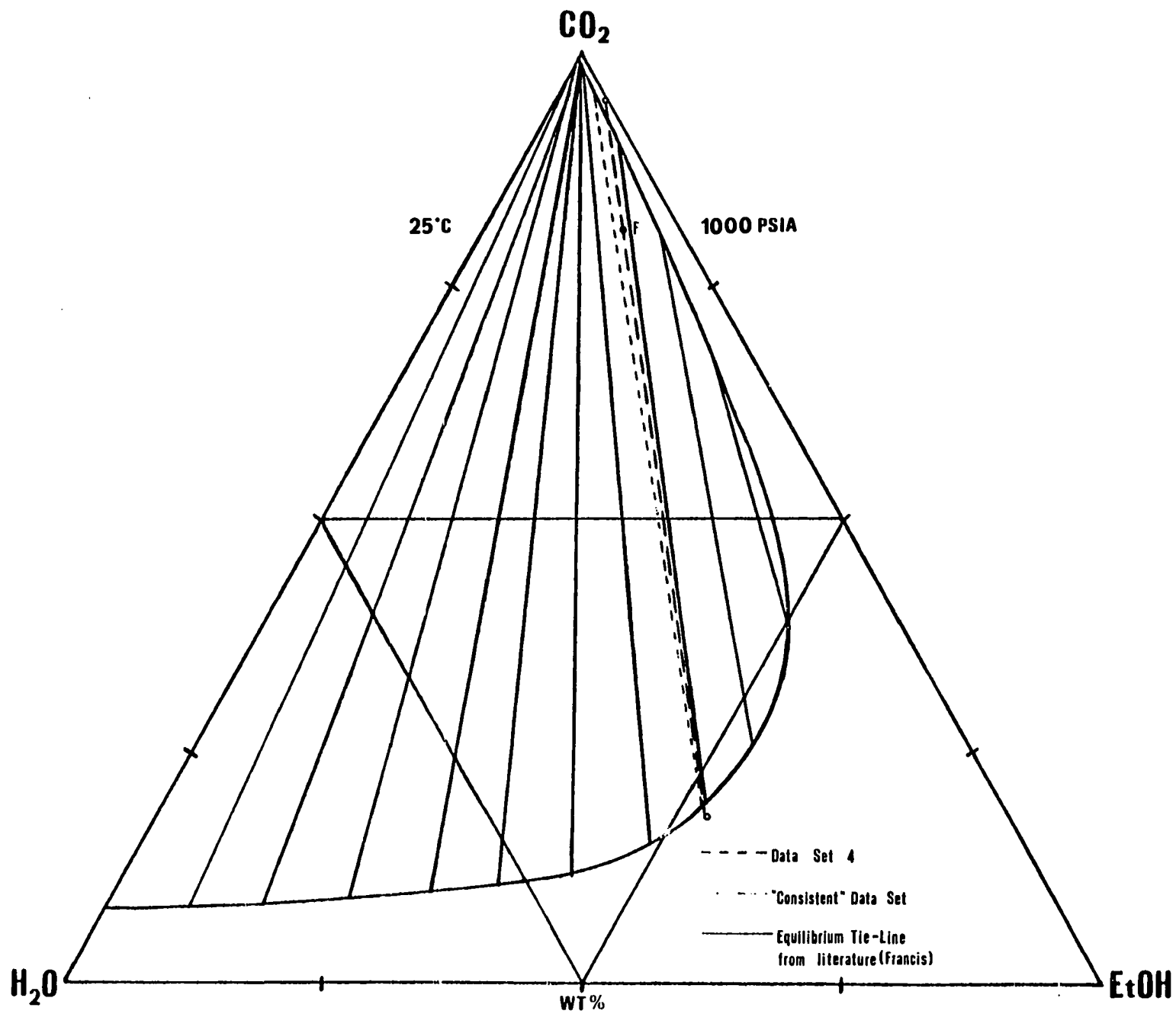


TABLE 8

SUMMARY OF THE EXPERIMENTAL RESULTS AND THE STATISTICALLY
 CONSISTENT MASS BALANCE FOR THE CO_2 - ETOH - H_2O
 SYSTEM AT 25°C AND 1000 PSIA

**	<u>Raw Experimental Data*</u>				<u>Consistent Data</u>
z_{CO_2}	.756				.757
z_{ETOH}	.122				.120
$z_{\text{H}_2\text{O}}$	.122				.123
	<u>1.000</u>				<u>1.000</u>
	<u>Run #1</u>	<u>Run #2</u>	<u>Run #3</u>	<u>Run #4</u>	
x_{CO_2}	.146	.111	.108	.132	.124
x_{ETOH}	.362	.370	.373	.360	.360
$x_{\text{H}_2\text{O}}$	.495	.510	.511	.506	.509
	<u>1.003</u>	<u>.991</u>	<u>.992</u>	<u>.998</u>	<u>.993</u>
y_{CO_2}	.953	.945	.960	.953	.941
y_{ETOH}	.037	.042	.034	.037	.047
$y_{\text{H}_2\text{O}}$	.012	.015	.011	.012	.006
	<u>1.002</u>	<u>1.002</u>	<u>1.005</u>	<u>1.002</u>	<u>.994</u>

* Both ethanol and water feed rate at 0.1 mole/min.

** Units in mole fraction.

***Consistent molar flow rates are $F/V=1.2920$ and $F/L=4.3138$.

TABLE 9

FLOW RATES* FOR THE STATISTICALLY CONSISTENT
 MASS BALANCE OF THE CO₂-ETOH-H₂O SYSTEM
 AT 25°C AND 1000 PSIA

<u>Component</u>	<u>Feed</u>	<u>Heavy</u>	<u>Light</u>
CO ₂	0.622	0.0236	0.598
ETOH	0.098	0.0684	0.030
H ₂ O	0.100	0.0961	0.004
ETOH %**	49.5%	41.6%	88.8%

* Flow rate is in units of moles per minute.

** ETOH mole percent on a CO₂free basis.

CHAPTER VIII

SUMMARY

The carbon dioxide-water-ethyl alcohol system has been investigated in a continuously fed apparatus. The results conclusively demonstrate that ethanol and water can be separated with a high pressure liquid carbon dioxide solvent. Future studies are recommended in the next chapter. Despite the limited experimental data obtained in this study the following conclusions are justified.

The goal of this dissertation has been to investigate the nature of the carbon dioxide-ethanol-water system at elevated pressures. The research shows that EtOH and H_2O can be separated by liquid carbon dioxide at elevated pressure. The research also shows, by a comparison of experimental results and literature data, that the subcritical region may yield characteristics which will prove as feasible as operation at some temperatures and pressures greater than the critical point.

The virial equation was used to predict the behavior of the $\text{CO}_2\text{-H}_2\text{O}$ binary. The prediction was found to give enhance solubility of water in the CO_2 phase at elevated pressures. The virial equation truncated after the second virial coefficient was used only as a standard for comparisons with the works of other authors. The virial EOS was never expected to give an accurate prediction. However, with the aide and benefit of the solubility equation rigorously derived in this dissertation research, a more advanced equation of state may now easily be employed. The Peng-Robinson and mBWRs are two EOS candidates which may fit the need.

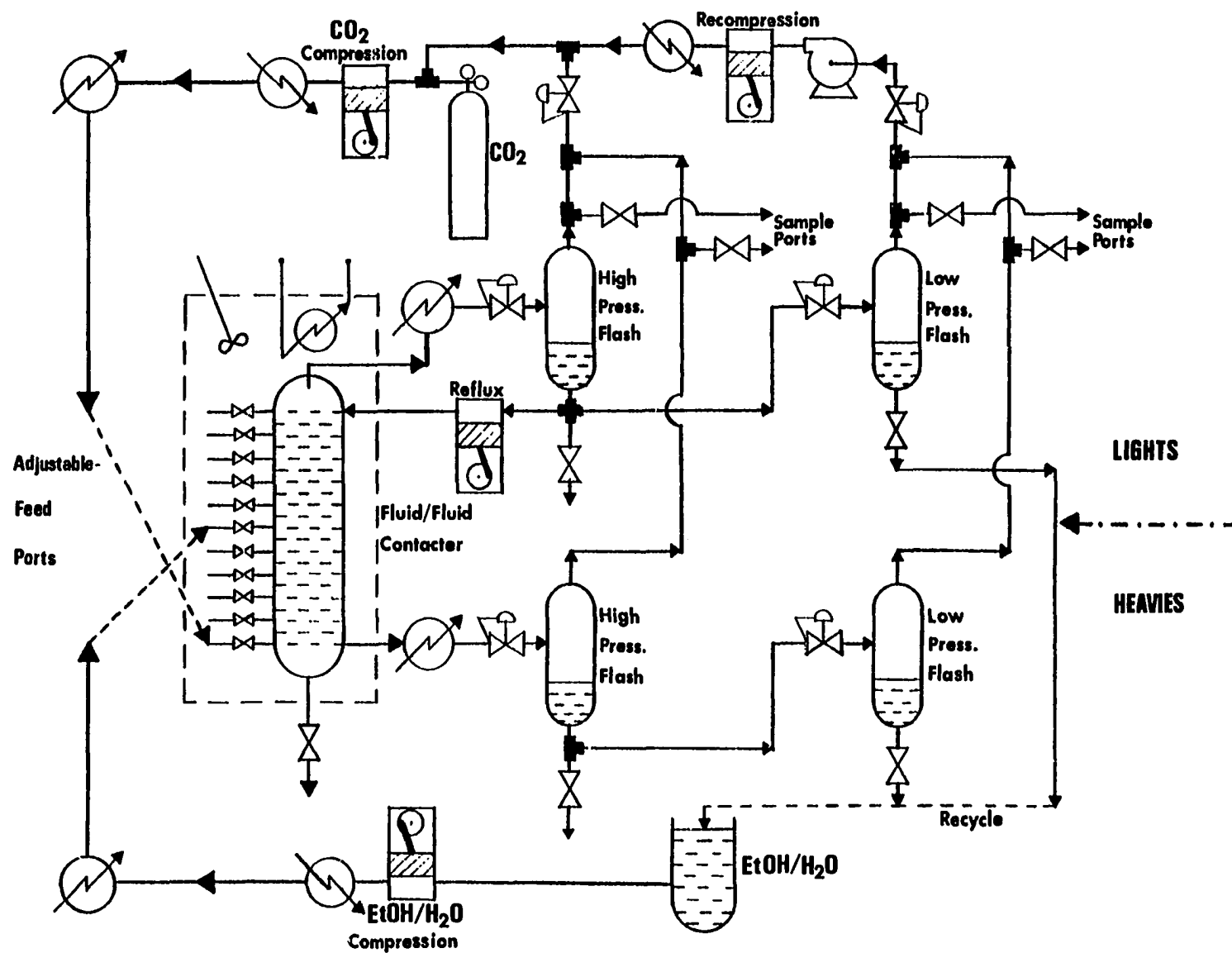
CHAPTER IX

RECOMMENDATIONS

The results of this dissertation research indicate two general recommendations: firstly, that an equation of state be developed which has the capability of predicting the thermodynamic properties of mixtures of isotropic, anisotropic, associative, and polar fluids, including water, and secondly, that an improved pilot plant be constructed for the study of supercritical solvent separation processes.

Even though only limited quantitative data were accumulated in this investigation, based on the extensive observations and operating experience on this equipment, the requirements for the experimental equipment in future studies have become clearly evident. The process flow diagram in Figure 24 presents the recommended design. The most important feature of this pilot plant is incorporation of adjustable feed locations for the solvent-solute contractor. Due to the lack of experimental data on the high mass transfer rates in supercritical solvents, the

FIGURE 25. PILOT PLANT DESIGN RECOMMENDED FOR FUTURE STUDIES. The process flow diagram illustrated in this figure presents the recommended design for future studies. This pilot plant is intended for continuing studies on systems for which the initial equilibrium data have previously been obtained. Three major modifications have been suggested over the previous design. The first modification is segregation of the atmospheric flash into two stages. The combination of a high pressure generator and a low pressure separator will provide for better control of the system. This first modification also enhances the ability to recycle the solvent stream, which is the second modification. The third modification is the contactor. The modified design encompasses multi-stage countercurrent contacting of feed streams. The adjustable feed ports may also serve as "tray" sample ports. Tray by tray analysis is a necessary determination need for scale-up parameters.

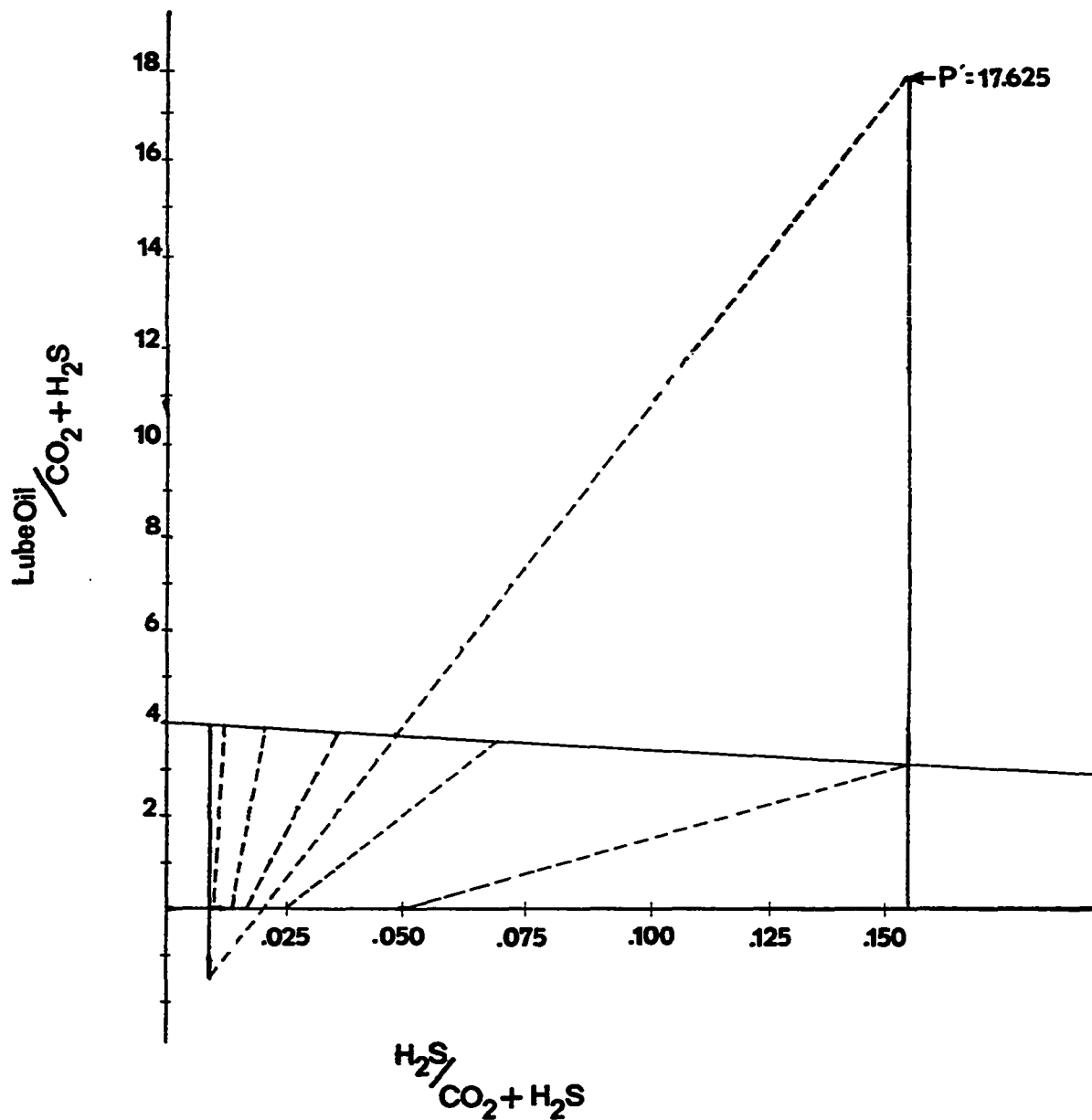


operational tie lines for a process are indeterminate from theory. The adjustable feed location option will provide more useful scale up parameters for design purposes.

Due to the unusual supercritical solvent behavior displayed in the $\text{CO}_2\text{-H}_2\text{O-ETOH}$ system, and a greater national need in more pressing areas at this time, it is recommended that the $\text{CO}_2\text{-H}_2\text{O-ETOH}$ system be incorporated as only one of many systems under investigation. Another system which may be more relevant at this time is the carbon dioxide-hydrogen sulfide-lubricating oil ternary system. This system is recommended because of the increased occurrence of hydrogen sulfide in recovered petroleum.

The $\text{CO}_2\text{-H}_2\text{S-Lub Oil}$ system is shown in Figure 25. This is a Ponchon-Savarit analysis showing that a feed stream of CO_2 containing 20,000 ppm H_2S can be separated into two streams: 1) a CO_2 rich phase containing 900 ppm H_2S , and 2) a lube oil rich phase containing 150,000 ppm H_2S . The $\text{CO}_2\text{-H}_2\text{S-Lub Oil}$ system leads the way for the class of systems which are recommended for further study. Petroleum reservoir systems exist at high pressures; this is especially true for the deeper wells currently being sought and delivered. With the availability of work already present in the system as a high pressure driving

FIGURE 26. PONCHON-SAVARIT DIAGRAM OF THE CO₂-H₂S-LUBRICATING OIL SYSTEM AT 25°C and 1000 PSIA.² The CO₂-H₂S-Lubricating Oil system is shown in this illustration. Ponchon-Savarit analysis predicts that a feed stream of CO₂ containing 20,000 ppm H₂S can be separated into two streams: 1) a CO₂ rich phase containing 900 ppm H₂S, and 2) a lubricating oil rich phase containing 150,000 ppm H₂S. Research towards on site surface separation and clean up of H₂S from production wells is within the scope of recommended research directions.



Total Reflux

Feed = 20,000 ppm H_2S
 X_D = 150,000 ppm H_2S
 X_W = 900 ppm H_2S
 Lube Oil: $\text{CO}_2 \rightarrow 4:1$
 no. of stages: 5

Minimum Reflux

Feed = 20,000 ppm H_2S
 X_D = 150,000 ppm H_2S
 X_W = 900 ppm H_2S
 no. of stages: infinite
 F/D = 12.933
 D/W = .0837
 W/F = .924
 D/F = .077

force, on site surface separation may be enhanced by supercritical solvent techniques. Research within this expanded scope is highly recommended.

Miscible CO₂ reservoir floods for enhanced oil recovery would also benefit from future studies. The recommended area of study within the scope of this dissertation work is the equilibrium phase behavior of such systems. Both the pure component derived systems (binary, ternary, etc.) and the actual reservoir fluids could be studied. However, the scope of this research would only cover the "compositionally" well defined systems. This limitation is placed on the research scope so that exacting data collection could enhance the viability of theoretical equations of state toward the oil reservoir. Study concentrated on the reservoir fluids would not satisfy the long term data base needs. As an example, the gasoline cut contains approximately 150 molecular species ranging from propane to n-dodecane and "unknown" C₁₂ aromatics. Mixtures of this type are not recommended for study in the next five year time frame.

Specifically the recommendations for future research which follow from the scope of this dissertation research are:

1. Construction of a "multiphase equilibrium" batch operation unit.

2. Construction of the two phase, continuously fed elevated pressure solvent extraction pilot plant.
3. Improvement of existing equations of state to encompass multicomponent, multiphase systems in the critical regions, for both hydrocarbons and their mixtures with polar and associative fluids.
4. The study of high pressure systems such as:
 - a) $\text{CO}_2\text{-H}_2\text{O-ETOH}$
 - b) $\text{CO}_2\text{-H}_2\text{S-Lube Oil}$
 $\text{CO}_2\text{-H}_2\text{S-Glycol Derivatives}$
 - c) $\text{CO}_2\text{-Light Hydrocarbons-Heavy Hydrocarbons}$
 - d) $\text{Light Hydrocarbons-Paraffins-Asphaltenes}$
 - e) $\text{CO}_2\text{-H}_2\text{O-Coal}$
 - f) $\text{Straight Chain and Ring Containing Hydrocarbons-Coal Fluids-Coal Solids}$

Research carried out within this recommended scope would require a large number of man-years before completion of any realistic goals.

More specifically the recommendations for a five year research plan are, first, the construction of an accurate equilibrium state determination unit. The accuracy should be for temperature = 0.001°C , for pressure = 0.001 psia, for volume = $1/10000$ the volume of the equilibrium cell, for composition = 1 ppm. The pressure range should be from 1 to 10,000 psia, the temperature range -150°F to 1000°F . (This temperature range may prove to over burden current technology).

The equilibrium states of the systems previously recommended could then be studied in the latter two years of this five year plan. Once the accuracy of the research unit is demonstrated, systems suggested for study would come from both fundamental and applied research.

NOMENCLATURE

VARIABLES

B_{ii}	Second virial coefficient of the pure component i .
B_{ij}	Second virial cross coefficient of the components i and j .
$\text{Exp}, \ln$	Natural exponent and log.
f_i	Fugacity of component i .
ϕ	Fugacity coefficient.
γ	Activity coefficient.
G	Gibb's free energy.
H	Enthalpy.
N	Number of nodes.
P	Pressure.
R	Ideal gas constant.
T	Absolute temperature.
$\underline{V}$	Specific volume.
$\underline{V}_m$	Specific volume of the mixture.
Z	Compressibility factor.

SUPERSCRIPTS

$\wedge$	Partial molar.
$\circ$	Pure component.
I	Phase number 1.
II	Phase number 2.

I.G. Ideal Gas.

Sat Value of the variable at the temperature of the system and saturation conditions.

V Vapor or fluid phase.

L Liquid phase.

SUBSCRIPTS

i,j,1 or 2 Respective component.

c Critical property.

R Reduced quantity.

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APPENDIX A

HAND CALCULATOR PROGRAM FOR THE PENG-ROBINSON
EQUATION OF STATE

HAND CALCULATOR PROGRAM FOR THE PENG-
ROBINSON EQUATION OF STATE

The Peng-Robinson equation of state is a current working version of the van der Waals equation of state [174, 175, 176]. The conciseness of this equation makes it an excellent candidate for programming on a hand calculator. The oil field, the process plant, and the board room are places where the hand calculator model would have it's greatest utility.

The Peng-Robinson EOS is a cubic equation with three independent parameters: T_{c_i} , P_{c_i} , and acentric factor i . A binary interaction parameter is included as a fourth parameter for each binary set in a fluid mixture. Table A-1 is a flow chart of the equation of state. This flow chart covers the introduction of all parameters (except for the number of components in the system). The flow chart ends at the point of deciding which form of the equation of state is to be used; the two alternatives are given.

One form that the P-R EOS may take is the solution of a cubic equation in compressibility factor (Z).

The compressibility factor for the system is then known. The solution of the cubic equation can be either by iterative search or by analytical solution. The analytical solution is outlined by Uspensky [2572]. The iterative search method is commonly found in the "plug in chip" library functions of most programmable calculators.

The pressure explicit form of the P-R EOS was used for the calculations and programming in this chapter. This form of the P-R EOS requires introduction of the specific volume of the fluid into the EOS to extract a pressure value. The flow diagram was tested by hand to check for consistency of logic. Results of the hand calculation are shown in Table A-2. The dew line of pure ethane is well predicted by the P-R EOS. The bubble line is not well predicted. A correction must be made to the P-R EOS ($\delta_{\text{ethane-ethane}} = 0.313546$) to yield an accurate prediction. This point will be discussed in conjunction with Table A-5.

A program for a Ti-58 or a Ti-59 Texas Instruments programmable hand calculator is listed in Table A-3. Table A-4 gives the key functions (memory locations) for the program. The Ti-58 must be repartitioned for 319 program steps. The Ti-59 has more than sufficient memory space for this program. This program was built for a Ti-58, so, only a binary system can be used.

Each component requires 8 memory locations. This program uses every register (memory) location available on a Ti-58. A multi-component system would require a Ti-59 or a Hewlett-Packard HP-41-CV.

Bubble and dew lines for pure ethane were calculated by this program. The results are listed in Table A-5. The prediction of the dew line from the critical point down to -210°F is very good, (less than 1% absolute normalized deviation). The bubble line prediction is very poor, 20 to 25,000% deviation. The δ column lists the necessary value of the binary interaction parameter to reduce the predicted error to a value of less than 0.05% absolute normalized deviation. Correlation of these interaction parameters to the degree of accuracy required (up to 6 places) would be equivalent to building a new equation of state. The large deviation in the bubble line is due to the $\pm 5\%$ error in the density prediction from the P-R EOS [174].

A correction in the order of $\pm 5\%$ for the volume specified will correct the pressure prediction to an acceptable level (0.05% AND).

Density prediction problems of the P-R EOS can be overcome by solving for the compressibility factor of each phase. The fugacity relation can then be used to equate the two phases. An iterative method could then be used to yield a value of the bubble point pressure. The resulting density should be within $\pm 5\%$ deviation [174].

The fugacity equation requires an additional 200 storage locations on a Ti-58. The additional storage locations make this method too memory intensive for the Ti series calculators, however, the Hewlett-Packard HP-41-CV series would be able to use this method, even for a large multi-component system.

TABLE A-1. (Continued)

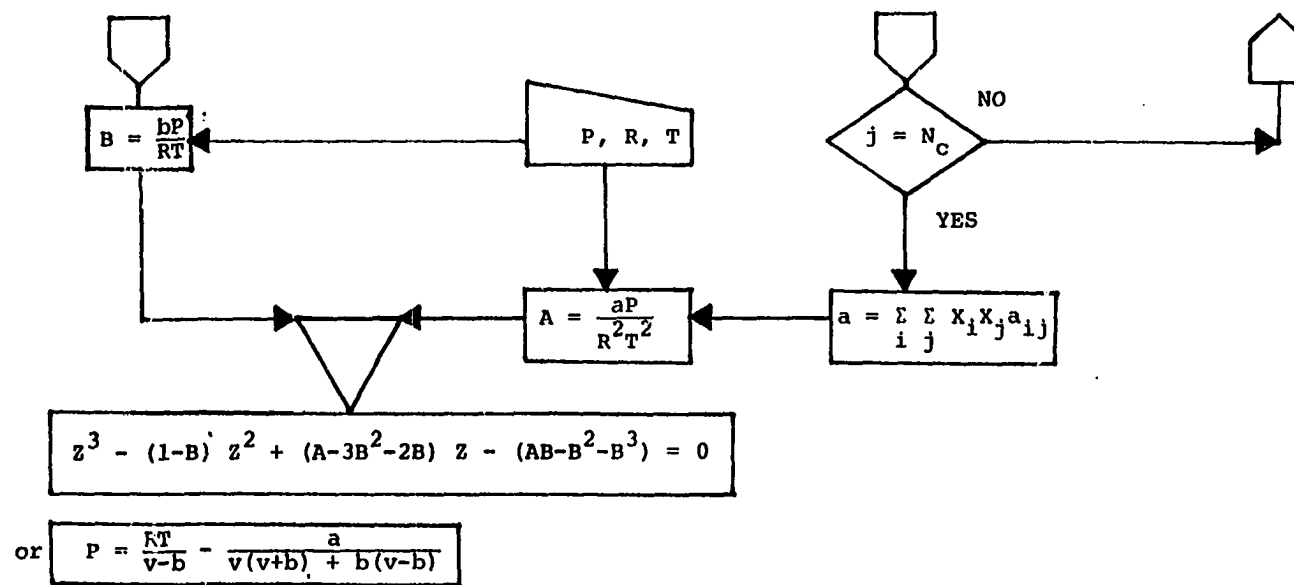


TABLE A-1.

THE PENG ROBINSON EQUATION OF STATE

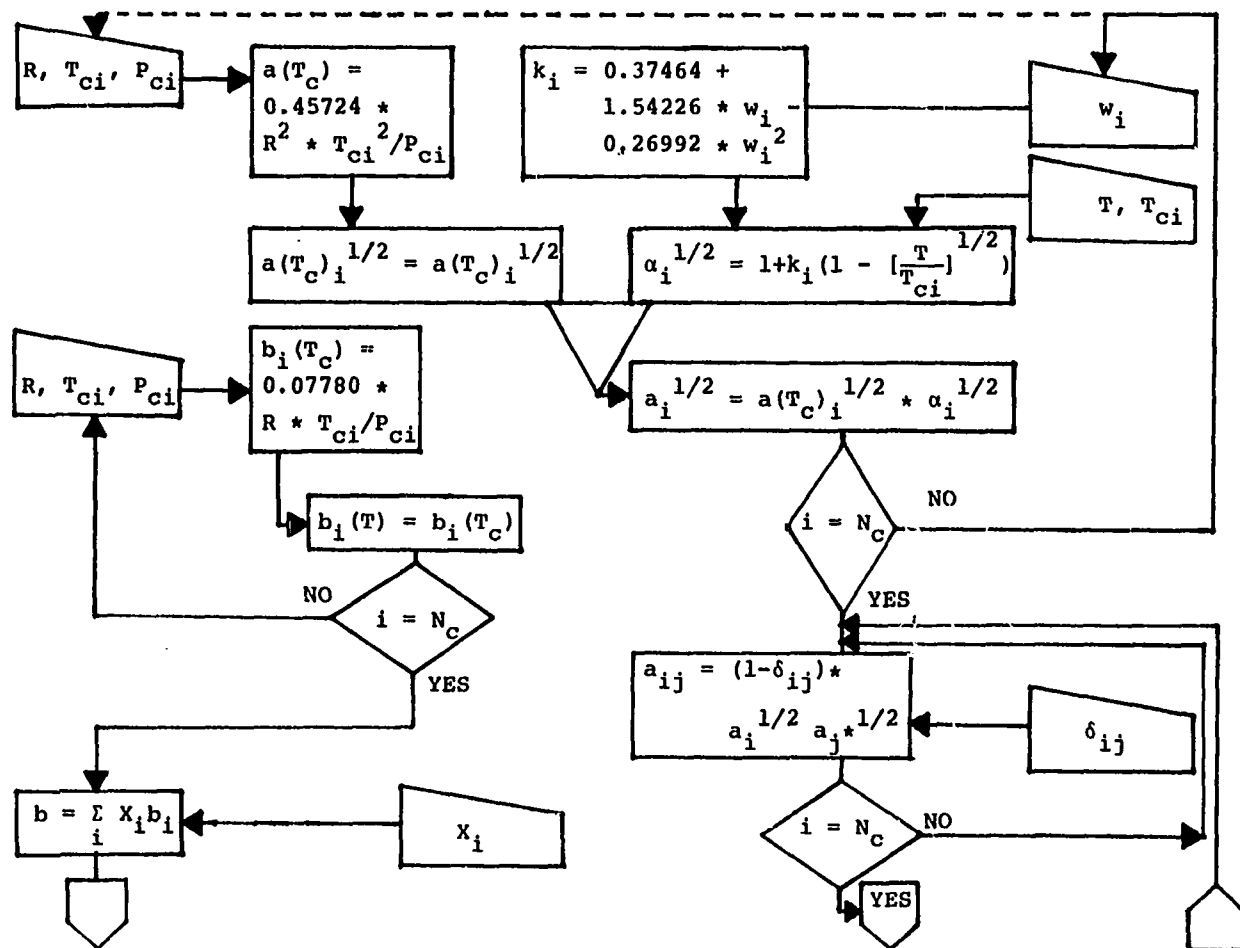


TABLE A-2.

Peng-Robinson EOS:

Calculations on Pure Ethane

Ethane C_2H_6

MW = 30.07

 $T_c = 305.4^\circ K$ $P_c = 48.2 \text{ ATM}$ $V_c = 148. \text{ cc/g-mole}$ $Z_c = 0.098$ $w = 0.098 = \text{acentric factor}$ $T_{\text{freeze}} = 89.9^\circ K$ $T_{\text{boil}} = 184.5$ $\rho_{183PK} = 0.548 \text{ gm/cc}$ $R = 82.057 \text{ cm}^3 \text{ ATM/g-mol } ^\circ K$ $a(T_c) = 0.45724 * R^2 * T_{ci}^2 / P_{ci}$

$$= 0.45724 * 82.057^2 \frac{\text{CM}^{3.2} \text{ ATM}^2}{\text{g-mol}^2 \text{ } ^\circ K^2} \left| \frac{305.4^2 \text{ } ^\circ K^2}{1} \right| \frac{1}{48.2 \text{ ATM}}$$

$$= 5957533.78 \frac{\text{CM}^6}{\text{g-mol}} \left| \frac{\text{ATM}^{1/2}}{1} \right|$$

 $k_i = 0.37464 + 1.54226 * w_i - 0.26992 * w_i^2$ $= 0.5231891683$

TABLE A-2. (Continued)

$$b_i(T_c) = 0.07780 * R T_{ci}/P_{ci}$$

$$= 0.07780 * 82.057 \frac{\text{CM}^3 \text{ ATM}}{\text{g-mol } ^\circ\text{K}} \left| \frac{305.4^\circ\text{K}}{1} \right| \frac{1}{48.2 \text{ ATM}}$$

$$= 40.44987898 \frac{\text{CM}^3}{\text{g-mol}}$$

$$b_i(T) = b_i(T_c)$$

$$\alpha_i^{1/2}(T) = 1 + k_i (1 - [T/T_{ci}]^{1/2})$$

$$\text{Choose } T = 510.78^\circ\text{K}$$

$$\alpha_i^{1/2}(T) = 1 + 0.5231891683 (1 - [510.78^\circ\text{K}/305.4^\circ\text{K}]^{1/2})$$

$$a_i^{1/2}(T = 510.78^\circ\text{K}) = 0.8465748723$$

$$a_i^{1/2}(T) = a_i^{1/2}(T_c) * \alpha_i^{1/2}(T)$$

$$= 2440.805969 \frac{\text{CM}^3}{\text{g-mole}} \left| \frac{\text{ATM}^{1/2}}{1} \right|$$

$$* 0.8465748723$$

$$a_i^{1/2}(T = 510.78^\circ\text{K}) = 2066.325002 \frac{\text{CM}^3}{\text{g-mole}} \left| \frac{\text{ATM}^{1/2}}{1} \right|$$

$$a_{PR} = \sum_i \sum_j X_i X_j (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2}$$

For a pure component a reduces to

$$a_{PR}(T) = (a_i^{1/2}(T))^2 = 4269699.014 \frac{\text{CM}^6}{\text{g-mole}^2} \left| \frac{\text{ATM}}{1} \right|$$

TABLE A-2. (Continued)

$$b_{P-R} = \sum_i X_i b_i$$

b_{P-R} for a pure component reduces to

$$b_{P-R} = b_i(T)$$

$$b_{P-R} = 40.44987898 \frac{\text{CM}^3}{\text{g-mol}}$$

The P-R EOS

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

$$P = 82.057 \frac{\text{CM}^3 \text{ ATM}}{\text{g-mol } ^\circ\text{K}} \left| \frac{510.78^\circ\text{K}}{1} \right| * \frac{1}{7508.1182 \frac{\text{CC}}{\text{g-mol}} - \frac{40.44987898 \frac{\text{CM}^3}{\text{g-mole}}}{40.44987898 \frac{\text{CM}^3}{\text{g-mole}}}]$$

$$- 4269699.014 \frac{\text{CM}^6}{\text{g-mole}^2} \left| \frac{\text{ATM}}{1} \right| * [$$

$$\frac{1}{7508.1182 \frac{\text{CC}}{\text{g-mol}} + (7508.1182 \frac{\text{CC}}{\text{g-mol}} + 40.44987898 \frac{\text{CC}}{\text{g-mol}})} + 40.44987898 \frac{\text{CC}}{\text{g-mole}} (7508.1182 \frac{\text{CC}}{\text{g-mol}} - 40.44987898 \frac{\text{CC}}{\text{g-mol}})$$

$$P = 5.6126053 \text{ ATM} \quad \left| \begin{array}{l} \text{Predicted Pressure} \\ - 0.0749364389 \text{ ATM} \end{array} \right|$$

$$P = 5.537668816 \text{ ATM}$$

$$\text{For } T = 510.78^\circ\text{K} \quad v = 7508.1182 \frac{\text{CM}^3}{\text{g-mol}}$$

TABLE A-2. (Continued)

Ethane: Bubble Line Calculations with Peng Robinson EOS

$$a(T_c)^{1/2} = 2440.805969 \quad \frac{\text{CM}^3}{\text{g-mol}} \bigg| \frac{\text{ATM}^{1/2}}{\text{ATM}^{1/2}}$$

$$\text{or } 4.961030572 \quad \frac{\text{Cuft}}{\text{lbm}} \bigg| \frac{\text{ATM}^{1/2}}{\text{ATM}^{1/2}}$$

$$k_i = 0.5231891683$$

$$b_i(T_c) = 40.44987898 \quad \text{CM}^3/\text{g-mol}$$

$$\text{or } 0.021331573 \quad \text{Cuft/lbm}$$

$$\text{At } -100^\circ\text{F} = 360^\circ\text{R}$$

$$v_e = 0.03029 \quad \text{Cuft/lbm}$$

$$P = 31.32 \quad \text{psia}$$

$$\alpha_i^{1/2}(T = 360^\circ\text{R}) = 1.099950612$$

$$a_i^{1/2}(T) = \alpha_i^{1/2}(T) a_i^{1/2}(T_c)$$

$$= 1.099950612 * 4.961030572$$

$$= 5.456888612 \quad \frac{\text{CM}^3}{\text{g-mol}} \bigg| \frac{\text{ATM}^{1/2}}{\text{ATM}^{1/2}}$$

$$\left[\frac{a_i^{1/2}(T)}{b_i} \right]^2 \quad \text{into P-R EOS gives } P_{\text{predicted}} = -2629.13$$

$$\text{For } \delta_{ij} = 0.313546 \quad X_1 = 0.5 \quad X_2 = 0.5$$

$$b_i(\delta_{ij} = 0) = b_i(\delta_{ij} \neq 0)$$

TABLE A-2. (Continued)

$$[a_i^{1/2}(T)]^2 = 29.77763332$$

$$a_{PR} = \sum_i \sum_j x_i x_j (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2} = 25.10930442$$

$$P_{\text{predicted}} = 31.31481223 \text{ } [\pm 0.05 \text{ \%AAD from Exper}]$$

TABLE A-3.

HAND CALCULATOR PROGRAM FOR THE PENG-ROBINSON EQUATION OF

STATE: FOR TEXAS INSTRUMENTS T_i-58 or T_i-59

<u>LOC</u>	<u>CODE</u>	<u>KEY</u>
00	68	2nd Nop
01	76	2nd Lbl
02	11	A
03	53	(
04	53	(
05	93	.
06	04	4
07	05	5
08	07	7
09	02	2
10	04	4
11	65	x
12	43	RC1
13	07	07
14	33	x ²
15	65	x
16	73	RC1 2nd Ind.
17	00	00
18	33	x ²
19	55	÷
20	69	2nd OP
21	30	30
22	73	RC1 2nd Ind.
23	00	00
24	54	)
25	34	√x
26	54	)
27	69	2nd OP
28	30	30
29	69	2nd OP
30	30	20
31	72	STO 2nd Ind.
32	00	00
33	53	(
34	43	RC1
35	00	00
36	85	+
37	03	03
38	54	)
39	42	STO
40	00	00
41	92	Inv SBR
42	76	2nd Lbl
43	16	2nd A'
44	53	(
45	53	(
46	53	(

TABLE A-3. (Continued)

<u>LOC</u>	<u>CODE</u>	<u>KEY</u>
47	53	(
48	73	Rc1 2nd Ind.
49	00	00
50	35	1/x
51	65	x
52	43	Rc1
53	08	08
54	54	)
55	34	$\sqrt{x}$
56	54	)
57	94	+/-
58	85	+
59	01	01
60	54	)
61	65	x
62	53	(
63	93	.
64	03	3
65	07	7
66	04	4
67	06	6
68	04	4
69	85	+
70	01	1
71	93	.
72	05	5
73	04	4
74	02	2
75	02	2
76	06	6
77	65	x
78	69	2nd OP
79	30	30
80	69	2nd OP
81	30	30
82	73	Rc1 2nd Ind.
83	00	00
84	75	-
85	73	Rc1 2nd Ind.
86	00	00
87	33	x^2
88	65	x
89	93	.
90	02	2
91	06	6
92	09	9
93	09	9
94	02	2
95	54	)
96	85	+

TABLE A-3. (Continued)

<u>LOC</u>	<u>CODE</u>	<u>KEY</u>
97	01	1
98	54	)
99	69	2nd OP
100	30	30
101	64	2nd Prd 2nd Ind.
102	00	00
103	53	(
104	43	RC1
105	00	00
106	85	+
107	03	3
108	54	)
109	42	STO
110	00	00
111	92	Inv SBR
112	76	2nd Lbl
113	12	B
114	53	(
115	93	.
116	00	0
117	07	7
118	07	7
119	08	8
120	00	0
121	65	x
122	43	RC1
123	07	07
124	65	x
125	73	RC1 2nd Ind.
126	00	00
127	55	÷
128	69	2nd OP
129	30	30
130	73	RC1 2nd Ind.
131	00	00
132	69	2nd OP
133	30	30
134	69	2nd OP
135	30	30
136	69	2nd OP
137	30	30
138	54	)
139	72	STO 2nd Ind.
140	00	00
141	53	(
142	43	RC1
143	00	00
144	85	+
145	04	4
146	54	)

TABLE A-3. (Continued)

<u>LOC</u>	<u>CODE</u>	<u>KEY</u>
147	42	STO
148	00	00
149	92	Inv SBR
150	76	2nd Lbl
151	17	2nd B'
152	53	(
153	53	(
154	43	RC1
155	15	15
156	65	x
157	43	RC1
158	05	05
159	85	+
160	43	RC1
161	04	04
162	65	x
163	43	RC1
164	10	10
165	54	)
166	42	STO
167	03	03
168	92	Inv SBR
169	76	2nd Lbl
170	13	C
171	53	(
172	43	RC1
173	05	05
174	33	x ²
175	65	x
176	43	RC1
177	16	16
178	33	x ²
179	85	+
180	43	RC1
181	04	04
182	33	x ²
183	65	x
184	43	RC1
185	11	11
186	33	x ²
187	85	+
188	02	2
189	65	x
190	43	RC1
191	05	05
192	65	x
193	43	RC1
194	04	04
195	65	x
196	43	RC1
197	16	16
198	65	x
199	43	RC1

TABLE A-3. (Continued)

<u>LOC</u>	<u>CODE</u>	<u>KEY</u>
200	11	11
201	65	x
202	53	(
203	01	1
204	75	-
205	43	RC1
206	06	06
207	54	)
208	54	)
209	42	STO
210	02	02
211	92	Inv SBR
212	76	2nd Lbl
213	18	2nd C'
214	53	(
215	43	RC1
216	02	02
217	55	÷
218	53	(
219	53	(
220	43	RCL
221	01	01
222	75	-
223	43	RC1
224	03	03
225	54	)
226	65	x
227	43	RC1
228	03	03
229	85	+
230	53	(
231	43	RC1
232	01	01
233	85	+
234	43	RC1
235	03	03
236	54	)
237	65	RX
238	43	RCL
239	01	01
240	54	)
241	94	+/-
242	85	+
243	43	RC1
244	07	07
245	65	x
246	43	RC1
247	08	08
248	55	÷
249	53	(
250	43	RC1
251	01	01

TABLE A-3. (Continued)

<u>LOC</u>	<u>CODE</u>	<u>KEY</u>
252	75	-
253	43	RC1
254	03	03
255	54	)
256	54	)
257	92	Inv SBR
258	76	2nd Lbl
259	49	2nd Prd
260	71	SBR
261	11	A
262	71	SBR
263	16	2nd A'
264	71	SBR
265	12	B
266	92	Inv SBR
267	76	2nd Lbl
268	15	E
269	71	SBR
270	49	2nd Prd
271	53	(
272	43	RC1
273	00	00
274	75	-
275	05	05
276	54	)
277	42	STO
278	00	00
279	71	SBR
280	49	2nd Prd
281	71	SBR
282	17	2nd B'
283	71	SBR
284	13	C
285	53	(
286	43	RC1
287	00	00
288	85	+
289	05	05
290	54	)
291	42	STO
292	00	00
293	71	SBR
294	18	2nd C'
295	92	Inv SBR
296	76	2nd Lbl
297	14	D
298	42	STO
299	06	06
300	71	SBR
301	13	C
302	71	SBR
303	18	2nd C'

TABLE A-3. (Continued)

<u>LOC</u>	<u>CODE</u>	<u>KEY</u>
304	92	Inv SBR
305	76	2nd Lbl
306	10	2nd E'
307	75	-
308	43	RC1
309	09	09
310	95	=
311	55	÷
312	43	RC1
313	09	09
314	65	x
315	01	1
316	00	0
317	00	0
318	95	=
319	92	Inv SBR

TABLE A-4.

KEY FUNCTIONS

USER DEFINED KEYS

- A: $a^{1/2} (T_{ci})$
 B: $b_i (T_{ci})$
 C: $\sum \sum X_i X_j a_{ij} = a$
 D: Run New δ_{ij}
 E: Run Mixture
 A': $a_i^{1/2} = a_i (T_{ci})^{1/2} \alpha_i^{1/2} (T)$
 B': $\sum X_i b_i = b$
 C': P-R EOS (a,b)
 D': N/A
 E': $[(P_{pred} - P)/P] * 100$

DATA REGISTERS

<u>STORAGE</u>	<u>INPUT</u>
00 Rindex	
01 v	SPECIFIC VOLUME OF MIXTURE
02 a	
03 b	
04 X ₂	MOLE FRACTION OF COMPONENT 2
05 X ₁	MOLE FRACTION OF COMPONENT 1
06 δ_{ij}	BINARY INTERACTION PARAMETER(P-R EOS)
07 R	GAS CONSTANT
08 T	TEMPERATURE OF SYSTEM

TABLE A-4. (Continued)

09 P	PRESSURE OF SYSTEM
10 b_2	
11 $a_2^{1/2}$	
12 w_2	ACENTRIC FACTOR COMPONENT 2
13 P_{c2}	CRITICAL PRESSURE OF COMPONENT 2
14 T_{c2}	CRITICAL TEMPERATURE OF COMPONENT 2
15 b_1	
16 $a_1^{1/2}$	
17 w_1	ACENTRIC FACTOR OF COMPONENT 1
18 P_{c1}	CRITICAL PRESSURE OF COMPONENT 1
19 T_{c1}	CRITICAL TEMPERATURE OF COMPONENT 1

TABLE A-5.

BUBBLE AND DEW LINES OF ETHANE AS PREDICTED BY THE PENG-ROBINSON WITHOUT THE
INCORPORATION OF THE FUGACITY COEFFICIENT

T	δ	% And	P _{pred}	v _L	P	v _g	P _{pred}	% And	δ
90.11	-0.0005	0.16	717.14	0.0755	716.0	0.0755	717.14	0.16	-0.0005
80	-0.043	19.79	755.54	0.05063	630.7	0.1411	633.50	0.44	-0.005
70	-0.05	28.32	716.40	0.04625	558.3	0.1795	559.40	0.20	-0.004
60	-0.0465	36.09	672.57	0.04358	494.2	0.2164	495.76	0.32	-0.007
50	-0.0409	39.45	618.1	0.04144	437.5	0.2596	435.99	-0.34	0.009
40	-0.0281	47.99	569.76	0.03990	385.0	0.3062	383.56	-0.37	0.0125
30	-0.0113	16.24	391.48	0.03866	337.1	0.3595	336.13	-0.29	0.0125
20	0.006	- 10.51	263.09	0.03754	294.0	0.4198	293.90	-0.03	0.0
10	0.0246	- 52.57	120.9	0.03655	254.9	0.4909	255.46	0.22	-0.01
0	0.04585	- 119.67	- 43.25	0.03570	219.7	0.5759	220.64	0.43	-0.025
- 10	0.06863	- 219.38	- 224.56	0.03444	188.1	0.6775	189.07	0.52	-0.035
- 20				0.03422	159.9	0.7983			
- 30				0.03359	135.0	0.9452			
- 40	0.1429	- 869.03	- 864.12	0.03303	113.1	1.127	114.33	1.09	-0.113
- 50				0.03249	93.76	1.355			
- 60	0.19683	- 1887.22	-1376.52	0.03199	77.02	1.638	77.92	1.17	-0.175
- 70				0.03152	62.63	1.994			
- 80				0.3108	50.34	2.451			
- 90				0.03067	39.98	3.043			
-100	0.313546	- 8494.42	-2629.13	0.03029	31.32	3.830			
-110				0.02991	24.17	4.876			
-120				0.02957	18.33	6.316			
-127.55	0.397691	-25089.2	-3672.41	0.02931	14.696	7.741	14.86	1.11	-0.64
-130				0.02923	13.68	8.282			
-140				0.02893	9.97	11.05			
-150				0.02861	7.14	15.10			
-160				0.02831	4.97	21.11			
-170				0.02802	3.36	30.32			
-180				0.02774	2.20	44.90			
-190				0.02746	1.40	68.43			

TABLE A-5. (Continued)

<u>T</u>	<u>δ</u>	<u>% And</u>	<u>P_{prod}</u>	<u>v_L</u>	<u>P</u>	<u>v_g</u>	<u>P_{prod}</u>	<u>% And</u>	<u>δ</u>
-200	0.628...	-0.85x10 ⁶	-7242.7	0.02720	0.85	107.8	0.858	0.94	-5.8
-210	..4086			0.02694	0.50	179.2			
°F	δ %AAD < ±0.05	$\frac{P_{pred}-P}{P} \times 100$	psia from	$\frac{CuFt}{lbm}$	psia exper	$\frac{CuFt}{lbm}$	psia from P-R EOS	$\frac{P_{pred}-P}{P} \times 100$	δ %AAD < ±0.05

BUBBLE LINE | DEW LINE

$$R/MW = 0.3568673096 = 10.731 \frac{ft^3 \text{ psi}}{lb-mol \text{ } ^\circ R} \bigg| \frac{lb-mol}{30.07 \text{ lb}}$$

% Absolute Normalized Deviation.

APPENDIX B

A TEST FOR THE CONSISTENCY OF
A MASS BALANCE

A Test for the Consistency of A Mass Balance

The consistency of experimental data is the primary concern in an analysis procedure. Consistency is judged on the basis of a statistical analysis. Choosing the best model for statistical analysis is thus a major duty of the experimentalist.

Obtaining the mass balance around the pilot plant is the major goal of the experimental work in this dissertation. Analysis of the mass balance follows the method developed by Dr. Kenneth Starling and Dr. Hemanth-Kumar at The University of Oklahoma, Norman, Oklahoma. This method was developed for testing the consistency of a mass balance around a two phase system. The mass balance around a flash tank is used to model a two phase system. Consistency of the "light" phase can be compared to the consistency of the "heavy" phase.

A linear relationship exists for the compositional mass balance in a steady state flow process, i.e. no accumulation of mass in the vessel. The mass balance around a 3 port (1 inlet and 2 outlet) vessel is given by the equation:

$$Z_i F = X_i L + y_i V$$

The molar (mass) flow rates of each stream are given by F (Feed), L (Liquid or "heavy"), and V (Vapor or "light"). The mole (mass) fraction of component i in each stream is given by Z_i (Feed i), X_i (heavy i), and y_i (light i). This equation can be arranged in the form of a straight line. Taking the reference such that the molar (mass) flow rate of the feed is unity, the relation is:

$$\frac{y_i}{Z_i} = \frac{1}{v} - \frac{X_i}{Z_i} \frac{(1-v)}{V}$$

This particular form of the mass balance can be used to test the overall consistency of the mass balance.

Another use of this equation is to test the consistency of the "heavy" phase with the "light" phase.

Using the equation above, vapor phase experimental data are used to draw a straight line through the liquid phase data. Compositions in the liquid phase must fall on the line if the experimental data are exactly consistent. When the liquid phase data do not fall on the predicted line, the experimental data must be adjusted. Adjusting the data is done statistically so that the error necessary for mass balance consistency can be determined. If the error encountered in adjusting the data is unacceptably too high, then the complete data set must be discarded.

The adjustment procedure results in a consistent set of data. In this case the vapor phase was used to adjust the liquid phase. Vapor phase measurements nominally gives better results than liquid phase measurements; however, if the liquid phase data is considered to be more exact than the vapor phase data, then the above procedure could be reversed. The liquid phase could be used to adjust the consistency of the vapor phase.

The consistency test requires a complete set of data. However, in many cases the feed flow rate is not experimentally measured by the experimentalist. The lack of an experimental feed rate results in a loss of an important degree of freedom. The consistency test can still be performed without this degree of freedom; however, the liquid and vapor consistencies cannot be determined independently (they must be grouped). If the feed rate is not determined then the liquid and vapor rates must be combined to give a value for F . The line drawn through the data points must now "float" between the vapor and liquid data points.

The experimental equipment used in this work did not include a CO_2 feed flow rate meter. The capital cost of a high pressure flow meter proved to be prohibitive. The $\text{ETOH-H}_2\text{O}$ feed stream flow rate was, however, measured accurately. Since the CO_2 stream feed

rate was not measured, the flow rate of CO_2 measured at the exit streams was summed to give a CO_2 feed flow rate. This resulted in the assumption that the feed rate of CO_2 exactly equals the measured exit flow rates of CO_2 as determined at room pressure and temperature. This is considered a valid assumption since the system contained no vapor leaks as determined with a "soap bubble leak detector." The only two sources of any experimental error would be at the wet test meter, and in the solubility of CO_2 in the low pressure liquid product streams. The results of the "consistency of mass balance" will indicate the utility of these assumptions concerning CO_2 feed rate.

A set of four experimental runs at the same feed conditions produced the independent sets of operating tie lines listed in Table B-1. The table lists the ratios of flow rates, feed: outlet stream, and lists the compositional ratios, outlet stream: feed. Given these dimensionless experimental quantities and the initial absolute feed rate of component species, the rate form of the mass balance is satisfied. Each of these sets of experimental data should produce a straight line when introduced into the mass balance around a flash tank:

$$[y_i/z_i] = [F/V] - [F/V][x_i/z_i]/[F/L]$$

Any deviation from the straight line indicates an error in determination of flow rates or composition. The data sets listed in Table R-1 are the same used to plot the points on Figure R-2. Data scatter is displayed both by the inconsistency of point grouping on the phase envelope and by the inconsistency of the feed location in relation to a tie drawn between the compositions of the two phases.

The particular form of the statistical analysis chosen to test consistency was necessarily limited by the fact that the feed flow rate of CO_2 was not independently measured. The feed flow rate of carbon dioxide, " $\text{ZCO}_2 * F$ " in each of the parameters was substituted with the equated term " $\text{XCO}_2 * L + \text{yCO}_2 * V$ ". This substitution for " $\text{ZCO}_2 * F$ " would not have been necessary if the feed flow rate of CO_2 had been determined experimentally. The substitution resulted in the loss of a much needed degree of freedom. For clarity, the case of a separate experimentally determined $\text{ZCO}_2 * F$ will be discussed.

Experimentally determining F , L , and V fixes the ordinate and abscissa intercepts on a mass balance consistency plot (y_i/Z_i versus X_i/Z_i). A statistically predicted line can then be drawn from the y_i/Z_i intercept (F/V), through the "light" species. The X_i/Z_i intercept (F/L), and the "heavy" species form a second

predicted line. If the "lights" and "heavies" predict the same line, then the original experimental data is consistent. If the predicted heavy and light lines are not consistent within an acceptable error level, then a decision must be made by the investigator as to which group is to be given a favorable weighting. Most experimental procedures give more accurate determination of "light" phase characteristics; therefore, the "light" phase is given an increased statistical weight factor. Confidence in the "lights" and inconsistencies in the "heavies" may push the weighting factor to the extent that the X_i/Z_i value of "heavies" is predicted entirely by the "lights".

The loss of a degree of freedom from inability to measure $XCO_2 * F$ for the pilot plant, used in this dissertation, resulted in an inability to construct the "light" and "heavy" lines. The intercepts F/V and F/L were not independent, so only one line can be drawn through the data. This is similar to the case above, with a weight factor evenly divided between lights and heavies.

Table B-2 lists the results of a statistical analysis on the four sets of data in Table R-1. In the first analysis, each component species was grouped as an independent set of samples points. Statistics on

TABLE B-1

ONE PROCESS TIE LINE FOR THE CO₂-ETOH-H₂O SYSTEM AT

25°C AND 1000 PSIA WITH A 50:50 MOLE RATIO

ETOH-H₂O FEED AND AN ETOH-H₂O MIXTURE

FEED RATE OF 460 ML/HR: FOUR

INDEPENDENT SETS OF DATA

	<u>F/V</u>	<u>CO₂</u>	<u>ETOH</u>	<u>H₂O</u>	<u>F/L</u>
Set #1					
X _i /Z _i	0.0	0.193	2.97	4.06	3.87
Y _i /Z _i	1.32	1.26	0.302	0.102	0.0
Set #2					
X _i /Z _i	0.0	0.147	3.03	4.18	4.82
Y _i /Z _i	1.32	1.25	0.346	0.120	0.0
Set #3					
X _i /Z _i	0.0	0.143	3.06	4.19	4.27
Y _i /Z _i	1.31	1.27	0.279	0.0918	0.0
Set #4					
X _i /Z _i	0.0	0.174	2.95	4.15	4.30
Y _i /Z _i	1.31	1.26	0.303	0.0974	0.0

Feed Rate for CO₂ of 37.2 Moles/Hour

TABLE B-2

CONFIDENCE INTERVALS FOR A TIE LINE OF THE CO₂-ETOH-H₂O SYSTEM AT 25°C AND 1000 PSIA
WITH 50:50 MOLE RATIO ETOH-H₂O FEED AT A MIXTURE FEED RATE OF 460 ML/HR

Component _i	X _i /Z _i [AVG]	Predicted y _i /z _i			
		Minimum	Predicted	Maximum	Confidence
Independent*					
CO ₂	0.1642	1.2455	1.26	1.2745	90%
		1.2101	1.26	1.3099	99%
ETOH	3.0025	0.2750	0.3075	0.3238	90%
		0.13635	0.3075	0.4786	99%
H ₂ O	4.145	0.0809	0.1027	0.1245	90%
		0.0277	0.1027	0.1777	99%
Consistent ⁺					
CO ₂	0.1642	1.2112	1.2428	1.2744	90%
		1.1744	1.2428	1.3111	99%
ETOH	3.0025	0.3707	0.3928	0.4149	90%
		0.3449	0.3928	0.4406	99%
H ₂ O	4.145	0.0217	0.0506	0.0795	90%
		-0.0119	0.0506	0.1131	99%

*Independent statistical determination on each component.

⁺Consistent mass balance as discussed in the text.

TABLE B-3

STATISTICAL ANALYSIS OF A TIE LINE: "LIGHTS"
 USED TO PREDICT "HEAVY" AND "HEAVY" USED
 TO PREDICT "LIGHTS"

	"Lights" y_i/z_i Predicts x_i/z_i	"Heavy" x_i/z_i Predicts y_i/z_i
Correlation Coefficient	-0.9932	-0.9932
Slope	-3.294	-3.339
F/L	4.2871	4.3138
F/V	1.3015	1.2920
Variation in x_i/z_i explained by y_i/z_i		
	7.0729	N/A
Variation in y_i/z_i explained by x_i/z_i		
	N/A	6.04356
Total Variance	7.1701	6.5188

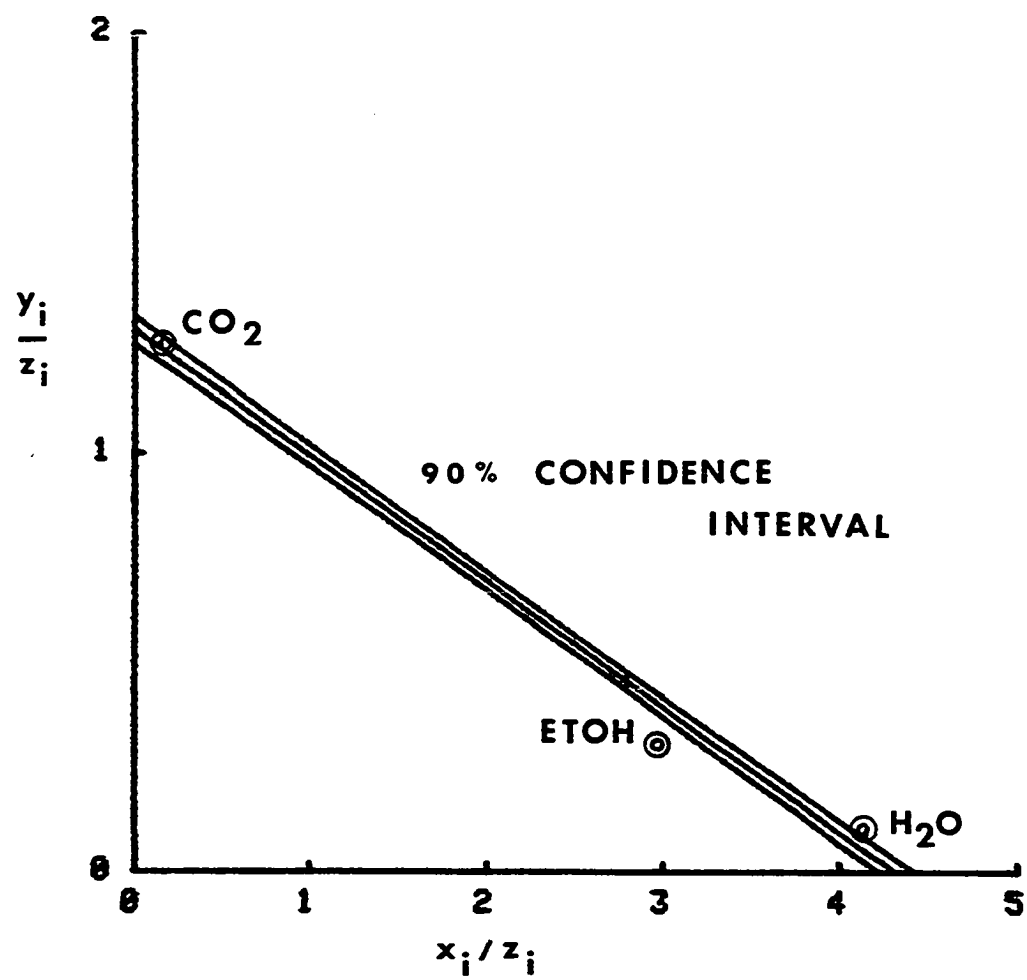
the y_i/z_i values for CO_2 give a predicted value of 1.26; the 99% confidence interval for this value is 1.2101 and 1.3099. Taking water as an independent group, the predicted y_i/z_i is 0.1027 with a 99% confidence interval of 0.0277 and 0.1777; likewise for ethanol 0.13635: 0.3075:0.4786. The predicted value of y_i/z_i in this case is the linear average of all the CO_2 data points (or H_2O , or ETOH).

Table B-2 also lists a consistent set of y_i/z_i and x_i/z_i values. The consistent set listed in this particular table is the y_i/z_i ' predicted by the x_i/z_i 's. The independent variable is chosen as x_i/z_i and the dependent variable as y_i/z_i . The dependent variables are assumed to follow a linear relationship with the independent variable [consistent data must yield a straight line]. The statistics result in an F/V equal to 1.2920, an F/V equal to 4.3138, and an L/V equal to 3.339. If x_i/z_i is chosen as the dependent variable, then the prediction yields $F/V = 1.3015$, $F/L = 4.2873$, and $L/V = 3.294$. The correlation coefficient is -0.9932 for both predictions. Further statistics are listed in Table B-3. The investigator must decide which predicted line to use. The decision cannot be based on the correlation coefficient because it is the same for both predicted tie lines. The choice might be based on

the variance. The variation in the X_i/Z_i data points will explain 92.7% of the total variation when X_i/Z_i is used to predicted the tie line. However, the y_i/Z_i data points will expalin 98.6% of the total variation when y_i/Z_i is used to predict the tie line. The decision as to which of the predicted tie lines should be used, "light" predicting "heavy" or "heavy" predicting "lights" is clouded by the loss of the degree of freedom associated with the inability to measure feed composition directly. The consistent set of data using X_i/Z_i to predict y_i/Z_i is shown in relation to the independently group averaged data in Figure B-1. The 90% confidence intervals around this predicted tie line are shown. The 90% confidence interval gives a 90% assurance that any data point collected will give a predicted tie line which will be within the confidence interval.

The predicted tie line, with X_i/Z_i as the independent variable, is in Figure 23 along with the equilibrium data of Francis [72]. The consistent tie line now runs through the feed composition location. The recovery of the tie line in weight fraction (or mole fraction) units from the consistency of the mass balance analysis requires that the feed compositions be entered back into the mass balance equation, along with the set of predicted parameters. Here again, is an example of how a lack of

FIGURE B-1. CONFIDENCE INTERVALS ON A CONSISTENT TIE LINE OF THE CO₂-ETOH-H₂O SYSTEM. The 90% confidence intervals around the consistent mass balance tie line is shown. This tie line is established by using X_i/Z_i values to "predict" the consistent Y_i/Z_i values. The data points marked on this figure are the statistically averaged data points for each component. This figure illustrates the deviation, particularly of ETOH, for each component from the mass balance consistent tie line.



independent data on feed composition can increase the difficulty in getting results from the final analysis. F was taken as L plus V. Both intercepts were therefore adjusted because neither is independent from the other. Thus, both L and V were adjusted. With no set of data on F from experimental determination, F was also adjusted. Therefore Z_{CO_2} , Z_{H_2O} , and Z_{ETOH} were adjusted. Iterative solution found the best values of Z_i , which were not too different from the average set; however, this addition procedure and possible source of error was, again, precipitated because the feed composition was not determined.