Supercritical Fluid Extraction:
A Study of Binary and
Multicomponent Solid-Fluid
Equilibria

by
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SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF
DOCTOR OF SCIENCE
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May, 1981

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Robert C. Reid
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Accepted by

Chairman, Departmental Committee on Graduate Students

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SUPERCRITICAL FLUID EXTRACTION:
A STUDY OF BINARY AND
MULTICOMPONENT SOLID-FLUID
EQUILIBRIA

by

RONALD TED KURNIK

Submitted to the Department of Chemical Engineering
on May 1981, in partial fulfillment of the
requirements for the degree of Doctor of Science

ABSTRACT

Solid-fluid equilibrium data for binary and multicomponent systems were determined experimentally using two supercritical fluids -- carbon dioxide and ethylene, and six solid solutes. The data were taken for temperatures between the upper and lower critical end points and for pressures from 120 to 280 bar.

The existence of very large ($10^6$) enhancement (over the ideal gas value) of solubilities of the solutes in the fluid phase was observed with these systems. In addition, it was found that the solubility of a species in a multicomponent mixture could be significantly greater (as much as 300 percent) than the solubility of that same pure species in the given supercritical fluid (at the same temperature and pressure).

Correlation of both pure and multicomponent solid-fluid equilibria was accomplished using the Peng-Robinson equation of state. In the case of multicomponent solid-fluid equilibrium it was necessary to introduce an additional binary solute-solute interaction coefficient.

The existence of a maximum in solubility of a solid in a supercritical fluid was observed both theoretically and experimentally. The reason for this maximum was explained.
Energy effects in solid-fluid equilibria were studied and it was shown that in the retrograde solidification region that the partial molar enthalphy difference for the solute between the fluid and solid phase is exothermic.

Thesis Supervisor: Robert C. Reid
Title: Professor of Chemical Engineering
May, 1981

Dear Professor Newton:

In accordance with the regulations of the Faculty I herewith submit a thesis entitled "Supercritical Fluid Extraction: A Study of Binary and Multicomponent Solid-Fluid Equilibria" in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Ronald Ted Kurnik
ACKNOWLEDGEMENTS

The author gratefully acknowledges the support and advice of Professor Robert C. Reid.

Many thanks are due to Dr. Val J. Krukonis for his enthusiastic support of this work and for his help in the experimental design of the equipment used in this thesis.

The help of Mike Mullins in constructing the equipment is gratefully acknowledged.

Dr. Herb Britt, Dr. Joe Boston, Dr. Paul Mathias, Suphat Watanasiri, and Fred Ziegler of the ASPEN project are thanked for their many helpful discussions.

The members of my thesis committee, Professor Modell, Professor Longwell, Professor Daniel I. C. Wang and Dr. Charles Apt provided many helpful comments and suggestions.

Samuel Holla was helpful in obtaining some of the equilibrium data used in this thesis.

The Nestle's Company is gratefully acknowledged for their financial support in terms of a three year fellowship.

Financial support of the National Science Foundation is appreciated.

To my many friends at MIT, especially those in the LNG lab, thanks for good advice, endless encouragement, and many fun filled hours when we were together. I wish you all
success, happiness, and lasting friendship in the years to come.

Finally, I am most indebted to my brother, parents, and grandmother for their continuous confidence and support throughout my schooling.

Ronald Ted Kurnik
Cambridge, Massachusetts
May, 1981
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1. SUMMARY

1-1 Introduction

Supercritical fluid extraction (SCF) is a rediscovered unit operation for purification of solid and/or liquid mixtures. It is of current interest and has potential utility in the chemical process industry due to six reasons:

I. Sensitivity to all Process Variables

For supercritical fluid extraction, both temperature and pressure may have a significant effect on the equilibrium solubility. Small changes of temperature and/or pressure, especially in the region near the critical point of the solvent, can affect equilibrium solubilities by two or three orders of magnitude. In liquid extraction, only temperature has a strong effect on equilibrium solubility.

II. Non-Toxic Supercritical Fluids can be Used

Carbon dioxide, a substance which is non-toxic, non-flammable, inexpensive, and has a conveniently low critical temperature (304.2 K), can be used as an excellent solvent for extracting substances. It is for this reason that many food and pharmaceutical industries are involved in supercritical CO$_2$ extraction research.
III. **High Mass Transfer Rates Between Phases**

A supercritical fluid phase has a low viscosity (near that of a gas) while also having a high mass diffusivity (between that of a gas and a liquid). Consequently, it is currently believed that the mass transfer coefficient (and hence the flux rate) will be higher for supercritical fluid extraction than for typical liquid extractions.

IV. **Ease of Solvent Regeneration**

After a given supercritical fluid has extracted the desired components, the system pressure can be reduced to a low value causing all of the solute to precipitate out. Then, the supercritical fluid is left in pure form and can be easily recycled. In typical liquid extraction using an organic solvent, the spent solvent must usually be purified by a distillation train.

V. **Energy Saving**

When compared to distillation, supercritical fluid extraction is usually less energy intensive. For example, it has been shown that dehydrating ethanol-water solutions is more energy efficient using supercritical carbon dioxide than azeotropic distillation (Krukonis, 1980).

VI. **Sensitivity of Solubility to Trace Components**

Solubility of components in supercritical fluids can sometimes be affected by several hundred percent by the addition to the fluid phase of small quantities (circa one mole percent) of a volatile, often polar, material (entrainer).
In addition, selectivities in the extraction can be significantly affected by an entrainer.

1-2 Background

Historical Summary

The earliest SCF extraction experiments were conducted by Andrews (1887)* who studied the solubility of liquid carbon dioxide in compressed nitrogen. Shortly thereafter, Hannay and Hogarth (1879, 1880) found that the solubilities of crystalline I₂, KBr, CoCl₂, and CaCl₂ in supercritical ethanol were in excess of values predicted from the vapor pressures of the solutes modified by the Poynting (1881) correction. There have been many other studies since these pioneering papers as summarized in the main body of this thesis. In most of the investigations until recently, emphasis was placed on developing phase diagrams for the fluid-solute systems investigated. The use of theory to correlate the experimental data began with the application of the virial equation of state, but the principal object was to employ the extraction data to determine interaction second virial coefficients (see, for example, Baughman et al., 1975; Najour and King 1966, 1970; King and Robertson, 1962).

Applications to the Food Industry

The most often cited example of SCF in the food industry

*The paper describing Andrew's work was published after his death. The experiments were carried out in the 1870's.
is in the decaffeination of green coffee (Zosel, 1978). British and German patents have been issued (Hag, A.G., 1974; Vitzthum and Hubert, 1975). While no data have been published, it is believed that the supercritical CO₂ is relatively selective for caffeine.

A patent has been issued to decaffeinate tea in a similar manner (Hag, A.G., 1973). SCF has also been suggested to remove fats from foods, prepare spice extracts, make cocoa butter, and produce hop extracts. These four applications are covered by patents of Hag, A.G. (1974b, 1973b, 1974c, 1975). In all these suggested processes, supercritical CO₂ is recommended as a non-toxic solvent that may be used in the temperature range where biological degradation is minimized. It is suspected that extensive in-house, non-published research is being conducted by the major food industries.

**Other Applications**

Hubert and Vitzthum (1978) suggest the use of supercritical CO₂ to separate nicotine from tobacco. Desalination of sea water by supercritical C_{11} and C_{12} paraffinic fractions has been successfully accomplished (Barton and Fenske, 1970; Texaco, 1967). Other applications include de-asphalting of petroleum fractions with supercritical propane/propylene mixtures (Zhuze, 1960), extraction of lanolin from wool fat (Peter et al., 1974), and the recovery of oil from waste gear oil (Studiengessellschaft Kohle M.B.H., 1967).
Holm (1959) discussed the use of supercritical CO₂ as a scavenging fluid in tertiary oil recovery. These and other processes are noted in reviews by Paul and Wise (1971), Wilke (1978), Irani and Funk (1977) and Gangoli and Thodos (1977).

Supercritical extraction in coal processing is being studied by a number of companies. In Great Britain, the National Coal Board has examined the de-ashing of coal with supercritical toluene and water (Bartle et al., 1975). The Kerr-McGee Company is said to have an operational process to de-ash coal using pentane or proprietary solvents (Knebal and Rhodes, 1978; Adams et al., 1978).

Modell et al., (1978, 1979) has proposed to regenerate activated carbon with supercritical CO₂.

Phase separations may be accomplished in some instances by contacting a liquid mixture with supercritical fluids. (Snedeker, 1955; Elgin and Weinstock, 1959; Newsham and Stigset, 1978; Balder and Prausnitz, 1966). The use of a supercritical fluid as the "third" component in a binary liquid mixture is analogous to the phase splits caused in the salting out process. The advantages of the use of a supercritical fluid over a soluble solid relate to the ease whereby the supercritical fluid may be removed by a pressure reduction. A current commercial venture is exploiting this technology to separate ethanol-water mixtures (Krukonis, 1980).
Supercritical-Fluid Chromatography

One quite promising application of SCF is in chromatography. While no commercial equipment is yet available, several investigators have fabricated their own prototype units (Sie et al., 1966; van Wasen et al., 1980; Klesper, 1978). Due to the higher operating pressures, there are significant problems in developing detectors and sample-injection techniques. The often drastic variation in solubility with pressure allows one to employ both temperature and pressure to optimize separations. Also, with the use of supercritical fluids with low critical temperatures, it would appear that separations could be made of high molecular weight thermodegradable biological materials. Ionic species which decompose in gas chromatography have been stabilized in supercritical fluids (Jentoft and Gouw, 1972).

Finally, supercritical chromatography has been employed to obtain a variety of physical and thermodynamic properties for infinitely dilute systems, e.g. diffusion coefficients, activity coefficients, and interaction second virial coefficients (Van Wasen et al., 1980; Bartmann and Schneider, 1973).

Theoretical Work

There are two ways to model solid-fluid equilibria: (a) the compressed gas model; (b) the expanded liquid model. The compressed gas model assumes that an equation of state can be used to estimate the fugacity coefficient of component \( i \) in a fluid phase. With the assumptions that
1. solid density is independent of pressure and composition

2. solubility of the fluid phase in the solid is sufficiently small so that $\gamma_i^S \approx 1$ and $x_i \approx 1$

3. no solid solutions form

4. vapor pressure of solid is sufficiently small so that $\phi_{vp_i}^S \approx 1$ and $P - P_{vp_i} \approx P$

the model can be written for component $i$ as

$$y_i = \frac{P_{vp_i}}{P} \cdot \frac{1}{\phi_i} \cdot \exp \left( \frac{P_{vp_i}^S}{RT} \right)$$  \hspace{1cm} (1-1.1)

Using the expanded liquid approach to solid-fluid equilibria, the solute activity in the fluid phase is expressed in terms of an activity coefficient. As a result, the mole fraction of component $i$ in a supercritical fluid is

$$y_i = \frac{1}{\gamma_i(y_i,P^R)} \cdot \frac{f_i^S(p^R)}{f_i^L(p^R)} \cdot \exp \left( \frac{(P-p^R)V_i^S}{RT} \right) \cdot \exp \left[ \frac{P}{P_R} \left( \frac{V_i^L}{RT} \right) dP \right]$$  \hspace{1cm} (1-1.2)

which can be simplified to give

$$y_i = \frac{\exp \left[ \Delta H_i^{FUS} \left( \frac{T}{T_i} - 1 \right) \right]}{\gamma_i(y_i,P^R)} \cdot \exp \left( \frac{(P-p^R)V_i^S}{RT} \right) \cdot \exp \left[ \frac{P}{P_R} \left( \frac{V_i^L}{RT} \right) dP \right]$$  \hspace{1cm} (1-1.3)
Mackay and Paulaitis (1979) have used a reference pressure of

\[ P^R = P_c, \]

with \( P_c \) the critical pressure of the pure fluid phase, and the assumption that

\[ \gamma_i(y_i, P^R) = \gamma_i^\infty(P_c) \quad (1-1.4) \]

\[ \bar{V}_i(y_i, P^R) = \bar{V}_i^\infty(P_c) \quad (1-1.5) \]

\( \bar{V}_i^\infty \) would then be found from an applicable equation of state and \( \gamma_i^\infty \) would be treated as an adjustable parameter.

Of the two methods to model solid-fluid equilibria, the first method (Equation 1-1.1) is preferred because it requires only one adjustable parameter, \( k_{ij} \) (whereas Equation 1-1.3 requires two: \( k_{ij} \) and \( \gamma_i^\infty(P_c) \)). Also, it is much easier to generalize Equation 1-1.1 to a multicomponent system than it is to generalize Equation 1-1.3.

1-3 Thesis Objectives

The objectives of this thesis can be divided into three parts: experimental, theoretical, and exploratory. Experimentally, equilibrium solubility data for both polar and non-polar solid solutes in supercritical fluids were to be measured over wide ranges of temperature and pressure. In addition, ternary equilibrium data (two solids, one fluid) were to be measured. Carbon dioxide and ethylene were the two supercritical fluids to be used.
Theoretically, correlation of equilibrium solubility data of both binary and multicomponent systems using rigorous thermodynamics was to be done.

Finally, after obtaining equilibrium solubility data and developing a thermodynamic model, it was desirable to use this model to explore the physics of solid-fluid equilibrium. Using the model that was to be developed, such phenomena as enthalpy changes of solvation of the solute in the supercritical solvent and changes in equilibrium solubility over wide ranges of temperature and pressure were to be studied.

1-4 Experimental Apparatus and Procedure

The experimental method used in this thesis to measure equilibrium solubilities was a one-pass flow through system. A schematic is shown in Figure 1-1.

A gas cylinder was connected to an AMINCO line filter, (model 49-14405) which feeds into an AMINCO single end compressor, (model 46-13411). The compressor was connected to a two liter magnet-drive packless autoclave (Autoclave Engineers) whose purpose was to dampen the pressure fluctuations. In addition, an on/off pressure control switch, Autoclave P481-P713 was used to control the outlet pressure from the autoclave.

Upon leaving the autoclave, the fluid entered the tubular extractor (Autoclave, CNLX16012) which consisted of a 30.5 cm tube, 1.75 cm in diameter. In the tube were alternate layers of the solute species to be extracted and Pyrex wool. The Pyrex wool was used to prevent entrainment. A
Equipment Flow Chart

Figure 1-1
LFE 238 PID temperature controller attached to the heating tape kept the extractor isothermal. The temperature was monitored by an iron-constantan thermocouple (Omega SH48-ICSS-116U-15) housed inside the extractor. At the end of the extraction system was a regulating valve (Autoclave 30VM4882), the outlet of which was at a pressure of 1 bar. All materials of construction were 316 stainless steel.

Following the regulating valve were two U-tubes in series (Kimax 46025) which were immersed in a 50% ethylene glycol-water/dry ice solution. Complete precipitation of the solids occurred in the U-tubes, while the fluid phase was passed into a rotameter and dry test meter (Singer DTM-115-3) and finally vented to a hood. An iron constantan thermocouple (Omega ICSS-116G-6) at the dry test meter outlet recorded the gas temperature. All thermocouple signals were displayed on a digital LED device (Omega 2170A). Analysis of the solid mixtures was done on a Perkin Elmer Sigma 2/Sigma 10 chromatograph/data station.

1-5 Results and Discussion

Phase Behavior for Binary Systems

Phase behavior resulting when a solid is placed in contact with a fluid phase at high pressures \( \left( P_r >> 1 \right) \) and at temperatures near and above the critical point of the pure fluid are of key importance. The phase diagram provides guidance to the possible operating regimes that exist in
supercritical fluid extraction.

In order to establish a basis, a general binary P-T-x diagram for the equilibrium between two solid phases, a liquid phase, and a vapor phase is shown in Figure 1-2. This diagram is drawn for the case of a solid of low volatility and high melting point and one of high volatility and slightly lower melting point. On the two sides of this diagram are shown the usual solid-gas and liquid-gas boundary curves for the two pure components. These boundary curves meet, three at a time, at the two triple points A and B. The line CDEF is an eutectic line where solid 1 (C), solid 2 (F), saturated liquid (E) and saturated vapor (D) join to form an invariant state of four phases. A projection of ABCEF on the T-x plane gives the usual solubility diagram of two immiscible solids, a miscible liquid phase, and a eutectic point that is the projection of point E. This projection is shown as the "cut" at the top of the figure, since pressure has little effect on the equilibrium between condensed phases.

In Figure 1-3 is shown a P-T projection of this P-T-x surface, indicating the three-phase locus (AFB) and the critical locus (MN). In this figure, the only region where solid is in equilibrium with a gaseous mixture is under the three-phase line AFB. Between the line AFB and MN, is a liquid-vapor region and above the locus MN is a one phase unsaturated fluid region. Consequently, if the pressure is raised isothermally starting at a pressure below the locus AFB, the solid will liquefy due to the presence of the fluid phase.
The Pressure - Temperature - Composition Surfaces for the Equilibrium Between Two Pure Solid Phases, A Liquid Phase and a Vapor Phase

(Rowlinson and Richardson, 1959)

Figure 1-2
P-T Projection of a System in Which the Three Phase Line Does Not Cut the Critical Locus

Figure 1-3
For some extractions, it is often desirable to keep the solute a solid phase, and so Figure 1-3 is an undesirable situation. Fortunately, Figure 1-3 in general, does not represent the usual situation, as discussed below.

When a high molecular weight solid is in equilibrium with a low molecular weight gas, the P-T projection that normally exists is as shown in Figure 1-4. Here, because the differences in temperature between the triple points and critical points of these substances is large, the three phase line AFB of Figure 1-3 can actually intersect the critical locus, so as to "cut" it at two points: p-the lower critical end point, and q-the upper critical end point. See Figure 1-4. In this figure, M and N are the critical points of the supercritical fluid and solid respectively. Critical end points are mixture critical points in the presence of excess solid, i.e., a liquid and gas of identical composition and properties in equilibrium with a solid.

The major consequence of a gap in the critical locus as shown in Figure 1-4 is to allow at least a region in temperature between Tp and Tq where one solid phase is in equilibrium with one fluid phase with no liquid phase present.

Presentation and Discussion of Data

In Figures 1-5 to 1-7 are shown experimental data and a correlation for the systems benzoic acid/CO₂, 2,3-dimethylnaphthalene (DMN)/CO₂, and 2,3-dimethylnaphthalene (DMN)/C₂H₄ respectively. In all cases, there are three pressure regimes: At low pressures an increase in temperature
P-T Projection of a System in Which the Three Phase Line Cuts the Critical Locus

Figure 1-4
Solubility of Benzoic Acid in Supercritical Carbon Dioxide

Figure 1-5
Solubility of 2,3-Dimethylnaphthalene in Supercritical Carbon Dioxide

Figure 1-6
Solubility of 2,3-Dimethylnaphthalene in Supercritical Ethylene

Figure 1-7
increases solubility; at intermediate pressures, an increase in temperature decreases solubility (retrograde solidification) -- more apparent for carbon dioxide than ethylene; and at high pressures an increase in temperature enhances solubility. The reason the retrograde solidification region is more significant for carbon dioxide than ethylene is because CO₂ is at a lower reduced temperature and therefore the density dependence on pressure is larger.

In all cases, the Peng-Robinson equation of state is able to correlate the data well providing that the proper binary interaction parameter is used. Although the binary parameters were independent of pressure and composition, they have a weak linear dependence on temperature.

The outstanding feature of all the data and simulations is the extreme sensitivity of equilibrium solubility to temperature and pressure. For example, consider Figure 1-5 (benzoic acid-carbon dioxide). There is about a two order of magnitude change in solubility when decreasing pressure and simultaneously increasing temperature from (318K, 180 bar) to (338K, 90 bar). Also shown for convenience in Figure 1-5 is the solubility predicted by the ideal gas law:

\[ \gamma_{i}^{ID} = \frac{P_{vP_{i}}}{P} \]  

(1-5.1)

The ratio of real to ideal solubilities is called the enhancement factor and can take on values of 10⁶ or larger.

Figure 1-8 shows a simulation of the case naphthalene
Solubility of Naphthalene in Supercritical Nitrogen

Figure 1-8
in supercritical nitrogen. At no pressure does the isothermal solubility of naphthalene even equal the solubility at one bar pressure. The reason is because under these temperature and pressure conditions, nitrogen is nearly an ideal gas with fugacity coefficients and compressibility factors near unity. Also, the density of nitrogen at high pressures is approximately 0.1 gm/cm$^3$ as compared to 0.8 gm/cm$^3$ for carbon dioxide under the same conditions of temperature and pressure. The dissolving power of supercritical fluids depends both on the density (the higher the greater) and the nonideality (fugacity coefficient) of the fluid phase.

**Ternary Solid-Fluid Equilibrium**

As in the case of binary solid-fluid equilibrium, it is useful to examine the P-T projection that results when two solids that form a eutectic solution (not a solid solution) are in equilibrium with a fluid phase. Such a P-T projection of the four dimensional surface is shown in Figure 1-9. In this diagram, $K_1$ and $K'_1$ are the first and second lower critical-end points. These end points are the intersection with the critical locus of the three-phase line formed by the solids in equilibrium, with a liquid and a gas phase. Similarly, $K_2$ and $K'_2$ are the first and second upper-critical end points. In the case where no solid solutions form, there will exist two eutectic points, and hence a four-phase line connecting them. However, the four phase line may intersect the critical locus at a lower double critical-end point and at a upper
P-T Projection of a Four Dimensional Surface of Two Solid Phases in Equilibrium with a Fluid Phase

Figure 1-9
double critical-endpoint -- shown as p and q respectively. Only for temperatures between those corresponding to $T_p$ and $T_q$, for any pressure, is one guaranteed that there are two solid phases in equilibrium with a fluid phase with no liquid phase forming.

**Presentation and Discussion of Data**

In Figures 1-10 and 1-11 are shown experimental data and a correlation for the ternary system naphthalene-phenanthrene-CO$_2$. The open circles represent the experimental solubilities of the pure component in supercritical CO$_2$, whereas the closed circles represent the solubilities of that component from a solid mixture in supercritical CO$_2$.

The most important conclusion that can be drawn from Figures 1-10 and 1-11 is, that by adding a more volatile component (naphthalene) to phenanthrene the solubilities of both components in the supercritical phase are increased. Component solubilities of phenanthrene in the supercritical fluid are about a maximum of 75% higher in the mixture than the pure phenanthrene alone in carbon dioxide; naphthalene concentrations in the mixture increase a maximum of about 20%. Similar findings were made on the following ternary systems with supercritical CO$_2$ with maximum increases of: benzoic acid (280% increase); naphthalene (107% increase) and 2,3-dimethylnaphthalene (144% increase); naphthalene (46% increase).

There is one set of ternary data available in the literature (Van Gunst, 1950) for the system hexachloroethane-
System: CO₂ - C₁₀H₈ - C₁₄H₁₀

Temperature = 308.2 K

Pure C₁₄H₁₀ in CO₂
Mixture C₁₄H₁₀ in CO₂
PR Equation of State

k₁₂ = 0.0959
k₁₃ = 0.115
k₂₃ = 0.05

Solubility of Phenanthrene from a Phenanthrene-Naphthalene Mixture in Supercritical Carbon Dioxide

Figure 1-10
SYSTEM: CO$_2$-C$_{10}$H$_8$-C$_{14}$H$_{10}$

(1) (2) (3)

TEMPERATURE = 308.2 K

○ PURE C$_{10}$H$_8$ IN CO$_2$

● MIXTURE C$_{10}$H$_8$ IN CO$_2$

PR EQUATION OF STATE

$\text{Pr Equation of State}$

$\begin{align*}
k_{12} &= 0.0959 \\
k_{13} &= 0.115 \\
k_{23} &= 0.05
\end{align*}$

+ DATA OF TSEKHANSKAYA et al. (1964)

Solubility of Naphthalene from a Phenanthrene-Naphthalene Mixture in Supercritical Carbon Dioxide

Figure 1-11
naphthalene-ethylene. Both the naphthalene and hexachlor-ethane solubilities increased by about 300% when they are used in a binary solid system as compared to a pure solid system.

For one case studied in this thesis, however, there was a slight (10%) decrease in component solubilities in a ternary mixture as compared to the binary system. This case was the system phenanthrene; 2,3-DMN; CO₂.

In most experiments, the ternary data were well correlated by the Peng-Robinson equation of state and Equation 1-1. There are two solute-solvent interaction parameters that are fixed from binary experiments and one solute-solute interaction coefficient that must be introduced. The solute-solvent interaction coefficients are those obtained by a nonlinear regression from binary data. Only for the solute-solute interaction coefficient is ternary data required.

To check whether there was physical meaning in the solute-solute parameter, the isomer system 2,3-DMN; 2,6-DMN was examined in both supercritical carbon dioxide and ethylene. Correlation of the resultant data showed that $k_{23}$ was dependent on the supercritical fluid (component 1). Thus, it can be concluded that $k_{23}$ is an adjustable parameter -- not a true binary constant.

Selectivities in the naphthalene-phenanthrene-CO₂ system are shown in Figure 1-12. At 1 bar, the selectivity is the ratio of solute vapor pressures. Increasing the system pressure dramatically decreases the selectivity until
System: CO₂-Naphthalene-Phenanthrene

(1) (2) (3)

Temperature = 308 K

PR Equation of State

\[ k_{12} = 0.0959 \]
\[ k_{13} = 0.115 \]
\[ k_{23} = 0.05 \]

\[ \alpha = \frac{Y_{\text{Naphthalene}}}{Y_{\text{Phenanthrene}}} \]

Selectivities in the Naphthalene-Phenanthrene-Carbon Dioxide System

Figure 1-12
it levels off at a nearly constant value just above the solvent critical pressure. This type of selectivity curve was found for all the ternary systems studied.

In conclusion, if in a given application, component solubilities of a solid in a supercritical fluid are not large, it may be possible to add to the original mixture a more volatile solid component which causes substantial increases in component solubilities of all species. Although this effect was shown only for solids in this thesis, it is believed that volatile liquids (entrainers) can also be added to accomplish the same effect.

**Solubility Maxima**

Of the data and correlations shown in Figures 1-5 to 1-7, the highest pressure attained was 280 bar. As these figures indicate, the isothermal solubilities are still increasing with pressure. It is interesting, therefore, to perform computer simulations to very high pressures (Kurnik and Reid, 1981). The results of such simulations are shown in Figure 1-13 for the solubility of naphthalene in supercritical ethylene for pressures up to 4 kbar and for several temperatures. Experimental data are shown only for the 285 K isotherm to indicate the range covered and the applicability of the Peng-Robinson equation.

For the naphthalene-ethylene system, the solubility attains a minimum value in the range of 15 to 20 bar and a maximum at several hundred bar.
Figure 1-13

Solubility of Naphthalene in Supercritical Ethylene—Indicating Solubility Maxima

SYSTEM:
NAPHTHALENE-ETHYLENE

- PENG-ROBINSON EQUATION OF STATE
  $k_{12} = 0.02$
- EXPERIMENTAL DATA OF TSEKHANSKAYA (1964); $T=285$ K
The existence of the concentration maxima for the naphthalene-ethylene system is confirmed by considering the earlier work of Van Welie and Diepen (1961). They also graphed the mole fraction of naphthalene in ethylene as a function of pressure and covered a range up to about 1 kbar. Their smoothed data (as read from an enlargement of their original graphs), are plotted in Figure 1-14. At temperatures close to the upper critical end point (325.3 K), a maximum in concentration is clearly evident. At lower temperatures, the maximum is less obvious. The dashed curve in Figure 1-14 represents the results of calculating the concentration maximum from the Peng-Robinson equation of state. This simulation could only be carried out to 322 K; above this temperature convergence becomes a problem as the second critical end point is approached and the formation of two fluid phases is predicted. Table 1-1 compares the theoretical versus experimental maxima.

Concentration maxima have also been noted by Czubryt et al. (1970) for the binary systems stearic acid-CO₂ and l-octadecanol-CO₂. In these cases, the experimental data were all measured past the solubility maxima -- which for both solutes occurred at a pressure of about 280 bar. An approximate correlation of their data was achieved by a solubility parameter model.

Theoretical Development

The solubility minimum and maximum with pressure can be
COMPUTER SIMULATION OF MAXIMUM CONCENTRATION USING THE PENG-ROBINSON EQUATION OF STATE

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Experimental Data Confirming Solubility Maxima of Naphthalene in Supercritical Ethylene

Figure 1-14
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<th>$P^T_{\text{max}}$ (bar)</th>
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<th>$y^E_{\text{max}}$</th>
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Notes: 1. Calculations were done using the Peng-Robinson Equation of State, $k_{12} = 0.02$

2. Experimental Data are from van Welie and Diepen (1961).

3. $P^E_{\text{max}}$ = experimental value of maximum pressure.

4. $P^T_{\text{max}}$ = theoretical value of maximum pressure.
related to the partial molar volume of the solute in the supercritical phase. With subscript 1 representing the solute, then with equilibrium between a pure solute and the solute dissolved in the supercritical fluid,

\[ \frac{d\ln f^F_1}{dT} = \frac{d\ln f^S_1}{dT} \]  

(1-5.2)

Expanding Eq. 1-5.2 at constant temperature and assuming that no fluid dissolves in the solute,

\[ \frac{\bar{v}_1^F}{RT} \frac{\partial}{\partial P} + \left( \frac{\partial \ln f^F_1}{\partial \ln y_1} \right)_{T,P} \frac{d\ln y_1}{dP} = \frac{\bar{v}_1^S}{RT} \frac{\partial \ln y_1}{dP} \]

(1-5.3)

Using the definition of the fugacity coefficient,

\[ \phi_1^F = \frac{f_1^F}{y_1 P} \]

(1-5.4)

Then Eq. 1-5.3 can be rearranged to give

\[ \left( \frac{\partial \ln y_1}{\partial P} \right)_T = \frac{\left( \frac{\bar{v}_1^S - \bar{v}_1^F}{RT} \right)}{1 + \left( \frac{\partial \ln \phi_1}{\partial \ln y_1} \right)_{T,P}} \]

(1-5.5)

\( \phi_1 \) may be expressed in terms of \( y_1, T, \) and \( P \) with an equation of state (Kurnik et al., 1981). For naphthalene as the solute in ethylene, \( \left( \frac{\partial \ln \phi_1}{\partial \ln y_1} \right)_{T,P} \) was never less than -0.4 over a pressure range up to the 4 kbar limit studied. Thus the extrema in concentration occur when \( \frac{\bar{v}_1^S}{\bar{v}_1} = \bar{v}_1^F \).
Again using the Peng-Robinson equation of state, $\bar{V}_1^F$ for naphthalene is ethylene as a function of pressure and temperature was computed. The 318 K isotherm is shown in Figure 1-15. At low pressures, $\bar{V}_1^F$ is large and positive; it would approach an ideal gas molar volume as $P \to 0$. With an increase in pressure, $\bar{V}_1^F$ decreases and becomes equal to $V_1^S$ (111.9 cm$^3$/mole) at a pressure of about 20 bar. This corresponds to the solubility minimum. $\bar{V}_1^F$ then becomes quite negative. The minimum in $\bar{V}_1^F$ corresponds to the inflection point in the concentration-pressure curve shown in Figure 1-13. At high pressures, $\bar{V}_1^F$ increases and eventually becomes equal to $V_1^S$; this then corresponds to the maximum in concentration described earlier.

In conclusion, the existence of a solubility maximum gives one a reference number that is useful to decide if a certain extraction scheme is economical. Furthermore, if it has been determined to perform a certain extraction, then it can be quickly ascertained what the optimal extraction pressure is.

1-6 **Recommendations**

The next research area for supercritical fluids should be in the area of multicomponent liquid -- SCF extraction -- since most industrial separations are with liquids. Some equilibrium data is available in the literature on binary liquid-fluid systems up to relatively low pressures (100
Partial Molar Volume of Naphthalene in Supercritical Ethylene

Figure 1-15
bar), but little is known about higher pressure solubilities and selectivities in multicomponent systems.

A rewarding research program in this area would include obtaining precise experimental data, correlating it with thermodynamic theory, and evaluating the selectivities as a function of temperature and pressure.
2. INTRODUCTION

2-1 Background

Supercritical fluid extraction can be considered to be a unit operation akin to liquid extraction whereby a dense gas is contacted with a solid or liquid mixture for the purpose of separating components from the original mixture. Advantages in using supercritical fluids over liquid extraction or distillation are many. Compared to distillation, supercritical fluid extraction has shown to be more energy efficient (Irani and Funk, 1977). The advantage of supercritical fluid extraction over liquid extraction is that (1) solvent recovery is much easier (the pure supercritical fluid can be obtained by expanding it to 1 bar pressure). (2) Non-toxic supercritical fluids can be used, such as carbon dioxide, to perform the extraction with solubilities comparable to those by using liquid extraction. (3) Solubility of the condensed phase in the supercritical fluid is strongly controlled by the temperature and pressure of the system, whereas in distillation and liquid extraction, the major independent variable to control is only temperature.

Historically, the use of supercritical fluids dates back to 1875 with the work of Andrews (1887). Although his work was not published until after his death, Andrews was the true pioneer in this field as a result of the data he obtained.
on the system liquid carbon dioxide in supercritical nitrogen. Shortly thereafter, Hannay and Hogarth (1879, 1880) found that the solubility of the crystals $I_2$, KBr, CoCl$_2$, and CaCl$_2$ in supercritical ethanol were in considerable excess of that predicted from the vapor pressure of the solute species and the Poynting (1881) correction.

This increase in solubility of solids in the supercritical phase after the discovery of Andrews has led to many studies, both experimental and theoretical, of solid fluid equilibrium. In Table 2-1 there is shown a compilation of available solid-fluid equilibrium data.

As is discussed in more detail in section 2-1, the phase diagrams for solid-fluid equilibria are of great importance. The reason for this is that there is only a selected temperature interval where it is feasible to carry out supercritical fluid extraction. For convenience, Table 2-2 provides a compilation of all available solid-fluid equilibrium phase projections.

The basic features of supercritical fluid extraction can be ascertained by studying the data of Diepan and Scheffer (1948a, 1948b, 1953) and Tsekhanskaya (1964). They measured the solubility of naphthalene in supercritical ethylene over a wide range of temperatures and pressures. Figure 2-1 shows a plot of their combined data. Many important trends can be observed. First, it is apparent that there are three regimes of pressure. In the low pressure region, an increase in temperature results in an increase in
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<td>C$_2$H$_4$</td>
<td>286-305</td>
<td>1.01-1.08</td>
<td>21-101</td>
<td>0.42-2.01</td>
<td>Ewald (1953)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>C$_2$H$_4$</td>
<td>313</td>
<td>1.11</td>
<td>138-551</td>
<td>2.74-10.94</td>
<td>Eisenbeiss (1964)</td>
</tr>
<tr>
<td>Coal tar</td>
<td>C$_2$H$_4$</td>
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<td>310</td>
<td>6.16</td>
<td>Wise (1970)</td>
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<td>Solvent</td>
<td>T(°C)</td>
<td>T_r(Solvent)</td>
<td>P(bar)</td>
<td>P_r(Solvent)</td>
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<td>C_2H_6</td>
<td>336-448</td>
<td>1.10-1.47</td>
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<td>0.02-2.05</td>
<td>Najour and King (1970)</td>
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<td>Naphthalene</td>
<td>C_2H_6</td>
<td>296-337</td>
<td>0.97-1.10</td>
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<td>0.02-22.52</td>
<td>King and Robertson (1962)</td>
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<td>Eisenbeiss (1964)</td>
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<tr>
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<td>CO_2</td>
<td>297-346</td>
<td>0.99-1.14</td>
<td>1-130</td>
<td>0.01-1.76</td>
<td>Najour and King (1966)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>CO_2</td>
<td>308-328</td>
<td>1.01-1.08</td>
<td>60-330</td>
<td>0.81-4.47</td>
<td>Tsekhanskaya et al. (1964)</td>
</tr>
<tr>
<td>Carbowax 4000</td>
<td>CO_2</td>
<td>313</td>
<td>1.03</td>
<td>300-2500</td>
<td>4.07-33.88</td>
<td>Czubyr et al. (1970)</td>
</tr>
<tr>
<td>Carbowax 1000</td>
<td>CO_2</td>
<td>313</td>
<td>1.03</td>
<td>300-2500</td>
<td>4.07-33.88</td>
<td>Czubyr et al. (1970)</td>
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<tr>
<td>1-Octadecanol</td>
<td>CO_2</td>
<td>313</td>
<td>1.03</td>
<td>300-2500</td>
<td>4.07-33.88</td>
<td>Czubyr et al. (1970)</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>CO_2</td>
<td>313</td>
<td>1.03</td>
<td>300-2500</td>
<td>4.07-33.88</td>
<td>Czubyr et al. (1970)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>CO_2</td>
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<td>1.03</td>
<td>138-551</td>
<td>1.87-7.47</td>
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<td>Diphenylamine</td>
<td>CO_2</td>
<td>305-310</td>
<td>1.00-1.02</td>
<td>50-225</td>
<td>0.68-3.05</td>
<td>Tsekhanskaya et al. (1962)</td>
</tr>
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<td>Phenol</td>
<td>CO_2</td>
<td>309-333</td>
<td>1.02-1.09</td>
<td>78-246</td>
<td>1.06-3.33</td>
<td>Van Leer and Paulaitis (1980)</td>
</tr>
<tr>
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<td>CO_2</td>
<td>309</td>
<td>1.02</td>
<td>79-237</td>
<td>1.06-3.21</td>
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<td>2,4-dichloro-</td>
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<td>309</td>
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<td>79-203</td>
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<td>Van Leer and Paulaitis (1980)</td>
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<td>phenol</td>
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<tr>
<td>Biphenyl</td>
<td>CO_2</td>
<td>308.8-328.5</td>
<td>1.02-1.08</td>
<td>105-484</td>
<td>1.42-6.56</td>
<td>McHugh and Paulaitis (1980)</td>
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Table 2-2

Phase Diagrams for Solid-Fluid Equilibria

<table>
<thead>
<tr>
<th>Solute</th>
<th>Solvent</th>
<th>T(K)</th>
<th>T_r(Solvent)</th>
<th>P(bar)</th>
<th>P_r(Solvent)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>N₂</td>
<td>H</td>
<td>10-130</td>
<td>0.30-3.92</td>
<td>0.01-10000</td>
<td>0-771</td>
<td>Dokoupel et al. (1955)</td>
</tr>
<tr>
<td>CO₂</td>
<td>CH₄</td>
<td>173-303</td>
<td>0.91-1.59</td>
<td>1-90</td>
<td>0.02-1.96</td>
<td>Rowlinson and Richardson (1959)</td>
</tr>
<tr>
<td>N₂</td>
<td>CH₄</td>
<td>89-311</td>
<td>0.47-1.63</td>
<td>1-95</td>
<td>0.02-2.06</td>
<td>Agrawal and Laverman (1974)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₂H₄</td>
<td>258-350</td>
<td>0.91-1.24</td>
<td>10-75</td>
<td>0.20-1.49</td>
<td>Dipen and Scheffer (1948)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₂H₄</td>
<td>285-333</td>
<td>1.01-1.18</td>
<td>40-270</td>
<td>0.79-5.36</td>
<td>Diepen and Scheffer (1953)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₂H₄</td>
<td>263-353</td>
<td>0.93-1.25</td>
<td>1-179</td>
<td>0.02-3.55</td>
<td>Van Gunst et al. (1953)</td>
</tr>
<tr>
<td>1,3,5-trichlorobenzene</td>
<td>C₂H₄</td>
<td>263-323</td>
<td>0.93-1.14</td>
<td>31-67</td>
<td>0.62-1.33</td>
<td>Diepen and Scheffer (1948)</td>
</tr>
<tr>
<td>p-dichlorobenzene</td>
<td>C₂H₄</td>
<td>258-318</td>
<td>0.91-1.13</td>
<td>31-95</td>
<td>0.61-1.89</td>
<td>Diepen and Scheffer (1948)</td>
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<td>p-chlorobromobenzene</td>
<td>C₂H₄</td>
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<td>0.93-1.16</td>
<td>31-82</td>
<td>0.62-1.63</td>
<td>Diepen and Scheffer (1948)</td>
</tr>
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<td>p-chloroiodobenzene</td>
<td>C₂H₄</td>
<td>263-319</td>
<td>0.93-1.13</td>
<td>24-68</td>
<td>0.48-1.35</td>
<td>Diepen and Scheffer (1948)</td>
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<td>p-dibromobenzene</td>
<td>C₂H₄</td>
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<td>0.93-1.25</td>
<td>32-82</td>
<td>0.64-1.63</td>
<td>Diepen and Scheffer (1948)</td>
</tr>
<tr>
<td>octacosane</td>
<td>C₂H₄</td>
<td>260-327</td>
<td>0.92-1.16</td>
<td>29-87</td>
<td>0.58-1.73</td>
<td>Diepen and Scheffer (1948)</td>
</tr>
<tr>
<td>hexatriacontane</td>
<td>C₂H₄</td>
<td>263-343</td>
<td>0.93-1.21</td>
<td>32-88</td>
<td>0.64-1.75</td>
<td>Diepen and Scheffer (1948)</td>
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<td>biphenyl</td>
<td>C₂H₄</td>
<td>278-328</td>
<td>0.98-1.16</td>
<td>43-85</td>
<td>0.85-1.69</td>
<td>Diepen and Scheffer (1948)</td>
</tr>
<tr>
<td>benzophene</td>
<td>C₂H₄</td>
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<td>0.93-1.10</td>
<td>30-87</td>
<td>0.60-1.72</td>
<td>Diepen and Scheffer (1948)</td>
</tr>
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<td>menthol</td>
<td>C₂H₄</td>
<td>258-300</td>
<td>0.91-1.06</td>
<td>21-92</td>
<td>0.42-1.82</td>
<td>Diepen and Scheffer (1948)</td>
</tr>
<tr>
<td>C₂Cl₆</td>
<td>C₂H₄</td>
<td>313-323</td>
<td>1.11-1.14</td>
<td>na</td>
<td></td>
<td>Holder and Maass (1940)</td>
</tr>
<tr>
<td>Solute</td>
<td>Solvent</td>
<td>T(K)</td>
<td>T_f(Solvent)</td>
<td>P(bar)</td>
<td>P_f(Solvent)</td>
<td>Reference</td>
</tr>
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<td>C_2Cl_6</td>
<td>C_2H_4</td>
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<td>0.93-1.01</td>
<td>32-53</td>
<td>0.64-1.05</td>
<td>Van Gunst et al. (1953)</td>
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<td>263-488</td>
<td>0.93-1.73</td>
<td>1-72</td>
<td>0.02-1.43</td>
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<td>Hexaethylbenzene</td>
<td>C_2H_4</td>
<td>263-401</td>
<td>0.93-1.42</td>
<td>1-64</td>
<td>0.02-1.27</td>
<td>Van Gunst et al. (1953)</td>
</tr>
<tr>
<td>Hexamethylbenzene</td>
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<td>0.93-1.55</td>
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<td>0.02-1.65</td>
<td>Van Gunst et al. (1953)</td>
</tr>
<tr>
<td>Stilbene</td>
<td>C_2H_4</td>
<td>263-395</td>
<td>0.93-1.40</td>
<td>1-78</td>
<td>0.02-1.55</td>
<td>Van Gunst et al. (1953)</td>
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<td>m-Dinitrobenzene</td>
<td>C_2H_4</td>
<td>263-362.9</td>
<td>0.93-1.29</td>
<td>1-78</td>
<td>0.02-1.55</td>
<td>Van Gunst et al. (1953)</td>
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<tr>
<td>Polyethylene</td>
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<td>533</td>
<td>1.89</td>
<td>1-2000</td>
<td>0.02-39.71</td>
<td>Bonner et al. (1974)</td>
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<tr>
<td>Naphthalene + C_2Cl_6</td>
<td>C_2H_4</td>
<td>263-328</td>
<td>0.93-1.16</td>
<td>1-180</td>
<td>0.02-3.57</td>
<td>Van Gunst et al. (1953)</td>
</tr>
</tbody>
</table>
Solubility of Naphthalene in Supercritical Ethylene

Figure 2-1
solubility; in the middle pressure regime, an increase in temperature results in a decrease in solubility, and finally in the high pressure regime, an increase in temperature results in an increase in solubility. It is also apparent that the solubility covers a wide range in magnitude -- about $10^4$. By operating an extraction process, say at point A, one can achieve the extract in pure form by changing the process conditions to point B. Going from point A to point B results in a two-order magnitude change in solubility for a small increase in temperature and simultaneous decrease in pressure. This, in short, is the significant feature of supercritical fluid extraction.

**Second Interaction Virial Coefficients**

Several investigators (Baughman et al., 1975; Najour and King; 1970, 1966; and King and Robertson, 1962) have calculated second interaction virial coefficients for solid-fluid equilibria systems. The virial equation of state is applicable to systems where the gas phase density is less than about one-half of the critical density of the gas phase. The study of Najour and King (1970) is typical of all the investigations performed and so their work will be discussed in more detail. They examined the system solid anthracene or solid phenanthrene in the supercritical fluids methane, ethylene, ethane, and carbon dioxide. Figure 2-2 shows the result of their calculations in the form of the reduced virial coefficient $B_{12}^R$ versus reduced mixture temperature $T_{12}^R$. The data
Reduced Second Cross Virial Coefficients of Anthracene in CO₂, C₂H₄, C₂H₆, and CH₄ as a Function of Reduced Temperature

\[ B_{12}^R = \frac{B_{12}(T)}{V_{12}^C}; \quad T_{12}^R = \frac{T}{T_{12}^C} \]

(Najour and King, 1970)

Figure 2-2
for all four gases, except for carbon dioxide coincide on a smooth curve. If, however, calculations are done to correct the pure component critical temperature and critical volume of carbon dioxide to those values that would exist without the quadrupolar moment, then the carbon dioxide data can be made to coincide with the other gases (Najour and King, 1970). Also, it is interesting to note that Najour and King found the reduced second interaction virial coefficients of phenanthrene to be identical to those of anthracene.

Applications of Supercritical Fluid Extraction

Food Industry

One of the most active research areas in supercritical fluid extraction is in the decaffination of coffee. Processes are described in a review article by Zosel (1978) and in two patents: a British patent granted to the German Company Hag Aktiengesellschaft (1974) and a German patent granted to Vitzthum and Hubert (1975). Basically, coffee is decaffinated by contracting moist green coffee beans before roasting with supercritical carbon dioxide. In a wet, unroasted coffee bean it is caffeine that has the highest vapor pressure of all substances present and is therefore selectively extracted by the carbon dioxide. In a similar manner, a

\[
B_{12}^R = B_{12}(T)/V_{12}^C, \quad \text{where} \quad V_{12}^C = \frac{1}{8}[(V_1^C)^{1/3} + (V_2^C)^{1/3}]
\]

\[
T_{12}^R = T/T_{12}^C, \quad \text{where} \quad T_{12}^C = [T_1 T_2]^1/2
\]
caffeine-free black tea can also be produced (Hag Aktiengesellschaft, 1973).

Other food-related applications of supercritical fluid extraction are removing of fats and oils from vegetables, obtaining spice extracts, producing cocoa butter, and hop extracts. These four applications are covered under the patents of the German company Hag Aktiengesellschaft (1974b, 1973b, 1974c, 1975) respectively. The major reason for the great interest in using supercritical carbon dioxide in the food industry is due to the non-toxic properties of carbon dioxide. Most other methods of purifying foods rely on using organic solvents such as dichloromethane (Hubert and Vitzhum, 1978) which may pose toxicological problems.

Some food applications, however, rely on liquid carbon dioxide (LCO₂) for extraction. For example, Schultz et al. (1967a, 1967b, 1970a, 1970b). Schultz and Randall (1970), and Randall et al. (1971) have studied the extraction of aromas and fruit juices from concord grapes, applies, oranges, and pineapples. The major emphasis of these studies was to find out the key chemical constituents which comprise the flavor of a given species. For instance, although concord grapes have over 100 chemical species, only one constituent; methyl anthranilate is principally responsible for its characteristic aroma. One reason to use LCO₂ extraction versus SCF extraction with carbon dioxide is that the selectivity is improved at the lower temperatures of LCO₂ (at the cost of lower solubilities), (Sims, 1979), see also Chapter 4-2.
Non-Food Industry

Other applications of supercritical fluid extraction industry are as follows. It has been suggested that a good way to remove nicotine from tobacco is by the use of supercritical carbon dioxide extraction (Hubert and Vitzthum, 1978; Hg Aktiengesellschaft, 1974). Desalination of seawater by supercritical C\textsubscript{11} and C\textsubscript{12} paraffinic fractions has been successfully accomplished (Barton and Fenske, 1970; Texaco, 1967). Other uses include de-asphalting of petroleum fractions using a supercritical propane/propylene mixture (Zhuze, 1960), extraction of lanolin from wool fat (Peter et al., 1974), and recovery of purified oil from waste gear oil (Studiengesellschaft Kohle M.B.H., 1967). Holm (1959) discusses the use of supercritical carbon dioxide (T = 311 K, P = 180 bar) as a scavenging fluid in tertiary oil recovery. The SCF carbon dioxide aids in displacing the oils from the pores of the reservoir rocks. Some of these applications are also discussed in the review articles by Paul and Wise (1971), Wilke (1978), Irani and Funk (1977), and Gangoli and Thodos (1977).

Application to Coal

Supercritical extraction of coal is under study by at least two industrial concerns. In England, the National Coal Board (NCB) has done extensive work on de-ashing coal (Bartle et al., 1975), with supercritical toluene and supercritical
water. In the United States, the Kerr-McGee Company is also interested in de-ashing coal (Knebel and Rhodes, 1978; and Adams et al. 1978).

A flow sheet of the Kerr-McGee process is shown in Figure 2-3. The feed consists of coal dissolved in pentane or proprietary solvents after having undergone hydrogenation. After the feed pump, ash-containing liquified coal is mixed with the recycled proprietary solvent (under supercritical conditions). In the first stage settler, mineral matter and undissolved coal separate from the coal solution as a heavy phase. This heavy phase (ash) is then stripped of solvent in Solvent Separator No. 1. The light phase from the first stage settler then flows to the second stage settler (while simultaneously heated to decrease the density of the solvent). This heating decreases the solubility of the coal in the fluid phase and therefore the deashed coal precipitates out and the supercritical fluid is recycled (in Solvent Separator No. 2). If necessary, an additional stage settler and solvent separator can be added to the process. Starting with an 11.7% ash content of Kentucky #9 coal, Kerr-McGee has been able to obtain a de-ashed coal of 0.1% ash by weight.

Regeneration of Activated Carbon

Modell et al. (1978, 1979) has studied the use of supercritical carbon dioxide to regenerate activated carbon. Granular activated carbon (GAC) is widely used to remove organic contaminants from water. After a given adsorption
Kerr-McGee Process to De-ash Coal
(Adams et al. 1978)

Figure 2-3
time period, however, the GAC must be taken out of service and re-activated.

Present technology for desorption of solutes is either by thermal regeneration, or by use of liquid solvents. Thermal regeneration has the drawback of significant loss of carbon during treatment due to oxidation of the carbon and attrition of fines. Liquid solvent regeneration suffers from the problems of very slow desorption, expensive solvent regeneration equipment, expensive solvents, and toxicity of solvents.

Most of the shortcomings can be overcome by using SCF carbon dioxide to re-activate the spent carbon. Supercritical fluids have a sufficiently high density to obtain liquid like solubilities, but with diffusivities about two order of magnitudes larger than for liquids. These properties give favorable mass transfer coefficients so that the desorption time to re-gerate GAC with a supercritical fluid is less than for ordinary liquids. Also, if carbon dioxide is chosen as the SCF, it is inexpensive and nontoxic.

Dehydration of Organic Liquids

(Salting Out Effect)

Another application of supercritical fluids is their use to perform phase separations in binary liquid mixtures. When binary liquid systems which are either partially or completely miscible are subjected to a supercritical fluid, the mutual solubility of the two liquid components is usually reduced
(Elgin and Weinstock, 1955, 1959; Snedeker, 1956; Weinstock 1954; Todd 1952; Close 1953). This use of a third component (the supercritical fluid) to induce immiscibility is analogous to adding a solid solute, normally an inorganic salt (Costellan, 1971), to cause phase splits between organic liquids and water. Thus, the name salting out effect. The advantages of using a supercritical fluid over a solid to "salt out" are obvious when the simplicity of separating and recovering the fluid from both phases, contrasted with removing a solid solute is considered. A current commercial venture to exploit this technology is the dehydration of ethanol-water solutions by supercritical solvents (Krukonis, 1980).

A better understanding of the salting out effect can be obtained by considering typical phase behavior for ternary systems of two liquids and a supercritical component. Elgin and Weinstock (1959), and Newsham and Stigset (1978) have shown that three types of phase behavior can be anticipated. In Figure 2-4 are shown three isobaric, isothermal sections for a type 1 system. In these diagram, S is the organic solvent, F is a fluid phase, and the supercritical fluid is considered to be ethylene. At a moderately low pressure $P_1$ (and also for higher pressures), the mutual solubility of ethylene and water are very low. At a fixed temperature, however, the solubility of ethylene in the organic solvent increases markedly with pressure so that at an intermediate pressure $P_2$, the solvent rich phase contains about 50% ethylene. At a still higher pressure (above the critical
Phase Diagrams for a Ternary Solvent-Water-Fluid Type I System (Elgin & Weinstock, 1959)

Figure 2-4
pressure of ethylene, the binary pair (organic solvent -- ethylene) become completely miscible.

In Figure 2-5 are shown three isobaric sections for a type 2 system. The only difference between a type 2 system and a type 1 system is the existence of a liquid phase miscibility gap within the pressure composition prism which does not extend to the ethylene-solvent face of the prism. Type 2b and 2c phase behavior are also typical for water-solvent-salt systems.

Finally, when the miscibility gap in the three component system is large enough to intersect the water-solvent face of the pressure-composition prism, a type 3 system is obtained. Three isobaric sections for this system are shown in Figure 2-6. The system methyl ethyl ketone-water-supercritical ethylene exhibits this type of behavior and will be used as an example for further discussion.

In Figure 2-7 is shown the pressure-composition prism for the ternary type III system methyl ethyl ketone (MEK)-water-ethylene at 35.5 bar and 288.1 K. MEK is an important industrial solvent which is used in lubricating oil and dewaxing and is also difficult to dehydrate to a low water content by conventional means. Using high pressure ethylene, however, the two liquid phases which exist in the invariant three-phase region have the following ethylene-free composition: 6.5% MEK in the heavy liquid and 98% MEK in the light liquid. Higher pressure would allow an even wider split, so that dehydration to a water content of less than 1% should
Phase Diagrams for a Ternary Solvent-Water-Fluid Type II System (Elgin & Weinstock, 1959)

Figure 2-5
Phase Diagrams for a Ternary Solvent - Water - Fluid Type III System (Elgin & Weinstock, 1959)

Figure 2-6
Phase Equilibrium Diagram for Ethylene - Water - Methyl Ethyl Ketone at 35.5 Bar and 288.1K (Elgin and Weinstock, 1959)

Schematic Flowsheet for Ethylene Dehydration of Solvents (Elgin & Weinstock, 1959)
be relatively easy to accomplish. A possible flowsheet for a dehydration facility for MEK is shown in Figure 2-7.

The phase behavior for two liquid components and a supercritical component can be modelled with standard thermodynamics (Balder and Prausnitz, 1966). Using a two suffix Margules equation for liquid phase activity coefficients, they have been able to obtain qualitative agreement for the seven systems studied by Elgin and Weinstock (1959). More theoretical work, however, needs to be done in this interesting area using more accurate models for the activities of the liquid phase and the fugacity of the fluid phase.

Supercritical Fluid Chromatography

Another application of supercritical fluid extraction that has developed is the use of supercritical fluids in chromatography. While no commercial equipment is yet available in this area, several investigators (Sie et al., 1966; van Wasen, et al., 1980; Klesper, 1978) have fabricated their own equipment. Major problems of the design of these chromatographs lie with the design of the detectors and the operation of a system capable of injecting a small sample into a column at pressures up to 300 bar.

The basic concept lying behind SCF chromatography is that if a supercritical fluid is used as the mobile phase, then by operating at sufficiently high pressures, the capacity ratio

\[
k_i = \frac{C_i^{\text{STAT}}}{C_i^{\text{MOB}}} \cdot \frac{V_i^{\text{STAT}}}{V_i^{\text{MOB}}} \tag{2-1.1}
\]
where $C_i^\text{STAT}$ and $C_i^\text{MOB}$ are the concentrations of component $i$ in the stationary (stat) and mobile (mob) phase and $V_i^\text{STAT}$ and $V_i^\text{MOB}$ are the total volume of the stationary and mobile phase in the column, will undergo a significant decrease with increasing pressure. Whereas in gas chromatography, only temperature has a significant role in determining the capacity ratio, in SCF chromatography, temperature and now, most significantly pressure, has a great effect on the capacity ratio. As a result, lower temperatures can be used so that high molecular weight thermodegradeable biological materials as complex as DNA may now be separated in SFC. Also, ionic species (Jentoft and Gouw, 1972) which would decompose in gas chromatography can be solubilized in a SCF and thus are amendable to supercritical chromatography.

The operating conditions where SFC will have its potential application is shown in Figure 2-8 in the form of a reduced pressure, reduced density plot. Table 2-3 lists a series of possible mobile phases for SFC. The "proper" supercritical phase to choose is one whose critical temperature is close to, but slightly below the desired temperature of operation.

An example application of SFC is in the resolution of oligomers. For instance, styrene oligomers of nominal molecular weight, $M_w = 2200$ were separated into more than 30 fractions (Klesper and Hartmann, 1978) using a supercritical phase of 95% n-pentane and 5% methanol.

Finally, SFC can be used to obtain thermodynamic
Supercritical Fluid (SCF) Operating Regimes for Extraction Purposes

Figure 2-8
Table 2-3

Critical Point Data for Possible Mobile Phases
for Supercritical Fluid Chromatography

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrous Oxide</td>
<td>309.7</td>
<td>72.3</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>304.5</td>
<td>73.9</td>
</tr>
<tr>
<td>Ethylene</td>
<td>282.4</td>
<td>50.4</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>430.7</td>
<td>78.6</td>
</tr>
<tr>
<td>Sulfur Hexafluoride</td>
<td>318.8</td>
<td>37.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>405.5</td>
<td>112.8</td>
</tr>
<tr>
<td>Water</td>
<td>647.6</td>
<td>229.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>513.7</td>
<td>79.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>516.6</td>
<td>63.8</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>508.5</td>
<td>47.6</td>
</tr>
<tr>
<td>Ethane</td>
<td>305.6</td>
<td>48.9</td>
</tr>
<tr>
<td>n-Propane</td>
<td>370.0</td>
<td>42.6</td>
</tr>
<tr>
<td>n-Butane</td>
<td>425.2</td>
<td>38.0</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>469.8</td>
<td>33.7</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>507.4</td>
<td>30.0</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>540.2</td>
<td>27.4</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>500.0</td>
<td>31.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>562.1</td>
<td>48.9</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>466.8</td>
<td>36.8</td>
</tr>
<tr>
<td>Methyl ethyl ether</td>
<td>437.9</td>
<td>44.0</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>384.9</td>
<td>39.9</td>
</tr>
<tr>
<td>Dichlorofluoromethane</td>
<td>451.7</td>
<td>51.7</td>
</tr>
<tr>
<td>Trichlorofluoromethane</td>
<td>469.8</td>
<td>42.3</td>
</tr>
<tr>
<td>Dichlorotetrafluoroethane</td>
<td>419.3</td>
<td>36.0</td>
</tr>
</tbody>
</table>
properties for the materials being used as the supercritical phase. van Wasen et al. (1980) and Bartmann and Schneider (1973) describe the proper data reduction to obtain partial molar volumes at infinite dilution, interaction second vivial coefficients, and diffusion coefficients.

Rules of Thumb as to What can be Extracted

Stahl et al. (1980) presents some "rules of thumb" as to what can be extracted into SCF carbon dioxide at 313 K. These rules were obtained by performing qualitative studies on many types of solid constituents.

1. Hydrocarbons and other typically lipophilic organic compounds of relatively low polarity, e.g., esters, lactones and epoxides can be extracted in the pressure range 70-100 bar.

2. The introduction of strongly polar functional groups (e.g. -OH, -COOH) makes the extraction more difficult. In the range of benzene derivatives, substances with three phenolic hydroxyls are still capable of extraction, as are compounds with one carboxyl and two hydroxyl groups. Substances in this range that cannot be extracted are those with one carboxyl and three or more hydroxyl groups.

3. More strongly polar substances, e.g. sugars and amino acids, cannot be extracted with pressures up to 400 bar.
2-2 Phase Diagrams

Binary Phase Behavior for Similar Components at Low Pressures

Phase behavior resulting when a solid is placed in contact with a fluid phase at temperatures near and above the critical point of the pure fluid are of key importance. The phase diagram provides guidance to possible operating regimes that exist in supercritical fluid extraction.

In order to establish a basis, a general binary P-T-x diagram for the equilibrium between two solid phases, a liquid phase, and a vapor phase is shown in Figure 2-9. This diagram is drawn for the case of a substance of low volatility and high melting point and one of high volatility and slightly lower melting point. On the two sides of the diagram are shown the usual solid-gas, solid-liquid, and liquid-gas boundary curves for the two pure components. These boundary curves meet, three at a time, at the two triple points A and B. The line CDEF is an eutectic line where solid 1(C), solid 2(F), saturated liquid (E), and saturated vapor (D) join to form an invariant state of four phases. A projection of ABCEF on the T-x plane gives the usual solubility diagram of two immiscible solids, a miscible liquid phase, and a eutectic point that is the projection of point E. This projection is shown as the "cut" at the top of the figure, since pressure has little effect on the equilibrium between condensed phases.
The Pressure - Temperature - Composition Surfaces for the Equilibrium Between Two Pure Solid Phases, A Liquid Phase and a Vapor Phase

(Rowlinson and Richardson, 1959)

Figure 2-9
It is also interesting to examine the P-x projections of this three dimensional surface. Below the eutectic temperature, the P-x projection is given by GHIJK, where H and K are the vapor pressures of the two pure solids. The total pressure of the two solids in equilibrium with the mixed vapor is given by GIJ which is very close to the sum of the vapor pressures of the two pure components. At temperatures above the melting point of component 1, a P-x projection has the shape shown by the dashed lines (of the isothermal cut) in Figure 2-9 and is drawn in more detail in Figure 2-10. Notice that there are two homogeneous regions, liquid and gas, and three heterogeneous regions, liquid + gas, solid + gas, and solid + liquid. At temperatures above the melting point of the second component, an increase in temperature causes points W and Y to move towards point Z. For temperatures between the melting point of the second component and the critical temperature of the light component, one obtains a P-x cross section similar to that shown in Figure 2-11. The locus (M-N) of the maxima of the (P,x) loops is the gas-liquid critical point line of the binary mixture.

Finally, in Figure 2-12 there is shown a P-T projection indicating the three-phase (AFB) locus and the critical locus (MN). In this figure, the only region where solid is in equilibrium with a gaseous mixture is in the area under the three-phase line AFB. Similarly, solid-gas equilibrium in Figure 2-9 exists on the curves HI and KI and in Figure 2-10 on the curve WX. Up until now, all of these diagrams
A Pressure Composition Section at a Constant Temperature Lying Between The Melting Points of the Pure Components (Rowlinson and Richardson, 1959)

Figure 2-10
A Pressure - Composition Section at a Constant Temperature above the Melting Point of the Second Component

Figure 2-11
P-T Projection of a System in Which the Three Phase Line Does Not Cut the Critical Locus

Figure 2-12
have been for similar substances and for relatively low pressures. The next section discusses the case of very dissimilar components and for very high pressures.

**Binary Phase Behavior for Dissimilar Components at High Pressures**

Supercritical fluid extraction of solid solutes usually operates with two very dissimilar substances (one is usually a low molecular weight gas at room conditions; one a high molecular weight solid at room conditions). Under these circumstances, the phase behavior discussed previously is not valid. Instead, entirely new phenomena exist in the P-T-x phase space. This phenomena, which is of most importance in understanding the use and limitations of supercritical fluid extraction, will be the topic of this section.

High pressure phase equilibria among dissimilar components has been previously investigated by Rowlinson (1969), Rowlinson and Richardson (1959), van Welie and Diepen (1961), van Gunst et al. (1953a, 1953b), Diepen and Scheffer (1948a, 1953), Morey (1957), Smits (1909), and Zernike (1955). The best way to introduce this subject is to reconsider the diagram shown in Figure 2-12. If the two components are so dissimilar that one is a low molecular weight gas at room conditions and one is a high molecular weight solid, then the difference in temperature between the triple points and critical points of these substances is so large that the three phase line AFB in Figure 2-12 can actually intersect
the critical locus so as to "cut" it into two points: p-the lower critical end point, and q- the upper critical end point. See Figure 2-13. In this figure, M and N are the critical points of the supercritical fluid and solid respectively. Critical end points are mixture critical points in the presence of excess solid. Following the notation of Morey (1954), these critical end points are commonly written as follows:

\[ p : (G \equiv L_1) + S \]

\[ q : (G \equiv L_2) + S \]

i.e., a liquid and gas of identical composition and properties in equilibrium with a pure solid.

The major consequence of a gap in the critical locus as shown in Figure 2-13 is to allow at least* a region in temperature between \( T_p \) and \( T_q \) where one solid phase is in equilibrium with one fluid phase with no liquid phase present.

In order to have a better visualization for the P-T projection of the P-T-x surface, it is necessary to understand various P-x and T-x projections. Figure 2-14 shows a P-T projection indicating where isothermal P-x projections are located in Figure 2-15. At \( T_1 \), the projection is

---

* A more general statement is discussed later in this section.
P-T Projection of a System in Which the Three Phase Line Cuts the Critical Locus

Figure 2-13
A P-T Projection Indicating Where the Isothermal P-x Projections of Figure 2-15 are Located

Figure 2-14
Isothermal P-X Projections For Solid-Fluid Equilibria

Figure 2-15
identical to Figure 2-10, i.e., equilibrium exists between two similar compounds. Isotherm $T_2$, the lower critical end point temperature, shows that the L-V branch has disappeared so that there is one homogeneous region -- which for convenience has been divided into two fictitious regions corresponding to the L-V equilibrium position that exists an infinitesimal position to the left. $T_3$ is a projection in the "window" between $T_p$ and $T_q$. Here, the solubility is unity at the vapor pressure of the solute, then decreases with increasing pressure, reaches a minimum, increases, reaches a maximum, and then decreases again. At $T_4$, the upper critical end point temperature, again there is one homogeneous fluid phase present, which for convenience has been divided into two fictitious regions corresponding to the top of the critical locus that exists an infinitesimal position to the right. $T_5$ is an isotherm between the upper critical end point and the triple point of the solid. Note the existence of a discontinuity in the two solid + liquid regions. This discontinuity is important from an experimental point of view in predicting the upper critical end point temperature. Also, the binary critical point for the mixture is located at the apex of the liquid-liquid equilibria region. At the triple point, the liquid-liquid region must disappear, and so there are now two homogeneous regions: $(S+L_2)$ and $(V+L_2)$. At $T_7$, the $(S+L_2)$ phase has broken off from the liquid-vapor region and will continue to shrink, until at some temperature before the critical point of the solid, only a liquid-vapor
equilibrium region remains.

**Construction of a T-x and P-x Diagram**

Modell et al. (1979) has constructed a T-x diagram for the system naphthalene-carbon dioxide as shown in Figure 2-16. Several important features should be brought out. First, the tie-lines connecting the three phase locus are isothermal lines. Second, in the region between the first and second critical end points, there exists a region of retrograde solidification, i.e., a region where an increase in temperature causes a decrease in solubility.

An analogous diagram for carbon dioxide-phenanthrene is shown in P-x coordinates in Figure 2-17. In this figure the extreme sensitivity of the equilibrium solubility to temperature and pressure is more apparent and the retrograde solidification region is clearly shown. All of these two-dimensional projections aid in providing a picture of the actual three-dimensional surface of this complex equilibria system.

**P-T-x Diagram for Solid-Fluid Equilibria**

Zernike (1955) and Smits (1909) have provided isometric, three-dimensional drawings for the case of solid-fluid equilibria. With the help of the many projections shown previously, a clear understanding of these diagrams is now possible. As both sketches are similar, only the diagram of Zernike will be discussed. Figure 2-18, shows this equilibrium surface. While the diagram indicates a perpendicular
Naphthalene - Carbon Dioxide Solubility Map
Calculated from the Peng - Robinson Equation;
k_{12} = 0.11

Figure 2-16

(After Hong, 1981)
Solubility of Phenanthrene in Supercritical Carbon Dioxide

Figure 2-17
Space Model in the Case Where the Critical Locus and the Three Phase Line Intersect (Zernike, 1955)

Figure 2-18
dividing surface extending infinitely upward at the upper and lower critical end point temperatures -- this surface is fictitious because there is no phase transition to the left or right of these critical end point temperatures. The dividing surface only indicates the uniqueness of the region between \( T_p \) and \( T_q \). It is also apparent that the isothermal \( P-x \) projections shown in Figure 2-15 "fit" nicely into the three-dimensional surface. Note in Figure 2-18 that the critical points of the two species and the upper and lower critical end points are on different planes of this surface. This is not obvious from two dimensional projections.

**Solid-Fluid Equilibria Outside The Critical End Point Bounds**

As is clearly shown by the many \( P-T \) projections of Figure 2-15, there exist regions of temperature other than \( T_p \leq T \leq T_q \) for which there is solid-fluid equilibrium. These other regions of temperature, therefore, offer unique possibilities for supercritical fluid extraction, but suffer from the drawback that the pressure must be kept between minimum and maximum bounds in order to guarantee that no liquid phase will form. A major advantage, however, of operating in these regions is that much higher solubilities of the solid in the fluid phase can be achieved compared to the solubilities that can be achieved in the region \( T_p < T < T_q \).

This particular phase behavior can be best understood
from Figure 2-15 isotherms, $T_3$, $T_4$ and $T_5$. Since the (S+F) isotherm $T_5$ and the apex of the ($L_1+L_2$) isotherm $T_5$ is on the critical locus of the binary mixture, then it follows that as long as the system pressure is greater than the maximum pressure on the critical locus connecting the upper critical end point with the critical point of the solid component, it is possible to operate with high solubilities in the S+F region for temperatures $T > T_q$. As the P-x diagrams of Figure 2-15 show, the solubilities in this region of solid-fluid equilibria will of necessity be higher than the solubility in the region of temperatures $T_p < T < T_q$. Consequently one can theoretically approach a solubility of 100 mole percent of solute in the fluid phase.

As an example, consider the system naphthalene-ethylene. Figure 2-19 shows experimental P-T data for the critical locus, the three-phase line and the upper critical end point. From this figure, it can be concluded that if the system pressure is greater than about 250 bar, that it is possible to operate in a solid-fluid regime for $T > T_q$. Verification of these ideas is shown in Figure 2-20. This is a graph of temperature versus mole percent at a constant pressure of 274 bar. The large change in solubility occurs near the upper critical end point temperature ($52.1^\circ C$). Also note the excellent agreement between the experimental data and theory (the solid line calculated from the Peng-Robinson equation of state, which is discussed later).
P-T Projection for Ethylene - Naphthalene (Van Welie and Diepen, 1961)

Figure 2-19
T-x Projection for Ethylene-Naphthalene for Temperatures and Pressures above the Critical Locus

Figure 2-20
Phase Behavior in Multicomponent Systems

Multicomponent systems (two or more solid phases in equilibrium with a fluid phase) have essentially the same type of phase behavior as binary systems with, however, a few peculiarities. Assuming the interesting case where the critical locus is broken into lower and upper critical end points, the P-T projection of a ternary phase diagram will appear similar to that shown in Figure 2-21. (Note: P-x projections cannot be drawn because the phase diagram is four dimensional).

Key points to be noted about Figure 2-21 are as follows. First, there are now six critical end points. K₁ and K'_1 are the first and second lower critical end points. These end points are the intersection with the critical locus of the three phase line formed by the two solids in equilibrium with a liquid and a gas phase. Similarly, K₂ and K'_2 are the first and second upper critical end points. In the case where no solid solutions form, there will exist two eutectic points and hence a four phase line connecting them. However, the four phase line may intersect the critical locus at a lower double critical end point and at an upper double critical end point -- shown as p and q respectively. The reason for calling these double critical end points is that they are actually formed by the intersection of the two first and second lower and upper critical end points respectively.

There are important physical implications that make the ternary system different from the binary system. As the
P-T Projection of a Four Dimensional Surface of Two Solid Phases In Equilibrium with a Fluid Phase

Figure 2-21
The upper double critical end point is formed by the intersection of the four phase line with the critical locus — and the four phase line starts at the eutectic point of the two solids, then it is apparent that the temperature of the upper double critical end point will be lower than either of the temperatures corresponding to the first and second upper critical end points.

As an example, consider the system supercritical fluid ethylene with the two solids naphthalene and hexachlorethane in comparison to the binary system supercritical ethylene with naphthalene. The critical end points of these two systems are shown in Table 2-4. Note the significant lowering of the upper critical end point temperature by 26.6 K.

**Mathematical Representation of Binary Phase Behavior**

By molecular thermodynamics, one can generate a binary-phase diagram for solid-fluid equilibria. All that is needed is an applicable mixture equation of state for the fluid phase, the vapor pressure, and the molar volume of the solid phase. The exact methodology to follow to generate such a phase diagram which includes the critical locus, the three phase line, and the critical end points is discussed in this section.

**Thermodynamics of the Binary Critical Locus**

A critical point is a stable position on a spinodal curve. Using the Legendre transform notation of Reid and Beegle (1977) and Beegle et al. (1974), the critical locus
Table 2-4
Comparison of Critical End Points for the System Supercritical Ethylene-Naphthalene with the System Supercritical Ethylene -Naphthalene -Hexachloroethane

<table>
<thead>
<tr>
<th>System</th>
<th>$T_p (K)$</th>
<th>$T_q (K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene-naphthalene$^1$</td>
<td>283.9</td>
<td>325.3</td>
</tr>
<tr>
<td>ethylene-naphthalene-hexachloroethane$^2$</td>
<td>288.5</td>
<td>298.7</td>
</tr>
</tbody>
</table>

1. Diepen and Scheffer (1953).
2. van Gunst et al. (1953).
are those states that satisfy

\[ Y^{(n)}_{(n+1)(n+1)} = 0 \]  \hspace{1cm} (2-2.1)

and

\[ Y^{(n)}_{(n+1)(n+1)(n+1)} = 0 \]  \hspace{1cm} (2-2.2)

In terms of the Helmholtz free energy, these transforms can be written (for a binary mixture) in terms of the two determinants

\[
 L_1 = \begin{vmatrix} A_{vv} & A_{v1} \\ A_{v1} & A_{11} \end{vmatrix} 
 = A_{vv}A_{11} - A_{v1}^2 = 0 \]  \hspace{1cm} (2-2.3)

where

\[
 A_{vv} = \left( \frac{\partial^2 A}{\partial v^2} \right)_{T,x} \]  \hspace{1cm} (2-2.4)

\[
 A_{11} = \left( \frac{\partial^2 A}{\partial x_1^2} \right)_{T,x} \]  \hspace{1cm} (2-2.5)

\[
 A_{v1} = \left( \frac{\partial^2 A}{\partial v \partial x_1} \right)_{T,x} \]  \hspace{1cm} (2-2.6)
and \[ M_1 = \begin{vmatrix} A_{vv} & A_{v1} \\ \frac{\partial L_1}{\partial V} & \frac{\partial L_1}{\partial x_1} \end{vmatrix}_{T,x} = 0 \] (2-2.7)

or,

\[ M_1 = A_{vv} A_{ll} A_{vv1} + A_{vv} A_{ll1} - 3 A_{vv} A_{v1} A_{v11} 
- A_{ll} A_{v1} A_{vvv} + 2 A_{v1} A_{lvv} = 0 \] (2-2.8)

Equations 2-2.3 and 2-2.8 are most conveniently solved simultaneously by a pressure explicit equation of state. Modell et al. (1979) have derived these critical criteria using the Peng-Robinson equation of state.

**Determination of the Three Phase SLG Line**

Thermodynamics requires that on the three-phase SLG line, that the following equalities must be satisfied:

\[ f^s_1(T,P) = \hat{f}^L_1(T,P,x_1) \] (2-2.9)

\[ f^s_1(T,P) = \hat{f}^V_1(T,P,y_1) \] (2-2.10)

\[ \hat{f}^V_1(T,P,y_1) = \hat{f}^L_2(T,P,x_1) \] (2-2.11)

\[ \hat{f}^V_2(T,P,y_1) = \hat{f}^L_2(T,P,x_1) \] (2-2.12)

Of these four equations, only three are independent and a convenient set to chose is the last three. The fugacity of the solid phase is given by
and the fugacity of the liquid and vapor phase by

\[
\hat{f}_L^V = x_1 p \phi_L^L \\
\hat{f}_L^V = y_1 p \phi_L^V
\]  

(2-2.14) (2-2.15)

where the fugacity coefficients \( \phi_L^L \) and \( \phi_L^V \) are found from an applicable equation of state. An iterative solution of Equations (2-2.10) through (2-2.12) coupled with the mass balance

\[
x_1 + x_2 = 1
\]

(2-2.16)

is sufficient to define the three-phase line. Numerical techniques helpful in solving for the three phase line are discussed by Francis and Paulaitis (1980).

**Determination of Binary Critical End Points**

There are two convenient methods whereby the upper and lower critical end points may be calculated. One is to generate the entire critical locus and the entire three-phase line, then plot the results on a P-T projection and graphically determine the end-points.

An easier way, however, is as follows. At a binary mixture critical point, the following thermodynamic equality must be satisfied.*

*See Appendix II for a derivation.
where \( x_1 \) is the mole fraction of component 1 in the liquid phase and subscript \( \sigma \) denotes differentiation along the three-phase curve. Thus, when the three-phase curve is generated on the computer, a numerical check can be performed to test for the equality of Equation 2-2.17. There will exist two such equalities -- one at the upper critical end point and one at the lower critical end point. Numerical techniques helpful in solving for the binary critical end points are discussed by Francis and Paulaitis (1980).

Experimental Methods to Determine Critical End Points of Binary Systems

There are two methods whereby one can determine experimentally the critical end points for binary systems. The first method makes use of the rigorous thermodynamic relationship that at a critical end point (see Appendix II).

\[
\left( \frac{\partial P}{\partial y_1} \right)_{T, \sigma} = 0 \quad (2-2.18)
\]

Thus, if careful experimental data are taken of isothermal solubilities versus pressure, then two isotherms will exhibit the zero slope criteria of Equation 2-2.18. These two conditions will be the upper and lower critical end points. Extremely precise solubility data must be taken for this
method to be reliable -- for the solubility is very sensitive to temperature and pressure near the critical end points.

Alternatively, one can make use of the special nature of the phase behavior near the critical end points to determine their values. Consider the isotherms $T_4$ and $T_5$ shown in Figure 2-15. These figures imply that if isothermal solubility data are taken at many pressures, that as the isotherm just exceeds the upper critical end point temperature (or is just less than the lower critical end point temperature), then there will be a discontinuity in the isothermal solubility curve. The temperature and pressure at which the discontinuity first occurs are the critical end point temperature and pressure respectively. McHugh and Paulaitis (1980) have obtained experimental values of the upper critical end points for a few systems by the second method.

Comparison of Experimental Critical End Points to Those Predicted by Theory

To date, there is only one system for which there are both experimental measurements of critical end points and also theoretical calculations of the critical end points. This system is naphthalene-ethylene. Diepen and Scheffer (1948a) and van Gunst et al. (1953) found the critical end points experimentally while Modell et al. (1979) calculated them using the Peng-Robinson (1976) equation of state. A comparison of experimental and theoretical results is shown in Table 2-5. The agreement is satisfactory.
Table 2-5
Comparison of Experimental vs Theoretical Values of the Critical End Points for the System Naphthalene-Ethylene

<table>
<thead>
<tr>
<th>System</th>
<th>Lower CEP</th>
<th>Upper CEP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T(K)</td>
<td>P(bar)</td>
</tr>
<tr>
<td>Naphthalene-ethylene, experimental</td>
<td>283.9</td>
<td>51.9</td>
</tr>
<tr>
<td>Naphthalene-ethylene, Peng-Robinson</td>
<td>282.8</td>
<td>50.6</td>
</tr>
</tbody>
</table>

1 Diepen and Scheffer (1953)
Equilibrium Conditions Using Compressed Gas Model

The criterion of equilibrium between a solid phase (pure or mixture) and a fluid phase for any component \( i \) is

\[
\hat{f}^S_i = \hat{f}^F_i \tag{2-3.1}
\]

Using a compressed gas model for the fluid phase, the fugacity coefficient in the fluid phase can be written

\[
\hat{f}^F_i = y_i P \phi_i^F \tag{2-3.2}
\]

where \( \phi_i \) is determined from an equation of state by the definition (Modell and Reid, 1974).

\[
\ln \phi_i = \frac{1}{RT} \int_{V}^{V_f} \left[ \frac{RT}{V} - \left( \frac{\partial P}{\partial N_i} \right)_T,V,N \right] dV - \ln Z \tag{2-3.3}
\]

Assuming that

1. solid density is independent of pressure and composition
2. no solid solutions form
3. solubility of the fluid in the solid is sufficiently small so that \( y_i^S \approx 1 \) and \( x_i = 1 \)
4. vapor pressure of the solid is sufficiently small so that \( \phi_{VP_i}^S \approx 1 \) and \( P - P_{VP_i}^S \approx P \)

Then, the solid phase fugacity can be written
\[ f_i^S = pVp_i \exp \left( \frac{pV_i}{RT} \right) \] (2-3.4)

Combining Equations 2-3.2 and 2-3.3 gives the equilibrium mole fraction of a component i in a supercritical fluid as

\[ y_i = \frac{pV_i^S}{p} \left[ \frac{l}{\phi_i} \right] \left[ \exp \left( \frac{pV_i^S}{RT} \right) \right] \] (2-3.5)

Equation 2-3.5 conveniently divided into three terms shown in brackets. The first bracketed term is the equilibrium solubility assuming the ideal gas law to be valid. The second term accounts for the nonideality of the fluid phase. The third term is the Poynting (1881) correction.

It is also often convenient to speak of the enhancement factor which is defined as the actual solubility compared to that assuming an ideal gas. Solving for the enhancement factor from Equation 2-3.5 gives

\[ E_i = \frac{\exp \left( \frac{pV_i^S}{RT} \right)}{\frac{pV_i}{RT}} \] (2-3.6)

**Equilibrium Condition Using Expanded Liquid Model**

Instead of treating the supercritical fluid phase as a compressed gas it may be advantageous to consider it as an expanded liquid. With this approach, at constant temperature, the fugacity of component i in the fluid phase can be
expressed as

$$\tilde{f}_i^F(y_i, P) = y_i \gamma_i(y_i, P^R) f_i^L(P^R) \exp \left[ \frac{P \left( \frac{V_i^L}{RT} \right)}{P_R \left( \frac{V_i^L}{RT} \right)} \right] dP$$

(2-3.7)

where $P^R$ is a reference pressure and $f_i^L$ is a hypothetical fugacity of pure liquid $i$ at the system temperature and at the reference pressure $P^R$. The solid phase fugacity can be written as

$$\tilde{f}_i^S = x_i \gamma_i^S(x_i, P^R) f_i^S(P^R) \exp \left[ \frac{P \left( \frac{V_i^S}{RT} \right)}{P_R \left( \frac{V_i^S}{RT} \right)} \right] dP$$

(2-3.8)

where $f_i^S(P^R)$ is the fugacity of pure solid at the system temperature and at the reference pressure $P^R$. Making the following assumptions: (1) the solid density is independent of pressure and composition; (2) the solubility of fluid in the solid is sufficiently small so that $\gamma_i^S = 1$ and $x_i = 1$ and (3) no solid solutions form, then equation 2-3.8 can be written as

$$f_i^S = f_i^S(P^R) \exp \left[ \frac{(P-P^R)V_i^S}{RT} \right]$$

(2-3.9)

Combining Equations 2-3.7 and 2-3.9 gives

$$y_i = \frac{1}{\gamma_i(y_i, P^R)} \frac{f_i^S(P^R)}{f_i^L(P^R)} \exp \left[ \frac{(P-P^R)V_i^S}{RT} \right] \exp \left[ \frac{P \left( \frac{V_i^L}{RT} \right)}{P_R \left( \frac{V_i^L}{RT} \right)} \right] \left[ \frac{P}{P_R \left( \frac{V_i^L}{RT} \right)} \right] dP$$

(2-3.10)
It can be shown (Prausnitz, 1969) that to a very good approximation

\[
\ln \frac{f_i^{L}(p^R)}{f_i^{S}(p^R)} = \frac{\Delta H_i^F}{RT} \left[ 1 - \frac{T}{T_{t_i}} \right] - \frac{\Delta C_p}{R} \left( \frac{T_{t_i} - T}{T} \right)
\]

\[+ \frac{\Delta C_p}{R} \ln \left( \frac{T_{t_i}}{T} \right) \quad (2-3.11)\]

where \( T_{t_i} \) is the triple point temperature of component \( i \). Furthermore, the last two terms on the right of Equation 2-3.11 are about equal in magnitude and opposite in sign.

Thus, Equation 2-3.11 can be approximated as

\[
y_i = \frac{\exp \left[ \frac{\Delta H_i^F}{RT} \left( \frac{T}{T_{t_i}} - 1 \right) \right]}{y_i(y_i, p^R)} \cdot \exp \left( \frac{p-p^R}{RT} \right) V_i^L \exp \int_{p^R}^{p} \frac{V_i^L}{RT} dP \quad (2-3.12)\]

An accurate representation of \( y_i(y_i, p^R) \) and \( V_i^L \) must now be obtained. Mackay and Paulaitis (1979) have used a reference pressure of

\[p^R = p_c\]

with \( p_c \) the critical pressure of the pure fluid phase, and the assumptions that

\[y_i(y_i, p^R) ≈ y_i^∞(p_c) \quad (2-3.13)\]
\[ \bar{V}_i(y_i, P) = \bar{V}_i^\infty(P_c) \]

(2-3.14)

\( \bar{V}_i^\infty(P_c) \) then can be found from an applicable equation of state by the definition

\[ \bar{V}_i^\infty = \lim_{N_i \to 0} \left( \frac{\partial V}{\partial N_i} \right)_{T, P_c, N_j[i]} \]

(2-3.15)

\( \gamma_i^\infty(P_c) \) is treated as an adjustable constant.

Using the Peng-Robinson (1976) equation of state, Mackay and Paulaitis (1979) were able to correlate naphthalene solubilities in supercritical carbon dioxide and supercritical ethylene at a constant value of the binary interaction parameter and for a temperature dependent infinite dilution activity coefficients. The infinite dilution activity coefficients they obtained, however, are quite large.

**Applicable Equations of State**

Both the compressed gas and the expanded liquid model approach to solid-fluid equilibrium require an equation of state to evaluate fluid phase fugacity coefficients (former case) and partial molar volumes (later case). This section will discuss the types of equations of state applicable to determine these thermodynamic quantities in the mixture state.

**Virial Equation of State**

The virial equation of state is applicable to the
correlation of the solubility of solids in compressed gases, but only for relatively low pressures. When the pressure is such that the density of the gas is less than about one-half of the critical density, the virial equation of state, truncated to the third term can be used. The virial equation can be written

\[
\frac{PV}{RT} = 1 + \frac{B_M}{V} + \frac{C_M}{V^2} + \ldots
\]

(2-3.16)

where:

\[
B_M = \sum_{ij} y_i y_j B_{ij}
\]

(2-3.17)

\[
C_M = \sum_{ijk} y_i y_j y_k C_{ijk}
\]

(2-3.18)

A major advantage of the virial equation is that the virial coefficients have a physical meaning in that they are related to the intermolecular potential function. Under conditions where the virial equation of state is applicable, the enhancement factor has been calculated for the compressed gas model (Ewald, 1955), (Ewald, et al., 1953) as:

\[
\ln E = \frac{V^s}{RT} (P-P_0) + \left( x_1^2 B_{11} - 2 x_1 x_2 B_{12} + x_2^2 B_{22} - 2 x_2 B_{22} \right) \frac{P}{RT}
\]

\[
+ \frac{1}{2} \left[ -x_1^2 B_{11}^2 - x_1^3 (2 C_{111} - 4 B_{11} B_{12}) + x_1^2 C_{112} 
\right.
\]

\[
+ \left. x_1^3 x_2 B_{11} B_{12} - x_1^2 x_2 (6 C_{112} - 4 B_{11} B_{22} + 8 B_{12}^2) \right]
\]
\[ +x_1 x_2^6 C_{122} - x_1 x_2^2 (6C_{112} + 12B_{12} B_{22}) + x_1 x_2^3 12B_{12} B_{22} + x_1 x_2^2 (12B_{12}^2 + 6B_{11} B_{22}) + x_2^4 B_{22}^2 \]

\[ -x_2^3 (2C_{222} + 4B_{22}^2) + x_2^3 C_{222} \left( \frac{P}{RT} \right)^2 \]  

(2-3.19)

where: subscript 2 is the solid  
subscript 1 is the fluid  
\( P_0 \) is the vapor pressure of the solid  
\( V_s \) is the molar volume of the solid

As an example, consider the application of the virial equation to solid-fluid equilibrium calculations in the correlation of solid carbon dioxide solubility in supercritical air. The resultant plot is shown in Figure 2-22. Clearly, for an accurate correlation past the solubility minimum, the third virial coefficient must be taken into account. As the virial equation is not valid for densities greater than about one-half of the critical density of the mixture, one has to resort to empirical equations of state for the high pressure region.

Cubic Equations of State

Of all the equations of state used today, the cubic equations of state are probably the most widely used. Evidence of this is in the continuing effort to produce modifications of the original cubic equation of state: that of van der Waals (1873). After the development of van der Waals
Solubility of CO₂ in Air (Prausnitz, 1969) at 143 K

Figure 2-22
equation, the most significant advance was the Redlich-Kwong (1949) equation which modified the attractive term of van der Waals. After Redlich-Kwong, Soave (1972) made the next major advance by introducing a temperature dependence on the attractive term. Following Soave, many other equations of state were developed (Peng and Robinson, 1976; Fuller, 1976; Won, 1976; and Graboski and Daubert, 1978). Also, two review articles on cubic equations of state were written (Abbott, 1973; Martin, 1979).

At the present time, it is believed that the best cubic equation of state is that of Peng and Robinson (1976). Their equation is:

\[
P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}
\]  

(2-3.20)

where

\[
a_i(T_C) = \omega_a \frac{R^2 T_C^2}{P_C}
\]  

(2-3.21)

\[
b_i(T_C) = \omega_b \frac{RT_C}{P_C}
\]  

(2-3.22)

\[
a_i(T) = a_i(T_C) \cdot \gamma_i(T_{r_i}, \omega_i)
\]  

(2-3.23)

\[
b_i(T) = b_i(T_C)
\]  

(2-3.24)

\[
\chi_i(T_{r_i}, \omega) = \left[ 1 + \kappa_i(1-T_{r_i}^{1/2}) \right]^2
\]  

(2-3.25)
\[ \kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (2-3.26) \]

\[ a = \sum_{ij} (1-k_{ij})a_i^{1/2}a_j^{1/2}x_ix_j \quad (2-3.27) \]

\[ b = \sum_i b_ix_i \quad (2-3.28) \]

By definition of the fugacity coefficient (Modell and Reid, 1974)

\[ \ln \phi_i = \frac{1}{RT} \int_V^{\infty} \left[ \left( \frac{RT}{V} \right) - \left( \frac{\beta P}{\beta N_i} \right)_{T,P,N_i[i]} \right] dV - \ln Z \quad (2-3.29) \]

The fugacity coefficient of component i can be calculated as

\[ \ln \phi_i = \frac{b_i}{B} (Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{B}} \ldots \]

\[ \left( \frac{2\Sigma x_j a_{ij} \frac{b_j}{a}}{A} - \frac{b_i}{B} \right) \ln \left( \frac{Z+(1+\sqrt{2})B}{Z-(1-\sqrt{2})B} \right) \quad (2-3.30) \]

where

\[ A = aP/R^2T^2 \quad (2-3.31) \]

\[ B = bP/RT \quad (2-3.32) \]

Benedict-Webb-Rubin Equation of State

The Benedict-Webb-Rubin (BWR) equation of state (Benedict et al., 1951, 1942, 1940), is another equation of state which is often used. Originally, the BWR constants were tabulated for only the light hydrocarbon systems. Later, Edmister et al. (1968) expressed the eight parameters in terms of critical
pressures, temperatures, and acentric factors. Starling and Han (1971, 1972a, 1972b) added three more parameters to the original BWR equation of state and developed a correlation for these parameters in terms of critical temperature, critical volume, and acentric factor. Yamada (1973) developed a forty four parameter BWR equation and a correlation of these parameters in terms of critical temperature, critical pressure, and acentric factor. Lee and Kesler (1975) developed a modified BWR equation within the context of Pitzer's three parameter correlation.

These many types of BWR equations have proved to be very successful for light hydrocarbon systems at conditions far removed from the critical point. Near the critical point, however, the BWR equations are less accurate as they do not satisfy the two pure component stability criteria at a critical point.

Perturbed Hard Sphere Equation of State

All of the cubic equations of state developed to date have used the same repulsive term that van der Waals used in 1893, i.e.,

\[ P_R = \frac{RT}{V-B} \]  \hspace{1cm} (2-3.33)

and have emphasized modifications on the attractive term. It can be shown, however, (Carnahan and Starling, 1972), that a more accurate representation of the repulsive term is
\[ P_R = \frac{RT}{V} \left[ \frac{1+\xi+\xi^2-\xi^3}{(1-\xi)^3} \right] \]  

(2-3.34)

where \( \xi = b/4V \)  

(2-3.35)

Equation 2-3.34 is quite precise since its virial expansion closely agrees with the exact expression for rigid spheres (Ree and Hoover, 1967). The equation of state that results when the repulsive term is replaced by Equation 2-3.34 is called a perturbed hard sphere (PHS) equation of state (Oellrich et al., 1978).

Preliminary use of the PHS equation of state, augmented by density dependent attractive forces (Alder et al., 1971) for solid-fluid equilibria has been encouraging (Johnston and Eckert, 1980). More development work, however, needs to be done.

Conclusions

The two general types of equation of state -- cubic and Benedict-Webb-Rubin (BWR) have been tested for their ability to correlate solid-fluid equilibrium data. For the cubic equations of state, the Peng-Robinson (1976) and Soave (1972) equations of state were used. Also, the Starling and Han (1971, 1972a, 1972b) modifications of the BWR equation of state were tried. In all cases the correlational ability of these equations were tested on the systems naphthalene-carbon dioxide and naphthalene-ethylene using the data of Tsekhanskaya (1964).
Extensive testing of the Starling and Han modification of the BWR equation of state showed that the solid-fluid equilibrium data could not be accurately correlated unless the binary interaction parameter was a function of both temperature and pressure. In the case of the two cubic equations of state (Soave and Peng-Robinson), the solid-fluid equilibrium data could be well correlated for a binary interaction parameter that is a weak function of temperature. The ability of both the Peng-Robinson and Soave equations of state to correlate the solubility data was essentially identical, but the two equations required different values of the binary interaction parameter.

Clearly, it is more desirable to have the binary interaction parameter a function of as few variables as possible -- and so the two cubic equations prove to be superior to the BWR equation. Of the two cubic equations of state, the Peng-Robinson equation predicts molar volumes of the liquid phase more accurately than the Soave equation of State (Peng and Robinson, 1976) and so the Peng-Robinson equation was chosen as the equation to use in this thesis.

A possible reason for the better predictive abilities of the cubic-type equation of state over the BWR-type equation of state can be explained as follows. Cubic equations of state contain two adjustable parameters. Typically, these adjustable parameters are found by forcing the cubic equations of state to satisfy the two pure component stability criteria:
\[
\left( \frac{\partial P}{\partial V} \right)_{T_c} = 0 \quad (2-3.36)
\]

\[
\left( \frac{\partial^2 P}{\partial V^2} \right)_{T_c} = 0 \quad (2-3.37)
\]

Consequently, isotherms for cubic equations of state have the correct slope in the critical region. BWR type equations, however, have typically eight to eleven adjustable parameters. These parameters are obtained by fitting the BWR equation to P-V-T data by use of a non-linear regression routine. Thus, the BWR equations may not satisfy pure component stability criteria and thus, will tend not to correlate data well in the critical region.

2-4 Thesis Objectives

The objectives of this thesis can be divided into three parts: experimental, theoretical, and exploratory. Experimentally, equilibrium solubility data for both polar and non-polar solid solutes in supercritical fluids were to be measured over wide ranges of temperature and pressure. In addition, ternary equilibrium data (two solids, one fluid) were to be measured. Carbon dioxide and ethylene were the two supercritical fluids to be used.

Theoretically, correlation of equilibrium solubility data of both binary and multicomponent systems using rigorous thermodynamics was to be done.
Finally, after obtaining equilibrium solubility data and developing a thermodynamic model, it was desirable to use this model to explore the physics of solid-fluid equilibria. Using the model that was to be developed, such phenomena as enthalpy changes of solvation of the solute in the supercritical solvent and changes in equilibrium solubility over wide ranges of temperature and pressure were to be studied.
3. EXPERIMENTAL APPARATUS AND PROCEDURE

3-1 Review of Alternative Experimental Methods

Experimentally, there are three feasible methods to determine equilibrium solubilities of slightly volatile solids in supercritical fluids. These are static methods, flow methods, and tracer methods.

Static Method

In the static method, the solute species to be extracted is contacted with the supercritical fluid in a batch vessel. After a sufficient length of time has passed so that an equilibrium solubility has been obtained, fluid samples are removed for analysis. Special care must be taken that no appreciable pressure perturbations occur during sampling. This is accomplished by taking very small samples or by a volumetric compensation technique (such as mercury displacement). Eisenbeiss (1964), Tsekhanskaya et al. (1962, 1964), and Diepen and Scheffer (1948b) measured equilibrium solubilities by this method.

Flow Method

In the flow method, the supercritical fluid is contacted with the solute species to be extracted in a flow extractor. The fluid stream exciting the extractor is then analyzed for composition. In order to assure that an equilibrium
solubility has been achieved, the solubility is determined at various flow rates and as long as the solubility is independent of flow rate, it can be assured that equilibrium is achieved. Several authors (Kurnik et al., 1981; Johnston and Eckert, 1981; McHugh and Paulaitis, 1981) have successfully used this method.

Tracer Method

Tracer methods of determining solubility are done typically by using a radioactive isotope of the desired solute species to be extracted. Using a static method, a Geiger counter is then attached to the fluid portion of the equilibrium cell. By careful calibration, the number rate of radioactive counts can be converted to an equilibrium solubility. Ewald et al. (1953) used this method to determine the equilibrium solubility of iodine in supercritical ethylene.

3-2 Description of Equipment

The experimental method used in this thesis to measure equilibrium solubilities was a one-pass flow system. A schematic is shown in Figure 3-1. Details of various sections of the equipment are discussed in Appendix VII.

A gas cylinder was connected to an AMINCO line filter, model 49-14405) which feed into an AMINCO single end compressor, model 46-13411). The compressor was connected to a two liter magendrive packless autoclave (Autovlave Engineers) whose purpose was to dampen the pressure fluctuations. In addition,
Figure 3-1

Equipment Flow-Chart

Key
TC - Temperature Controller
PC - Pressure Controller
P - Pressure Gauge
T - Thermocouple
an on/off pressure control switch, Autoclave P481-P713 was used to control the outlet pressure from the autoclave.

Upon leaving the autoclave, the fluid entered the tubular extractor (Autoclave, CNLX16012) which consisted of a 30.5 cm tube, 1.75 cm in diameter. In the tube were alternate layers of the solute species to be extracted and Pyrex wool. The Pyrex wool was used to prevent entrainment. A LFE 238 PID temperature controller attached to the heating tape kept the extractor isothermal. The temperature was monitored by an iron-constantan thermocouple (Omega SH48-ICSS-116U-15) housed inside the extractor. At the end of the extraction system was a regulating valve (Autoclave 30VM4882), the outlet of which was at a pressure of 1 bar. All materials of construction were 316 stainless steel.

Following the regulating valve were two U-tubes in series (Kimax 46025) which were immersed in a 50% ethylene glycol-water/dry ice solution. Complete precipitation of the solids occurred in the U-tubes, while the fluid phase was passed into a rotameter and dry test meter (Singer DTM-115-3) and finally vented to a hood. An iron-constantan thermocouple (Omega ICSS-116G-6) at the dry test meter outlet recorded the gas temperature. All thermocouple signals were displayed on a digital LED device (Omega 2170A). Analysis of the solid mixtures was done on a Perkin Elmer Sigma 2/Sigma 10 chromatograph/data station.
3-3 Operating Procedure

Approximately 40 gm of solid or solid mixture to be extracted was inserted into the extractor between alternate layers of glass wool. In order not to damage the thermocouple which was lodged in the center of the extractor, a 0.6 cm O.D. copper tube was inserted around the thermocouple while the extractor was being filled. Finally, the extractor was closed with an Autoclave coupling 20F41666.

The extraction assembly was mounted on the specially designed mounting bracket and all connections fastened. Heating tape was carefully wrapped around the extractor and connected to the temperature controller. The pressure controller switch was set to the desired operating pressure and the compressor started. Heating tape was also wrapped around the depressurization valve and attached to a variac to maintain a temperature greater than the melting point of the solid.

The data recorded was (1) the initial and final weights of both U-tubes; (2) the initial and final reading on the dry test meter; (3) the extraction temperature and pressure; (4) the barometric pressure, and (5) the temperature of the gas leaving the dry test meter.

To start the experiment, the depressurization valve was opened so that a steady flow rate of about 0.4 standard liters* per minute is obtained. The extraction was then continued

---

*At 1 atm pressure and 294 K.
until the amount of solid collected gave no more than one percent error in the experimental solubility. During this time, no operator intervention was necessary since the extraction temperature and pressure were automatically controlled.

3-4 Determination of Solid Mixture Composition

After precipitating solid mixtures in the U-tubes, it was necessary to determine their composition. In all cases, this was done by dissolving the solids in methylene chloride and injecting the sample into a gas chromatograph. A Perkin-Elmer Sigma 2/Sigma 10 chromatograph/data station was used with a FID detector. In Appendix VIII there is given complete documentation for using the gas chromatograph for all of the solid mixtures studied.

It was imperative to show that the solid mixtures extracted formed an eutectic solution -- not a solid solution. First, a melting point analysis was done on all of the solid mixtures and, in each case, an eutectic solution was found (see Appendix III). The extraction temperature for a given solid mixture was always below the eutectic temperature. Then, 50/50 solid mixtures of naphthalene and phenanthrene were melted, recrystallized, and then extracted. The extracted mixture had identical component solubilities as when the solids were physically mixed.

Also, the system phenanthrene-2,3-DMN was extracted with different ratios (50/50 and 30/70) of the two solids changed to the extractor. The extracted mixture had component
solubilities independent of the ratio charged. Thus, it can be concluded that eutectic solutions were formed for the solid systems studied.

3-5 Safety Considerations

Due to the high pressures used in this research (350 bar), special safety precautions had to be observed. These are as follows:

- The autoclave was fitted with a rupture disk rated for 411 bar at 295 K; the outlet was vented to a hood.
- Hydrocarbon leak detectors were used at all times when ethylene was used as the supercritical fluid.

In addition, care must be exercised that rapid pressure reductions do not occur. A rapid release in pressure of carbon dioxide has the potential of creating vapor explosions and shock waves. For details, see Kim-E (1981), Kim-E and Reid (1981) and Reid (1979).
4. RESULTS AND DISCUSSION OF RESULTS

In this section, experimental solid-fluid equilibrium data are given for both binary and multicomponent systems. Also, graphs of the data points correlated with the Peng-Robinson equation of state are shown.

4-1 Binary Solid-Fluid Equilibrium Data

Presented in Tables 4-1 through 4-9 are experimental equilibrium data for the solubility of pure component solids in supercritical carbon dioxide and ethylene at several temperatures and pressures. Also shown with the data are isothermal Peng-Robinson binary interaction coefficients obtained by use of a non-linear least squares regression. Figures 4-1 through 4-9 show the experimental data are correlated with the Peng-Robinson equation of state.

Binary Interaction Coefficients

In modelling the binary solid-fluid equilibrium problem using the Peng-Robinson equation of state, there exists an unknown binary interaction parameter, $k_{ij}$, which must be determined from experimental data (refer to Eq. 2-3.27). The binary interaction parameter has been found to be a weak function of temperature, but independent of pressure and composition -- at least over the range studied here. One
<table>
<thead>
<tr>
<th>T=308 K</th>
<th>T=318 K</th>
<th>T=328 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(bar)</td>
<td>y</td>
<td>P(bar)</td>
</tr>
<tr>
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<td>2.20x10^{-3}</td>
<td>99</td>
</tr>
<tr>
<td>143</td>
<td>4.40x10^{-3}</td>
<td>145</td>
</tr>
<tr>
<td>194</td>
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</tr>
<tr>
<td>242</td>
<td>5.83x10^{-3}</td>
<td>242</td>
</tr>
<tr>
<td>280</td>
<td>6.43x10^{-3}</td>
<td>280</td>
</tr>
</tbody>
</table>

k_{12} = 0.0996  
0.102  
0.107
Table 4-2

C\textsubscript{2}H\textsubscript{4}; 2,3-Dimethylnaphthalene Data

<table>
<thead>
<tr>
<th>T=308 K</th>
<th>T=318 K</th>
<th>T=328 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(bar)</td>
<td>y</td>
<td>P(bar)</td>
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<td>9.66x10\textsuperscript{-3}</td>
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</tr>
<tr>
<td>240</td>
<td>1.27x10\textsuperscript{-2}</td>
<td>240</td>
</tr>
<tr>
<td>280</td>
<td>1.51x10\textsuperscript{-2}</td>
<td>280</td>
</tr>
</tbody>
</table>

k\textsubscript{12} 0.0246 0.0209 0.0147
Table 4-3

$\text{CO}_2; \ 2,6-$Dimethylnaphthalene Data

<table>
<thead>
<tr>
<th>$T=308 \text{ K}$</th>
<th>$T=318 \text{ K}$</th>
<th>$T=328 \text{ K}$</th>
</tr>
</thead>
<tbody>
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<td>$\text{P (bar)}$</td>
<td>$\text{y}$</td>
<td>$\text{P (bar)}$</td>
</tr>
<tr>
<td>97</td>
<td>$1.91 \times 10^{-3}$</td>
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</tr>
<tr>
<td>145</td>
<td>$2.97 \times 10^{-3}$</td>
<td>146</td>
</tr>
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<td>195</td>
<td>$3.83 \times 10^{-3}$</td>
<td>194</td>
</tr>
<tr>
<td>245</td>
<td>$4.01 \times 10^{-3}$</td>
<td>244</td>
</tr>
<tr>
<td>280</td>
<td>$4.47 \times 10^{-3}$</td>
<td>280</td>
</tr>
</tbody>
</table>

$k_{12}$          | 0.102            |                  | 0.0989            |                  | 0.100            |
Table 4-4

\( \text{C}_2\text{H}_4; \) 2,6-Dimethylnaphthalene Data

<table>
<thead>
<tr>
<th>( P(\text{bar}) )</th>
<th>( T=308 \text{ K} )</th>
<th>( T=318 \text{ K} )</th>
<th>( T=318 \text{ K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( y )</td>
<td>( y )</td>
<td>( y )</td>
</tr>
<tr>
<td>80</td>
<td>( 4.84 \times 10^{-4} )</td>
<td>( 1.89 \times 10^{-4} )</td>
<td>( 2.36 \times 10^{-4} )</td>
</tr>
<tr>
<td>120</td>
<td>( 2.35 \times 10^{-3} )</td>
<td>( 2.20 \times 10^{-3} )</td>
<td>( 2.20 \times 10^{-3} )</td>
</tr>
<tr>
<td>159</td>
<td>( 4.62 \times 10^{-3} )</td>
<td>( 5.56 \times 10^{-3} )</td>
<td>( 6.74 \times 10^{-3} )</td>
</tr>
<tr>
<td>200</td>
<td>( 6.95 \times 10^{-3} )</td>
<td>( 9.08 \times 10^{-3} )</td>
<td>( 1.30 \times 10^{-2} )</td>
</tr>
<tr>
<td>240</td>
<td>( 9.28 \times 10^{-3} )</td>
<td>( 1.39 \times 10^{-2} )</td>
<td>( 2.00 \times 10^{-2} )</td>
</tr>
<tr>
<td>280</td>
<td>( 1.10 \times 10^{-2} )</td>
<td>( 1.71 \times 10^{-2} )</td>
<td>( 2.75 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

\( k_{12} \) 0.0226               0.0201               0.0167
### Table 4-5

**CO$_2$ - Phenanthrene Data**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P$ (bar)</th>
<th>$k_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T=308 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>7.86x10$^{-4}$</td>
<td>0.115</td>
</tr>
<tr>
<td>160</td>
<td>1.38x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>1.58x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>1.70x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>1.78x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td><strong>T=318 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>8.50x10$^{-4}$</td>
<td>0.113</td>
</tr>
<tr>
<td>160</td>
<td>1.40x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>1.71x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>2.23x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>2.29x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td><strong>T=328 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>4.65x10$^{-4}$</td>
<td>0.108</td>
</tr>
<tr>
<td>160</td>
<td>1.52x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.14x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>2.79x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>3.20x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td><strong>T=338 K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>3.29x10$^{-4}$</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>1.19x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.37x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>3.28x10$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>3.84x10$^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

$k_{12}$ values are given for each temperature to indicate the contribution of phenanthrene to the CO$_2$ adsorption at different pressures.
Table 4-6

C$_2$H$_4$ - Phenanthrene Data

<table>
<thead>
<tr>
<th>T=318 K</th>
<th>T=328 K</th>
<th>T=338 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(bar)</td>
<td>y</td>
<td>P(bar)</td>
</tr>
<tr>
<td>120</td>
<td>8.16x10^{-4}</td>
<td>120</td>
</tr>
<tr>
<td>160</td>
<td>1.75x10^{-3}</td>
<td>160</td>
</tr>
<tr>
<td>200</td>
<td>2.67x10^{-3}</td>
<td>200</td>
</tr>
<tr>
<td>240</td>
<td>3.71x10^{-3}</td>
<td>240</td>
</tr>
<tr>
<td>280</td>
<td>4.56x10^{-3}</td>
<td>280</td>
</tr>
</tbody>
</table>

$k_{12}$ 0.0459 0.0356 0.0318
Table 4-7

**CO$_2$ - Benzoic Acid Data**

<table>
<thead>
<tr>
<th>$T=308$ K</th>
<th>$T=318$ K</th>
<th>$T=328$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$(bar)</td>
<td>$y$</td>
<td>$P$(bar)</td>
</tr>
<tr>
<td>120</td>
<td>$1.38 \times 10^{-3}$</td>
<td>120</td>
</tr>
<tr>
<td>160</td>
<td>$2.37 \times 10^{-3}$</td>
<td>160</td>
</tr>
<tr>
<td>200</td>
<td>$3.01 \times 10^{-3}$</td>
<td>200</td>
</tr>
<tr>
<td>240</td>
<td>$3.10 \times 10^{-3}$</td>
<td>240</td>
</tr>
<tr>
<td>280</td>
<td>$3.31 \times 10^{-3}$</td>
<td>280</td>
</tr>
</tbody>
</table>

$k_{12} = 0.0183$  

$T=338$ K

<table>
<thead>
<tr>
<th>$P$(bar)</th>
<th>$y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>$3.21 \times 10^{-4}$</td>
</tr>
<tr>
<td>160</td>
<td>$1.72 \times 10^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>$4.11 \times 10^{-3}$</td>
</tr>
<tr>
<td>240</td>
<td>$6.96 \times 10^{-3}$</td>
</tr>
<tr>
<td>280</td>
<td>$9.84 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

$k_{12} = -0.0124$
<table>
<thead>
<tr>
<th>P (bar)</th>
<th>( \gamma )</th>
<th>P (bar)</th>
<th>( \gamma )</th>
<th>P (bar)</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>5.76x10^{-4}</td>
<td>120</td>
<td>5.48x10^{-4}</td>
<td>120</td>
<td>5.44x10^{-4}</td>
</tr>
<tr>
<td>160</td>
<td>1.36x10^{-3}</td>
<td>160</td>
<td>1.61x10^{-3}</td>
<td>160</td>
<td>1.93x10^{-3}</td>
</tr>
<tr>
<td>200</td>
<td>1.90x10^{-3}</td>
<td>200</td>
<td>2.61x10^{-3}</td>
<td>200</td>
<td>3.51x10^{-3}</td>
</tr>
<tr>
<td>240</td>
<td>2.90x10^{-3}</td>
<td>240</td>
<td>3.61x10^{-3}</td>
<td>240</td>
<td>4.94x10^{-3}</td>
</tr>
<tr>
<td>280</td>
<td>2.91x10^{-3}</td>
<td>280</td>
<td>4.01x10^{-3}</td>
<td>280</td>
<td>6.19x10^{-3}</td>
</tr>
</tbody>
</table>

\( k_{12} \) = -0.0563, \ -0.0642, \ -0.0756
Table 4-9

CO₂ - Hexachloroethane Data

\[
\begin{array}{ccc}
\text{T=308 K} & \text{T=318 K} & \text{T=328 K} \\
\hline
P(\text{bar}) & y & P(\text{bar}) & y & P(\text{bar}) & y \\
\hline
99 & 1.45 \times 10^{-2} & 100 & 1.04 \times 10^{-2} & 97 & 3.80 \times 10^{-3} \\
149 & 1.86 \times 10^{-2} & 148 & 2.40 \times 10^{-2} & 145 & 2.32 \times 10^{-2} \\
199 & 1.97 \times 10^{-2} & 198 & 2.60 \times 10^{-2} & 195 & 3.89 \times 10^{-2} \\
248 & 2.00 \times 10^{-2} & 247 & 2.78 \times 10^{-2} & 245 & 3.94 \times 10^{-2} \\
280 & 1.80 \times 10^{-2} & 280 & 2.71 \times 10^{-2} & 280 & 3.90 \times 10^{-2} \\
\hline
k_{12} & 0.129 & 0.123 & 0.116 \\
\end{array}
\]
Solubility of 2,3-Dimethylnaphthalene in Super-critical Carbon Dioxide

**Figure 4-1**

Solubility of 2,3-Dimethylnaphthalene in Super-critical Carbon Dioxide
Solubility of 2,3-Dimethylnaphthalene in Super-critical Ethylene

Figure 4-2
Solubility of 2,6-Dimethylnaphthalene in Supercritical Carbon Dioxide

Figure 4-3
Solubility of 2,6-Dimethylnaphthalene in Supercritical Ethylene

**Figure 4-4**
Figure 4-5

Solubility of Phenanthrene in Supercritical Carbon Dioxide
Solubility of Phenanthrene in Supercritical Ethylene

Figure 4-6
Solubility of Benzoic Acid in Supercritical Carbon Dioxide

Figure 4-7
Solubility of Benzoic Acid in Supercritical Ethylene

Figure 4-8
Solubility of Hexachloroethane in Supercritical Carbon Dioxide

Figure 4-9
data point is sufficient (mathematically) to determine the value of \( k_{ij}(T) \) at each temperature, but an optimum value of \( k_{ij}(T) \) can be found by regressing isothermal experimental data. It has been found that minimizing the objective function \( J \), where

\[
J = \min \sum_{i} \left( \frac{\ln y_i^0 - \ln y_i^E}{y_i^E} \right)^2
\]

subject to

\[
f_{li}^S = f_{li}^F
\]

where \( y_i^0 \) = mole fraction of component \( i \) predicted from Peng-Robinson equation of state \( y_i^E \) = experimental value of mole fraction.

enables one to obtain \( k_{ij}(T) \) from isothermal experimental data. The computer software necessary to perform these calculations is given in Appendix VI.

Holla (1980) has shown that if it is desired to model isothermal binary solid-fluid equilibrium data, one experimental compositional datum point is sufficient to determine an accurate value of \( k_{ij}(T) \) if this one point is measured at a pressure \( P' \), where

\[
P' = 3.8 \sqrt{P_{c1}P_{c2}}
\]

If \( k_{ij}(T) \) is calculated at \( P' \), then the complete isotherm
can be generated almost as accurately as if $k_{ij}(T)$ were obtained by regressing all isothermal data.

Discussion of Binary Solid-Fluid Equilibrium Results

As Figures 4-1 through 4-9 show, the effects of temperature and pressure solubility for all the solid species are similar. There are three pressure regimes: At low pressures an increase in temperature increases solubility; at intermediate pressures, an increase in temperature decreases solubility (retrograde solidification) — more apparent for carbon dioxide than ethylene; and at high pressures an increase in temperature enhances solubility. The reason that retrograde solidification region is more significant for carbon dioxide than ethylene is because CO₂ is at a lower reduced temperature and therefore the density dependence on pressure is larger.

In all cases, the Peng-Robinson equation of state is able to correlate the data well providing that the proper binary interaction parameter is used. Although the binary parameters were independent of pressure and composition, examination of Tables 4-1 through 4-9 shows a weak linear dependence on temperature.

The outstanding feature of all the data and simulations is the extreme sensitivity of equilibrium solubility on temperature and pressure. For example, consider Figure 4-10 (benzoic acid-carbon dioxide). There is about a two order of magnitude change in solubility when decreasing pressure and simultaneously increasing temperature from (318 K, 180 bar)
Solubility of Benzoic Acid in Super-critical Carbon Dioxide

Figure 4-10
to (338 K, 90 bar). Also shown for convenience in Figure 4-10 is the solubility predicted by the ideal gas law:

$$y_i^{ID} = \frac{P_{vp_i}}{P}$$

(4-1.4)

The ratio of real to ideal solubilities is called the enhancement factor and can take on values of $10^6$ or larger.

Figure 4-11 shows a simulation of the case naphthalene in supercritical nitrogen. In no case does the isothermal solubility of naphthalene even equal the solubility at one bar pressure. The reason is because under these temperature and pressure conditions, nitrogen is nearly an ideal gas with fugacity coefficients and compressibility factors near unity. Also, the density of nitrogen at high pressures is approximately 0.1 gm/cm$^3$ as compared to 0.8 gm/cm$^3$ for carbon dioxide under the same conditions. The dissolving power of supercritical fluids depends both on the density (the higher the greater) and the nonideality (fugacity coefficient) of the fluid phase.

4-2 Ternary Solid-Fluid Equilibrium Data

Presented in Tables 4-10 through 4-20 are experimental equilibrium data for the solubility of solid mixtures in supercritical carbon dioxide and ethylene at several temperatures and pressures. Also shown with the data are isothermal binary solute-solute interaction coefficients. Figures 4-12 through 4-23 show the experimental data correlated with the
Solubility of Naphthalene in Supercritical Nitrogen

Figure 4-11
Table 4-10

CO₂ (1); Benzoic Acid (2); Naphthalene (3) Mixture Data

\( T = 308K \)

<table>
<thead>
<tr>
<th>( P (\text{bar}) )</th>
<th>( y(\text{Benzoic acid}) )</th>
<th>( y(\text{Naphthalene}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>( 2.93 \times 10^{-3} )</td>
<td>( 1.44 \times 10^{-2} )</td>
</tr>
<tr>
<td>160</td>
<td>( 4.01 \times 10^{-3} )</td>
<td>( 1.73 \times 10^{-2} )</td>
</tr>
<tr>
<td>200</td>
<td>( 5.22 \times 10^{-3} )</td>
<td>( 2.06 \times 10^{-2} )</td>
</tr>
<tr>
<td>240</td>
<td>( 5.46 \times 10^{-3} )</td>
<td>( 2.08 \times 10^{-2} )</td>
</tr>
<tr>
<td>280</td>
<td>( 5.61 \times 10^{-3} )</td>
<td>( 2.12 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

\( k_{12} = 0.0183 \)
\( k_{13} = 0.0959 \)
\( k_{23} = 0.060 \)
### Table 4-11

CO$_2$ (l); Benzoic Acid (2); Naphthalene (3) Mixture Data

T=318K

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>y(Benzoic acid)</th>
<th>y(Naphthalene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>3.49x10^{-3}</td>
<td>1.76x10^{-2}</td>
</tr>
<tr>
<td>160</td>
<td>6.96x10^{-3}</td>
<td>2.61x10^{-2}</td>
</tr>
<tr>
<td>200</td>
<td>1.00x10^{-2}</td>
<td>3.25x10^{-2}</td>
</tr>
<tr>
<td>240</td>
<td>1.21x10^{-2}</td>
<td>3.67x10^{-2}</td>
</tr>
<tr>
<td>280</td>
<td>1.26x10^{-2}</td>
<td>3.66x10^{-2}</td>
</tr>
</tbody>
</table>

$k_{12} = 0.00994$

$k_{13} = 0.0968$

$k_{23} = 0.015$
# Table 4-12

CO$_2$ (1); 2,3-DMN (2); Naphthalene (3) Mixture Data

\[ T=308K \]

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>$y(2,3$-DMN)</th>
<th>$y$(Naphthalene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>6.52x10$^{-3}$</td>
<td>1.85x10$^{-2}$</td>
</tr>
<tr>
<td>160</td>
<td>8.80x10$^{-3}$</td>
<td>2.41x10$^{-2}$</td>
</tr>
<tr>
<td>200</td>
<td>9.34x10$^{-3}$</td>
<td>2.39x10$^{-2}$</td>
</tr>
<tr>
<td>240</td>
<td>9.95x10$^{-3}$</td>
<td>2.58x10$^{-2}$</td>
</tr>
<tr>
<td>280</td>
<td>9.90x10$^{-3}$</td>
<td>2.62x10$^{-2}$</td>
</tr>
</tbody>
</table>

$k_{12} = 0.0996$

$k_{13} = 0.0959$

$k_{23} = 0.04$
Table 4-13

$\text{CO}_2$ (1); Naphthalene (2); Phenanthrene (3) Mixture Data

$T=308K$

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>$y$ (Naphthalene)</th>
<th>$y$ (Phenanthrene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>$1.47 \times 10^{-2}$</td>
<td>$1.65 \times 10^{-3}$</td>
</tr>
<tr>
<td>140</td>
<td>$1.62 \times 10^{-2}$</td>
<td>$1.92 \times 10^{-3}$</td>
</tr>
<tr>
<td>160</td>
<td>$1.76 \times 10^{-2}$</td>
<td>$2.32 \times 10^{-3}$</td>
</tr>
<tr>
<td>180</td>
<td>$1.84 \times 10^{-2}$</td>
<td>$2.54 \times 10^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>$1.88 \times 10^{-2}$</td>
<td>$2.59 \times 10^{-3}$</td>
</tr>
<tr>
<td>220</td>
<td>$2.08 \times 10^{-2}$</td>
<td>$2.90 \times 10^{-3}$</td>
</tr>
<tr>
<td>240</td>
<td>$2.14 \times 10^{-2}$</td>
<td>$2.93 \times 10^{-3}$</td>
</tr>
<tr>
<td>260</td>
<td>$2.13 \times 10^{-2}$</td>
<td>$3.01 \times 10^{-3}$</td>
</tr>
<tr>
<td>280</td>
<td>$2.14 \times 10^{-2}$</td>
<td>$3.21 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

$k_{12} = 0.0959$

$k_{13} = 0.115$

$k_{23} = 0.05$
Table 4-14

CO₂ (1); 2,3-DMN (2); 2,6-DMN (3) Mixture Data

T=308K

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>y(2,3-DMN)</th>
<th>y(2,6-DMN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>3.92x10⁻³</td>
<td>3.04x10⁻³</td>
</tr>
<tr>
<td>140</td>
<td>4.34x10⁻³</td>
<td>3.36x10⁻³</td>
</tr>
<tr>
<td>160</td>
<td>4.94x10⁻³</td>
<td>3.87x10⁻³</td>
</tr>
<tr>
<td>180</td>
<td>5.21x10⁻³</td>
<td>4.02x10⁻³</td>
</tr>
<tr>
<td>200</td>
<td>5.68x10⁻³</td>
<td>4.38x10⁻³</td>
</tr>
<tr>
<td>220</td>
<td>6.00x10⁻³</td>
<td>4.62x10⁻³</td>
</tr>
<tr>
<td>240</td>
<td>6.03x10⁻³</td>
<td>4.57x10⁻³</td>
</tr>
<tr>
<td>260</td>
<td>6.16x10⁻³</td>
<td>4.62x10⁻³</td>
</tr>
<tr>
<td>280</td>
<td>6.40x10⁻³</td>
<td>4.74x10⁻³</td>
</tr>
</tbody>
</table>

k₁₂ = 0.0996
k₁₃ = 0.102
k₂₃ = 0.20
Table 4-15

\( \text{CO}_2 (1); \text{2,3-DMN} \ (2); \text{2,6-DMN} \ (3) \) Mixture Data

\( T=318K \)

<table>
<thead>
<tr>
<th>( P ) (bar)</th>
<th>( y(2,3-\text{DMN}) )</th>
<th>( y(2,6-\text{DMN}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>3.67x10^{-3}</td>
<td>3.40x10^{-3}</td>
</tr>
<tr>
<td>140</td>
<td>5.18x10^{-3}</td>
<td>4.47x10^{-3}</td>
</tr>
<tr>
<td>160</td>
<td>6.51x10^{-3}</td>
<td>5.48x10^{-3}</td>
</tr>
<tr>
<td>180</td>
<td>7.36x10^{-3}</td>
<td>6.14x10^{-3}</td>
</tr>
<tr>
<td>200</td>
<td>7.95x10^{-3}</td>
<td>6.59x10^{-3}</td>
</tr>
<tr>
<td>220</td>
<td>8.24x10^{-3}</td>
<td>6.78x10^{-3}</td>
</tr>
<tr>
<td>240</td>
<td>9.01x10^{-3}</td>
<td>7.39x10^{-3}</td>
</tr>
<tr>
<td>260</td>
<td>9.45x10^{-3}</td>
<td>7.58x10^{-3}</td>
</tr>
<tr>
<td>280</td>
<td>1.01x10^{-3}</td>
<td>8.13x10^{-3}</td>
</tr>
</tbody>
</table>

\( k_{12} = 0.102 \)

\( k_{13} = 0.0989 \)

\( k_{23} = 0.1 \)
Table 4-16
C$_2$H$_4$ (1); 2,3-DMN (2); 2,6-DMN (3) Mixture Data
T=308K

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>y(2,3-DMN)</th>
<th>y(2,6-DMN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>5.35x10^{-3}</td>
<td>4.41x10^{-3}</td>
</tr>
<tr>
<td>140</td>
<td>7.46x10^{-3}</td>
<td>5.97x10^{-3}</td>
</tr>
<tr>
<td>160</td>
<td>9.70x10^{-3}</td>
<td>7.73x10^{-3}</td>
</tr>
<tr>
<td>180</td>
<td>1.19x10^{-2}</td>
<td>9.45x10^{-3}</td>
</tr>
<tr>
<td>200</td>
<td>1.40x10^{-2}</td>
<td>1.08x10^{-2}</td>
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<tr>
<td>220</td>
<td>1.62x10^{-2}</td>
<td>1.24x10^{-2}</td>
</tr>
<tr>
<td>240</td>
<td>1.62x10^{-2}</td>
<td>1.25x10^{-2}</td>
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<tr>
<td>260</td>
<td>1.76x10^{-2}</td>
<td>1.34x10^{-2}</td>
</tr>
<tr>
<td>280</td>
<td>1.85x10^{-2}</td>
<td>1.40x10^{-2}</td>
</tr>
</tbody>
</table>

$k_{12} = 0.0246$
$k_{13} = 0.0226$
$k_{23} = 0.05$
Table 4-17

CO₂ (1); Benzoic Acid (2); Phenanthrene (3) Mixture Data
T=308K

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>y(Benzoic acid)</th>
<th>y(Phenanthrene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>1.84x10⁻³</td>
<td>1.02x10⁻³</td>
</tr>
<tr>
<td>160</td>
<td>2.44x10⁻³</td>
<td>1.36x10⁻³</td>
</tr>
<tr>
<td>200</td>
<td>2.95x10⁻³</td>
<td>1.63x10⁻³</td>
</tr>
<tr>
<td>240</td>
<td>3.28x10⁻³</td>
<td>1.87x10⁻³</td>
</tr>
<tr>
<td>280</td>
<td>3.70x10⁻³</td>
<td>2.05x10⁻³</td>
</tr>
</tbody>
</table>

k₁₂ = 0.0183
k₁₃ = 0.115
k₂₃ = 0.2
The correlation of mixture data by the Peng-Robinson Equation of State is not possible.
### Table 4-19

**CO$_2$; 2,3-DMN; Phenanthrene Mixture Data**  
**T=308K**

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>$y(2,3\text{-DMN})$</th>
<th>$y(\text{Phenanthrene})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>2.89x10$^{-3}$</td>
<td>7.33x10$^{-4}$</td>
</tr>
<tr>
<td>160</td>
<td>3.56x10$^{-3}$</td>
<td>1.00x10$^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>4.23x10$^{-3}$</td>
<td>1.24x10$^{-3}$</td>
</tr>
<tr>
<td>240</td>
<td>4.43x10$^{-3}$</td>
<td>1.43x10$^{-3}$</td>
</tr>
<tr>
<td>280</td>
<td>4.50x10$^{-3}$</td>
<td>1.48x10$^{-3}$</td>
</tr>
</tbody>
</table>

The correlation of mixture data by the Peng-Robinson equation of state is not possible.
Table 4-20

CO$_2$; 2,3-DMN; Phenanthrene Mixture Data

$T$=318K

<table>
<thead>
<tr>
<th>$P$ (bar)</th>
<th>$y$(2,3-DMN)</th>
<th>$y$(Phenanthrene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>2.47x10$^{-3}$</td>
<td>5.27x10$^{-4}$</td>
</tr>
<tr>
<td>160</td>
<td>4.33x10$^{-3}$</td>
<td>1.19x10$^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>5.54x10$^{-3}$</td>
<td>1.71x10$^{-3}$</td>
</tr>
<tr>
<td>240</td>
<td>5.85x10$^{-3}$</td>
<td>1.96x10$^{-3}$</td>
</tr>
<tr>
<td>280</td>
<td>6.97x10$^{-3}$</td>
<td>2.33x10$^{-3}$</td>
</tr>
</tbody>
</table>

The correlation of mixture data by the Peng-Robinson equation of state is not possible.
Solubility of Naphthalene from a Phenanthrene-Naphthalene Mixture in Supercritical Carbon Dioxide

Figure 4-12
Solubility of Phenanthrene from a Phenanthrene-Naphthalene Mixture in Supercritical Carbon Dioxide

Figure 4-13
Solubility of Phenanthrene from a Phenanthrene-Naphthalene Mixture in Supercritical Carbon Dioxide

Figure 4-13
Figure 4-14

Solubility of 2,3-Dimethylnaphthalene from a 2,3-Dimethylnaphthalene-Naphthalene Mixture in Supercritical Carbon Dioxide at 308 K.

System CO₂; 2,3-DMN; Naphthalene
(1) (2) (3)
Temperature = 308 K
Pure 2,3-DMN in CO₂
Mixture 2,3-DMN in CO₂
PR Equation of State

\[ k_{12} = 0.0996 \]
\[ k_{13} = 0.0959 \]
\[ k_{23} = 0.04 \]

PRESSURE (BARS)

PRESSURE (BARS)

Y₂₃-DMN
Solubility of Naphthalene from a 2,3-Dimethyl-naphthalene-Naphthalene Mixture in Supercritical Carbon Dioxide at 308 K.

Figure 4-15
Solubility of Benzoic Acid from a Benzoic Acid-Naphthalene Mixture in Supercritical Carbon Dioxide at 308 K.

Figure 4-16
**System:** CO\textsubscript{2}: Naphthalene: Acid (1) (2) (3)

- **Temperature** = 308 K
- **Pure Naphthalene in CO\textsubscript{2}**
- **Mixture Naphthalene in CO\textsubscript{2}

**PR Equation of State**

- \( k_{12} = 0.0959 \)
- \( k_{13} = 0.0183 \)
- \( k_{23} = 0.000 \)

† Data of Tsakhanskaya et al. (1964)

**Solubility of Naphthalene from a Benzoic Acid-Naphthalene Mixture in Supercritical Carbon Dioxide at 308 K.**

**Figure 4-17**
Solubility of 2,6-Dimethylnaphthalene from a 2,6-Dimethylnaphthalene; 2,3-Dimethylnaphthalene Mixture in Supercritical Carbon Dioxide at 308 K.

Figure 4-18
Solubility of 2,3-Dimethylnaphthalene from a 2,6-Dimethylnaphthalene; 2,3-Dimethylnaphthalene Mixture in Supercritical Carbon Dioxide at 308 K.

Figure 4-19
Solubility of 2,3-Dimethylnaphthalene from a 2,3-Dimethylnaphthalene; 2,6-Dimethylnaphthalene Mixture in Supercritical Ethylene at 308 K.

Figure 4-20
Solubility of 2,6-Dimethylnaphthalene from a 2,3-Dimethylnaphthalene; 2,6-Dimethylnaphthalene Mixture in Supercritical Ethylene at 308 K.

Figure 4-21
System: CO₂: 2,3-DMN; 2,6-DMN

Temperature = 318 K

Pure 2,3-DMN in CO₂
● Mixture 2,3-DMN in CO₂

PR Equation of State

\[ k_{12} = 0.102 \]
\[ k_{13} = 0.0989 \]
\[ k_{23} = 0.1 \]

Solubility of 2,3-Dimethylnaphthalene from a 2,3-Dimethylnaphthalene; 2,6-Dimethylnaphthalene Mixture in Supercritical Carbon Dioxide at 318 K.

Figure 4-22
Solubility of 2,6-Dimethylnaphthalene from a 2,3-Dimethylnaphthalene; 2,6-Dimethylnaphthalene Mixture in Supercritical Carbon Dioxide at 318 K.

Figure 4-23
Peng-Robinson equation of state.

**Binary Solute-Solute Interaction Coefficients**

In modelling ternary solid-fluid equilibrium problems using the Peng-Robinson equation of state, it was found that in most cases the ternary data could not be well correlated unless non-zero values of the binary solute-solute interaction coefficients \( k_{23} \) were used. For an appropriately determined pressure, and composition independent solute-solute parameter, correlation of isothermal ternary data was generally successful. The evaluation of the solute-solute parameter was done by a trial and error procedure.

**Selectivities in Ternary Solid-Fluid Equilibria Systems**

Selectivities (ratios) of component solute concentrations in supercritical fluids have been found to have the characteristic shape as shown in Figure 4-24 for the system naphthalene-phananthrene-CO\(_2\) and Figure 4-25 for the system naphthalene-2,3-DMN-CO\(_2\). At 1 bar, the selectivity is just the vapor pressure ratio. As the pressure increases, there is a sharp drop in selectivity, especially near the solvent critical point. Finally, at pressures well above the solvent critical point, the selectivity is nearly constant -- at a relatively low value. The effect of temperature on selectivity is shown in Figure 4-26 for the system naphthalene-benzoic acid. Only at pressures at and below the critical pressure does temperature have an effect on selectivity.

The conclusion to be drawn from the selectivity curves
Selectivities in the Naphthalene-Phenanthrene-Carbon Dioxide System

Figure 4-24
Selectivities in the Naphthalene-2,3-Dimethyl-naphthalene-Carbon Dioxide System

\[ \alpha = \frac{Y_{\text{Naphthalene}}}{Y_{2,3-\text{DMN}}} \]

Temperature = 308 K

- PR Equation of State
  \[ k_{12} = 0.0959 \]
  \[ k_{13} = 0.0996 \]
  \[ k_{23} = 0.04 \]

**Figure 4-25**
Selectivities in the Naphthalene-Benzolic Acid-
Carbon Dioxide System

**Figure 4-26**
is that at high reduced pressures ($P_r \gg 1$), the selectivity is low and therefore, both "high" and "low" volatile species will be extracted. In order to get a good separation of solute materials, the pressure must be kept less than the solvent critical pressure, but here, the solubilities are also low. (At pressures of about 1000 bar, computer simulations predict that selectivities increase slightly.)

Discussion of Ternary Solid-Fluid Equilibrium Results

Ternary solid-fluid equilibria exhibits similar phenomena to binary solid-fluid equilibrium. There are, however, some unique characteristics: component solubilities in ternary systems can be significantly higher than the solubility of the pure component in a supercritical fluid under identical operating conditions.

Careful examination of the ternary solid-fluid equilibrium data taken shows that component solubilities are significantly increased when an additional solid component of high solubility ($> 10^{-2}$ mole fraction) is added to the first solid. If, however, the solubilities of both pure components are low ($< 10^{-3}$ mole fraction), then the solubility of the components in the mixture will be almost identical to the pure component solubilities. If the solubilities of both components are high ($> 10^{-2}$ mole fraction), then the solubilities of both components in the mixture are significantly increased.

Physically, what seems to be happening is that a high
concentration of a hydrocarbon solute in the supercritical fluid phase aids in dissolving other hydrocarbon solutes --- by using the rule that "like dissolves like." In one case studied in this thesis, however, there was a slight (10%) decrease in component solubilities in a ternary mixture as compared to the binary system. This case was the system phenanthrene; 2,3-DMN; CO₂.

In most cases, the ternary data can be correlated well by the Peng-Robinson equation of state. Correlation of these ternary systems requires, however, the use of a solute-solute interaction coefficient (k₂₃). To check the physical meaning of this solute-solute parameter, the isomer system 2,3-DMN; 2,6-DMN was examined in both supercritical carbon dioxide and ethylene. Correlation of the resultant data showed that k₂₃ was dependent on the supercritical fluid (component 1). Thus it can be concluded that k₂₃ is an adjustable parameter -- not a true binary constant.

4-3 Experimental Proof that T < Tq

As discussed in Chapter 2-2, it is only for system temperatures less than the upper critical end point temperature (Tq) that one is guaranteed that no liquid phase will form. Since all of the thermodynamic modelling used in this thesis incorporated the assumption of T < Tq, it is necessary to obtain experimental proof that this assumption was valid. Such a proof can be inferred with experiments using the system naphthalene-ethylene. For this system (Diepen and
Scheffer, 1953):

\[ T_\text{q} = 325.3 \text{ K} \]
\[ P_\text{q} = 176 \text{ BAR} \]

Experimental data at 318 K and 328 K and for many pressures are shown for naphthalene in supercritical ethylene in Figure 4-27. At 318 K, the solubility data agree well with (Tsekhanskaya, 1964). At 328 K, however, \( T > T_\text{q} \) and the experimental isothermal data show entirely different behavior. By examining the P-T space for this isotherm, the large discontinuity in concentration can be explained and the lack of such a discontinuity in concentration in the binary and ternary systems studied in this thesis suggest that \( T < T_\text{q} \).

Explanation of the discontinuity in concentration is as follows. Consider isotherms \( T_3 \) and \( T_5 \) of Figure 2-15. Upon raising the system pressure on isotherm \( T_3 \), which is below \( T_\text{q'} \), there is a continuous change in concentration for a saturated solution. However, for temperature \( T_5 \), which is greater than \( T_\text{q'} \), it is apparent that upon increasing the system pressure while keeping the fluid phase saturated with solid, that the concentration will have a discontinuity because of the \( L_1+L_2 \) region which is "jumped". Furthermore, for \( T \geq T_\text{q'} \), the discontinuity will occur at a pressure \( P<P_\text{q'} \). This discontinuity predicted by P-T phase space is what was found experimentally for the system ethylene-naphthalene at 328 K in Figure 4-27. Scattering of the data at high...
A Close Examination of the System Naphthalene-Ethylene Near the Upper Critical End Point

System: Ethylene - Naphthalene

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>318</td>
<td>O</td>
</tr>
<tr>
<td>328</td>
<td>●</td>
</tr>
</tbody>
</table>

T (UCEP) = 325.3 K
P (UCEP) = 176 BAR

Figure 4-27
pressures (and concentrations) results because of plugging problems in the pressure let-down value. Finally, the lack of such a discontinuity in the binary (and by analogy ternary) systems studied in this thesis certainly indicates that in all cases $T < T_q$. 
5. UNIQUE SOLUBILITY PHENOMENA OF SUPERCRITICAL FLUIDS

Solubility of solids in supercritical fluids exhibit several unique phenomena not present in typical phase equilibria situations. These phenomena are the existence of a maximum in isothermal solubilities at high pressures, a solubility minimum at low pressures, and a method to achieve essentially 100% solubility of a solid in a supercritical phase. Solubility maxima (Kurnik and Reid, 1981) and a method to achieve 100% solubilities of a solid in a supercritical phase are new findings in this thesis.

5-1 Solubility Minima

As is clearly shown in typical isothermal solubility diagrams of mole fraction versus pressure, a definite solubility minimum exists at relatively low pressures (10 - 30 bar). At these pressures, the virial equation of state is applicable and so it is possible to solve analytically for the pressure and mole fraction at the solubility minimum. As is shown by Hinckley and Reid (1964), the pressure and mole fraction at the solubility minimum for binary systems is:

\[ y(\text{min}) = \frac{2eB_{12}Pv_{1}}{RT} \] (5-1.1)
Knowing the pressure for the minimum solubility is important in deciding optimum operating pressures for low temperature purification systems such as in heat exchangers used to remove carbon dioxide from air.

5-2 Solubility Maxima

Of the data and correlations shown in Figures 4-1 to 4-9, the highest pressure attained was 280 bar. As these figures indicate, the isothermal solubilities are still increasing with pressure. It is interesting, therefore, to perform computer simulations to very high pressures (see Kurnik and Reid, 1981). The results of such simulations are shown in Figure 5-1 for the solubility of naphthalene in supercritical ethylene for pressures up to 4 kbar and for several temperatures. Experimental data are shown only for the 285 K isotherm to indicate the range covered and the applicability of the Peng-Robinson equation.

For the naphthalene-ethylene system, the solubility attains a minimum value in the range of 15 to 20 bar and a maximum at several hundred bar.

The existence of the concentration maxima for the naphthalene-ethylene system is confirmed by considering the earlier work of Van Welie and Diepen (1961). They also graphed the mole fraction of naphthalene in ethylene as a function of
Solubility of Naphthalene in Supercritical Ethylene—
Indicating Solubility Maxima

Figure 5-1
pressure and covered a range up to about 1 kbar. Their smoothed data (as read from an enlargement of their original graphs), are plotted in Figure 5-2. At temperatures close to the upper critical end point (325.3 K), a maximum in concentration is clearly evident. At lower temperatures, the maximum is less obvious. The dashed curve in Figure 5-2 represents the results of calculating the concentration maximum from the Peng-Robinson equation of state. This simulation could only be carried out to 322 K; above this temperature convergence becomes a problem as the second critical end point is approached, and the formation of two fluid phases is predicted. Table 5-1 compares the theoretical versus experimental maxima.

Concentration maxima have also been noted by Czubryt et al. (1970) for the binary systems stearic acid-CO₂ and 1-octadecanol-CO₂. In these cases, the experimental data were all measured past the solubility maxima -- which for both solutes occurred at a pressure of about 280 bar. An approximate correlation of their data was achieved by a solubility parameter model.

Theoretical Development

The solubility minimum and maximum with pressure can be related to the partial molar volume of the solute in the supercritical phase. With subscript $I$ representing the solute, then with equilibrium between a pure solute and the solute dissolved in the supercritical fluid,
Experimental Data Confirming Solubility Maxima of Naphthalene in Supercritical Ethylene

Figure 5-2
Table 5-1

Comparison between Experimental and Theoretical Solubility
Maxima and the Pressure at these Maxima

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$P_{\text{max}}^E$ (bar)</th>
<th>$P_{\text{max}}^T$ (bar)</th>
<th>% error, P</th>
<th>$y_{\text{max}}^E$</th>
<th>$y_{\text{max}}^T$</th>
<th>% error, y</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>612</td>
<td>680</td>
<td>11.1</td>
<td>4.31x10^{-2}</td>
<td>4.83x10^{-2}</td>
<td>12.1</td>
</tr>
<tr>
<td>308</td>
<td>590</td>
<td>648</td>
<td>9.8</td>
<td>5.68x10^{-2}</td>
<td>6.06x10^{-2}</td>
<td>6.9</td>
</tr>
<tr>
<td>313</td>
<td>576</td>
<td>576</td>
<td>0.0</td>
<td>7.84x10^{-2}</td>
<td>8.43x10^{-2}</td>
<td>7.5</td>
</tr>
<tr>
<td>318</td>
<td>477</td>
<td>472</td>
<td>1.0</td>
<td>1.17x10^{-1}</td>
<td>1.19x10^{-1}</td>
<td>1.7</td>
</tr>
<tr>
<td>321</td>
<td>398</td>
<td>357</td>
<td>10.3</td>
<td>1.35x10^{-1}</td>
<td>1.60x10^{-1}</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Notes:
1. Calculations were done using the Peng-Robinson Equation of State, $k_{12}$=0.02.
2. Experimental Data are from Van Welie and Diepen (1961).
3. $P_{\text{max}}^E$ = experimental value of maximum pressure.
4. $P_{\text{max}}^T$ = theoretical value of maximum pressure.
\[ \frac{d \ln f^F}{d P} = \frac{d \ln f^S}{d P} \] (5-2.1)

Expanding Eq. 5-2.1 at constant temperature and assuming that no fluid dissolves in the solute,

\[ \frac{\overline{V}_1^F}{RT} \frac{dP}{T,P} + \left( \frac{\partial \ln f_1^F}{\partial \ln y_1} \right)_{T,P} d \ln y_1 = \frac{\overline{V}_1^S}{RT} dP \] (5-2.2)

Using the definition of the fugacity coefficient,

\[ \phi_1^F = \frac{\overline{z}_1^F}{y_1^P} \] (5-2.3)

Then Eq. 5-2.2 can be rearranged to give

\[ \left( \frac{\partial \ln y_1}{\partial P} \right)_T = \left[ \frac{\overline{V}_1^S - \overline{V}_1^F}{\overline{V}_1^F} \right] \left[ \frac{1 + \left( \frac{\partial \ln \phi_1}{\partial \ln y_1} \right)_{T,P}}{1 + \left( \frac{\partial \ln y_1}{\partial \ln y_1} \right)_{T,P}} \right] \] (5-2.4)

\[ \phi_1 \] may be expressed in terms of \( y_1, T, \) and \( P \) with an equation of state (Kurnik et al., 1981). For naphthalene as the solute in ethylene, \( \left( \frac{\partial \ln \phi_1}{\partial \ln y_1} \right)_{T,P} \) was never less than -0.4 over a pressure range up to the 4 kbar limit studied. Thus the extrema in concentration occur when \( \overline{V}_1^S = \overline{V}_1^F \).

Again using the Peng-Robinson equation of state, \( \overline{V}_1^F \) for naphthalene in ethylene as a function of pressure and temperature was computed. The 318 K isotherm is shown in Figure 5-3. At low pressures, \( \overline{V}_1^F \) is large and positive; it would approach
Partial Molar Volume of Naphthalene in Supercritical Ethylene

Figure 5-3
an ideal gas molar volume as $P \to 0$. With an increase in pressure, $\bar{V}_1^F$ decreases and becomes equal to $V_1^s$ ($111.9 \text{ cm}^3/\text{mole}$) at a pressure of about 20 bar. This corresponds to the solubility minimum. $\bar{V}_1^F$ then becomes quite negative. The minimum in $\bar{V}_1^F$ corresponds to the inflection point in the concentration-pressure curve shown in Figure 5-1. At high pressures, $\bar{V}_1^F$ increases and eventually becomes equal to $V_1^s$; this then corresponds to the maximum in concentration described earlier.

5-3 A Method to Achieve 100% Solubility of a Solid in a Supercritical Phase

Due to the unusual phase behavior of the solid-supercritical fluid surface described in Chapter 2-2, it is possible to delineate regions of solid-fluid equilibria other than between the lower and upper critical end points. Moreover, in these regions, one can obtain significantly higher solubilities than between the critical end points and actually approach a solubility of 100% mole fraction. These unique features of supercritical fluids are discussed in this section.

Consider the $P$-$x$ isotherms shown in Figure 2-15 of the $P$-$T$ projection shown in Figure 2-14. These projections are for the case where the three phase line intersects the critical locus. On isotherms $T_5$, $T_6$ and $T_7$, there is a distinct solid + fluid (S+F) region existing for temperatures greater than the upper critical end point temperature ($T_4$).

One can, nevertheless, operate in the (S+F) region, provided that the pressure is greater than the highest
pressure on the critical locus connecting the critical point of the solute with the upper critical end point. In this situation, a limiting composition of 100% solubility of the solute in the supercritical phase may be achieved when the temperature just equals the pure solid melting point temperature at the operating pressure.

Consider the system naphthalene-ethylene. The maximum pressure on the critical locus connecting the critical point of the pure solid to the upper critical end point is approximately 250 bar (see Figure 5-4). Thus, at an operating pressure greater than 250 bar, say 274 bar, one can achieve 100% solubility of a solid in a supercritical fluid by choosing the operating temperature equal to the melting point temperature of pure naphthalene at 274 bar. Diepen and Scheffer (1953) give the melting point of pure naphthalene at 274 bar as 363 K.

A computer simulation of the ethylene-naphthalene system at a constant pressure of 274 bar and for temperatures between 285 K and 363 K is shown in Figure 5-5. For comparison, experimental data of Diepen and Scheffer (1953) under these conditions is also shown. The Peng-Robinson equation appears to simulate these extremely concentrated solutions quite well.

5-4 Entrainers in Supercritical Fluids

Solubilities of desired species in supercritical fluids may not always be sufficiently large enough for certain applications. In order to further increase component
Critical Locus -- UCEP
Fusion Line
Three Phase Line

P - T Projection for Ethylene - Naphthalene (Van Welie and Diepen, 1961)

Figure 5-4
System Ethylene-Naphthalene
Pressure = 274 Bar
- PR Equation of State
e_{12} = 0.02
- Experimental Data of Diepen and Scheffer (1953)
- Melting Point of Naphthalene at 274 Bar

T-x Projection for Ethylene-Naphthalene for Temperatures and Pressures above the Critical Locus

Figure 5-5
solubilities in supercritical fluids, it is possible in some circumstances to add an additional component of higher solubility -- called an entrainer.

At present, there is only one published case where entrainers were systematically used. This case is the separation of glyceride mixtures using supercritical carbon dioxide. Quoting from Panzer et al. (1978): "Little separation was achieved using pure carbon dioxide, but considerable improvements resulted by the addition of the entrainers carbon tetrachloride and n-hexane." Peter and Brunner (1978) made similar observations with the system carbon dioxide- glycerides, but with acetone as the entrainer. Selectivities of the glycerides were different, however, with the different entrainers.

Brunner (1980) has also noted that entrainers can significantly change the retrograde temperature region.

Some exploratory investigations done in this thesis have also shown the effect of entrainers. Several experiments were performed whereby the solubility of natural alkaloids in supercritical carbon dioxide were determined. Upon adding water as an entrainer (about one weight percent in the fluid phase), component solubilities of the alkaloids could be increased from 10 to 50 percent.

Finally, the ternary solid-fluid systems that were systematically studied in this thesis show that small amounts of a volatile component in a supercritical phase can significantly effect the solubility of all components in the supercritical
Little is really known about the important topic of entrainers in supercritical fluids. Clearly much more research remains to be done.

5-5 Transport Properties of Supercritical Fluids

Mass transfer in supercritical fluids is of importance for the design engineer in sizing equipment -- for rarely will industrial applications operate at equilibrium. Very little work has been done in this area -- a few binary diffusion and self diffusion coefficients have been measured and flux rates for one system have been measured.

It is the purpose of this section of the thesis to review the literature on transport properties in supercritical fluids and to make suggestions for further research.

Tsekhsanskaya (1968, 1971) has made measurements of the diffusivity for the systems p-nitrophenol-water and naphthalene-carbon dioxide near the critical region. In dense fluids, the diffusivities are slightly larger than those of liquids ($D_{12} \approx 10^{-4} \text{cm}^2/\text{s}$), but when the critical point is approached, the binary diffusivity approaches zero as suggested by theory (Reid et al., 1977).

Iomtev and Tsekhsanskaya (1964) and Morozov and Vinkler (1975) have made extensive measurements on the diffusivity of naphthalene in ethylene, carbon dioxide, and nitrogen. Except for the measurements of Morozov and Vinkler, all diffusivities were measured in static diffusion cells.
Morozov and Vinkler designed a dynamic method to obtain diffusion coefficients which appears to give good results and is also quite simple to construct and use.

Finally, Rance and Cussler (1974) measured flux rates of iodine into supercritical carbon dioxide. Their data are interesting as it suggests that there is no retrograde solidification region with this system. Also, if equilibrium solubility measurements are made on the system iodine-carbon dioxide, then it would be possible to calculate mass transfer coefficients from their flux data.

Suggestions for further research are to obtain binary diffusivity data for additional solid-fluid systems and to measure mass transfer coefficients to these systems. A generalized correlation of the Sherwood number as a function of the Reynold and Schmidt number would then be obtained.
6. ENERGY EFFECTS

Enthalpy changes when a solid dissolves in a supercritical fluid are of importance in evaluating the energy requirements of a supercritical fluid extractor. Although no work has been previously reported in this field, and no calorimetric measurements were made in this thesis, it is possible to obtain quantitative values of the differential heat of solution by applying an equation of state to model systems.

6-1 Theoretical development

Consider the situation where solute (1) is added to originally pure fluid (2) at constant temperature and pressure. Applying the First Law:

\[ dU^F = dQ - dW + H^S_1dN_1 \]  \hspace{1cm} (6-1.1)

\[ d\bar{H}^F - Pd\bar{V}^F = dQ - Pd\bar{V}^F + H^S_1dN_1 \] \hspace{1cm} (6-1.2)

\[ d\bar{H}^F = dQ + H^S_1dN_1 \] \hspace{1cm} (6-1.3)

But, for the fluid mixture,

\[ \bar{H}^F_1 = N_1\bar{H}^F_1 + N_2\bar{H}^F_2 \] \hspace{1cm} (6-1.4)

\[ d\bar{H}^F = (N_1d\bar{H}^F_1 + N_2d\bar{H}^F_2) + (H^S_1dN_1 + H^S_2dN_2) \] \hspace{1cm} (6-1.5)
At constant temperature and pressure,

\[ N_1 d\bar{H}_1 + H_2 d\bar{H}_2 = 0 \]

by the Gibb's Duhem Equation. Since only solid is added to the mixture,

\[ dH_F^\text{F} = \bar{H}_1^\text{F} dN_1 \quad (6-1.6) \]

Combining Eq. (6-1.3) and (6-1.6) gives

\[ \frac{dQ}{dN_1} = (\bar{H}_1^\text{F} - \bar{H}_1^\text{S}) \quad (6-1.7) \]

or, the differential heat of solution is equal to the difference between the partial molar enthalpy of component 1 in the fluid phase minus the enthalpy of pure solid 1. As shown in Appendix III, this enthalpy difference is given by

\[ (\bar{H}_1^\text{F} - \bar{H}_1^\text{S}) = -R \left[ \ln y_1 \right]_{T,P} \left[ 1 + \frac{\partial \ln y_1}{\partial T} \right]_{T,P} \quad (6-1.8) \]

The integral heat of solution is defined as

\[ Q = \int_0^{N_1} (\bar{H}_1^\text{F} - \bar{H}_1^\text{S}) dN_1 \quad (6-1.9) \]

Equation (6-1.9) can be simplified to give
Physically, the molar differential heat of solution is the heat interaction with the system by dissolving 1 mole of solute in an infinite amount of fluid; the integral heat of solution is total heat interaction with the system for a given amount of solute and solvent.

6-2 Presentation and Discussion of Theoretical Results

Using an equation of state, the differential heat of solution can be evaluated for the model systems studied in this thesis. These simulations were made for many cases and several numerical results are shown in Tables 6-1 to 6-3.

In the low pressure region, the enthalpy difference $(H_f^F - H_l^S) - \Delta H_{SUB}$, as expected. In the high pressure region $(P \sim 300$ bar), $(H_f^F - H_l^S) = 2\Delta H_{FUS}$, and in the retrograde region (where an increase in temperature decreases solubility), $(H_f^F - H_l^S)$ is exothermic. This exothermic enthalpy difference may prove beneficial in minimizing the energy requirements of a supercritical fluid (SCF) extraction plant.
Table 6-1

Differential Heats of Solution for Phenanthrene-Carbon Dioxide at 328K

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>(-R \left( \frac{\delta \ln y_1}{\delta 1/T} \right)_P)</th>
<th>(\left( \frac{\delta \ln \phi_1}{\delta \ln y_1} \right)_{328, P})</th>
<th>(-\frac{H^P}{H^S}_1), cal./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20,734</td>
<td>0</td>
<td>20,734</td>
</tr>
<tr>
<td>5</td>
<td>20,382</td>
<td>0</td>
<td>20,382</td>
</tr>
<tr>
<td>10</td>
<td>19,930</td>
<td>0</td>
<td>19,930</td>
</tr>
<tr>
<td>120</td>
<td>-11,087</td>
<td>-0.03928</td>
<td>-11,540</td>
</tr>
<tr>
<td>300</td>
<td>6,849</td>
<td>-0.1555</td>
<td>8,110</td>
</tr>
</tbody>
</table>

\[ \Delta H\text{(fusion)}^2 = 4,456 \text{ cal./mole} \]

\[ \Delta H\text{(sublimation)}^3 = 20,870 \text{ cal./mole} \]

Notes:
1. Calculations were done using the Peng-Robinson Equation of State; \(k_{12} = k_{12}^0(T)\) as given in Table 4-5.
2. Date from Perry and Chilton (1973).
3. Calculated from vapor pressures of de Kruif et al. (1975).
Table 6-2

Differential Heats of Solution for Phenanthrene-Ethylene at 328K₁

<table>
<thead>
<tr>
<th>P(bar)</th>
<th>(-R)(\frac{\partial \ln y_1}{\partial \frac{1}{T}})₁</th>
<th>(\frac{\partial \ln \phi_1}{\partial \ln y_1})₁,328,P</th>
<th>(\frac{\phi_{F}^1 - \phi_{S}^1}{\phi_{1}^1},\text{cal./mole})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20,724</td>
<td>0</td>
<td>20,724</td>
</tr>
<tr>
<td>5</td>
<td>20,339</td>
<td>0</td>
<td>20,339</td>
</tr>
<tr>
<td>10</td>
<td>19,834</td>
<td>0</td>
<td>19,834</td>
</tr>
<tr>
<td>120</td>
<td>-1,951</td>
<td>-0.04224</td>
<td>-2,037</td>
</tr>
<tr>
<td>300</td>
<td>7,706</td>
<td>-0.2819</td>
<td>10,731</td>
</tr>
</tbody>
</table>

\(\Delta H(\text{fusion})^2 = 4456\ \text{cal./mole}\)

\(\Delta H(\text{sublimation})^3 = 20,870\ \text{cal./mole}\)

Notes: 1. Calculations were done using the Peng-Robinson Equation of State; \(k_{12} = k_{12}^P(T)\) as given in Table 4-6.
2. Data from Perry and Chilton (1973)
3. Calculated from vapor pressures of de Kruif et al. (1975)
Table 6-3

Differential Heats of Solution for
Benzoic acid-Carbon Dioxide at 328K

<table>
<thead>
<tr>
<th>P(bar)</th>
<th>(-R\left(\frac{\partial \ln y_1}{\partial 1/T}\right)_P)</th>
<th>(\frac{\partial \ln \phi_1}{\partial \ln y_1})</th>
<th>((H^F_1-H^S_1)), cal./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21,030</td>
<td>0</td>
<td>21,030</td>
</tr>
<tr>
<td>5</td>
<td>20,766</td>
<td>0</td>
<td>20,766</td>
</tr>
<tr>
<td>10</td>
<td>20,436</td>
<td>0</td>
<td>20,436</td>
</tr>
<tr>
<td>120</td>
<td>-10,114</td>
<td>-0.04245</td>
<td>-10,562</td>
</tr>
<tr>
<td>300</td>
<td>7,191</td>
<td>-0.2236</td>
<td>9,262</td>
</tr>
</tbody>
</table>

\(\Delta H(\text{fusion})^2 = 4,139\) cal./mole

\(\Delta H(\text{sublimation})^3 = 21,096\) cal./mole

Notes: 1. Calculations were done using the Peng-Robinson Equation of State, \(k_{12} = k_{12}(T)\) as given in Table 4-7.


3. Calculated from vapor pressures of de Kruif et al. (1975).
7. OVERALL CONCLUSIONS

Supercritical fluid extraction processes are seeing a resurgence of interest -- both in academic institutions and in industry. In academia, many of the phase equilibrium and transport properties of a condensed phase in equilibrium with a fluid phase are being studied. In industry, the emphasis is on process development and solving the design and engineering problems.

There are six major reasons why supercritical fluids are receiving a widespread interest.

* High Mass Transfer Rates Between Phases

A supercritical fluid phase has a low viscosity (near that of a gas) while also having a high mass diffusivity (between that of a gas and a liquid). Consequently, it is currently believed that the mass transfer coefficient (and hence the flux rate) will be higher than for typical liquid extractions.

* Ease of Solvent Regeneration

After a given supercritical fluid has extracted the desired components, the system pressure can be reduced to a low value (20-30 bar) causing all of the solute to precipitate out. Then, the supercritical fluid is left in pure form and can be easily recycled. In typical liquid extractions, using an organic solvent, the spent solvent must usually be purified by distillation.
- Sensitivity to all Process Variables

For supercritical fluid extraction, both temperature and pressure have a significant effect on the equilibrium solubility. Small changes of temperature and/or pressure -- especially in the region near the critical point of the solvent, can affect equilibrium solubilities by two or three orders of magnitude. In liquid extraction, only temperature has a strong effect on equilibrium solubility.

- Non-Toxic Supercritical Fluids Can Be Used

Carbon dioxide -- a chemical which is non-toxic, non-flammable, inexpensive, and has a low critical temperature (304.2 K) can be used as a solvent for extracting substances. It is for this reason that many food and pharmaceutical industries are quite interested in supercritical CO₂ extraction research.

- Energy Saving

When compared to distillation, supercritical fluid extraction is usually less energy intensive. A study by Arthur D. Little, Inc. on dehydrating ethanol-water solutions by using supercritical CO₂ has shown to be more energy efficient than azeotropic distillation (Krukonis, 1980).

- Sensitivity of Solubility to Trace Components

Solubility of components in supercritical fluids can be changed by several hundred percent by the addition to the fluid phase of small quantities (one mole percent) of a volatile, often polar, material (entrainer). In addition, selectivities of the extraction can be significantly affected by the entrainer. More research on entrainers in multicomponent
systems will give a better physical understanding of the enhanced solubility as well as to enable one to develop guidelines to choose the best entrainer.

New developments in supercritical fluid extraction discovered in this thesis are (1) the existence of a maximum in isothermal solubilities with increasing pressure; (2) enhancement of component solubilities in supercritical fluids by the addition of a second volatile solid component; (3) differential heats of solution from solid to fluid phase changing from endothermic in the low pressure regime to exothermic in the middle pressure regime back to endothermic in the high pressure regime; and (4) correlation and prediction of equilibrium solubilities of binary and multicomponent solids in supercritical fluids by use of rigorous thermodynamic theory.
8-1 Solid-Fluid Equilibria

In the area of solid-fluid equilibria, there are several research topics which warrant further study. First, in this thesis, only ternary systems were studied (two solids, one fluid). It would be interesting to extend this work to even higher order systems (more solid components) to answer several questions:

a) Does the "temperature window" between p and q close?

b) Can one model a complex equilibria problem like coal in supercritical CO₂ by considering it to be made up of many model compounds?

c) Do component solubilities in multicomponent systems keep increasing in value over their value in a binary system (when they do increase)?

Along with the experimental data of these higher order systems, it would be interesting to examine the Peng-Robinson equation (and others, such as Perturbed-Hard-Chain) to test their ability to correlate higher order systems.

As solid-fluid extractions are most conveniently performed in the region between the upper and lower critical end points, a convenient way of theoretically and experimentally determining these end points for multicomponent systems is a topic for further study.
Correlation of the solid-fluid equilibrium data taken in this thesis and the data available in the literature proved satisfactory by using the Peng-Robinson model for the fluid phase fugacity coefficient. A drawback of this model, however, is that there is a temperature dependent binary parameter, \( k_{ij} \), which up to now, cannot be determined apriori. Perhaps correlation methods to predict \( k_{ij}(T) \) could be developed, or better yet, a model for the fluid phase fugacity coefficient that has a more theoretical framework (and without adjustable parameters) than the Peng-Robinson equation of state could be developed.

As discussed in Chapter 5-3 of this thesis, there are temperature and pressure regimes other than those between the upper and lower critical end points where solid is in equilibrium with a fluid phase. Furthermore, in these other regimes, it is possible to reach extremely high solubilities of solid components in the fluid phase. As the experimental equipment was designed in this thesis, however, it was impossible to obtain reproducible data for high solubilities (30 percent mole fraction or higher) due to plugging problems inside the let-down valve. Perhaps with a refinement of the experimental apparatus, equilibrium data in this very interesting regime could be obtained (and correlated with theory).

8-2 **Liquid-Fluid Extraction**

The area of liquid-fluid extraction has much wider applications in industry than solid-fluid extraction -- since most
industrial separation problems are with liquids. Some
equilibrium data is available in the literature on binary
liquid-fluid systems up to relatively low pressures (100 bar),
but little is known about higher pressure solubilities and
solubilities in multicomponent systems.

An interesting research program would be to determine
experimentally the solubility of multicomponent liquids in
supercritical fluids and successfully model and correlate the
data. The effect of temperature and pressure on the distri-
bution coefficients in multicomponent systems could then be
examined.

8-3 Equipment Design

A visual observation extraction would be useful in
locating critical end points (in the case of solid-fluid
equilibria) by observing the appearance and disappearance
of a liquid phase.

As discovered in this thesis, there exists an iso-
thermal solubility maxima (with pressure) of component
solubilities of solids in supercritical fluids. This
maxima however, exists at relatively high pressures (600 bar),
and so it would be useful to have the capability to take
solubility measurements in this region, and therefore
give more support to this finding. A similar solubility
maxima will probably exist with some liquid-fluid
equilibria systems -- and this may be of value to
test.
APPENDIX I
PARTIAL MOLAR VOLUME USING THE PENG-ROBINSON EQUATION OF STATE

The partial molar volume of component i in a fluid is by definition

\[ \bar{V}_i = \left( \frac{\partial V_i}{\partial N_i} \right)_{T,P,N_j[i]} \]  \hspace{1cm} (I-1)

The partial molar volume can be evaluated from an equation of state for the fluid mixture. Since most equations of state are explicit in pressure, rather than in volume, it is convenient to rewrite Equation (I-1):

\[ \bar{V}_i = - \frac{\left( \frac{\partial P}{\partial V} \right)_{T,P,N_j[i]}}{\left( \frac{\partial V}{\partial N} \right)_{T,N_j}} \]  \hspace{1cm} (I-2)

Evaluating Equation (I-2) using the Peng-Robinson Equation of State gives

\[ \bar{V}_i = \left[ \frac{RT}{V-b} \left( 1 + \frac{b_i}{V-b} \right) - \frac{2}{\sqrt{\sum_{j=1}^{\infty} Y_j a_{ij}}} \right] \frac{2ab_i(V-b)}{V(V+b) + b(V-b)} - \frac{\left( \frac{RT}{(V-b)^2} - \frac{2a(V+b)}{[V(V+b)+b(V-b)]^2} \right)}{2} \]  \hspace{1cm} (I-3)
A similar derivation has been made by Lin and Daubert (1980).
APPENDIX II
DERIVATION OF SLOPE EQUALITY
AT A BINARY MIXTURE CRITICAL POINT

Consider a binary mixture of two substances that has a molar Gibbs energy of mixing as shown in Figure II-1. Compositions $x'_1$ and $x''_1$ correspond to points on a binodial curve while points B and C correspond to the limits of material stability of this system. If, however, points A, B, C, and D of Figure II-1 were made to coincide to form a stable point $E$, then $E$ is called a critical point and satisfies the relations:

$$g_{2x}^c = 0, g_{3x}^c = 0, g_{4x}^c > 0$$  \hspace{1cm} (II-1)

where $g_{nx}^c = \left( \frac{\partial^n g}{\partial x^n} \right)_{T,P, \text{CRITICAL POINT}}$

By performing a Taylor expansion of $g$ (in terms of $P$ and $x$) around the critical point, it can be shown (Rowlinson, 1969) that for component 1 that:

$$\left( \frac{\partial P}{\partial x_1} \right)'_{T,\sigma} = - \left( \frac{\partial P}{\partial x_1} \right)''_{T,\sigma} = - \frac{\Delta x_1 g_{4x}^c}{6V_{2x}^c}$$  \hspace{1cm} (II-2)

where $\Delta x_1 = x'_1 - x''_1$
The Molar Free Energy of Mixing as a Function of Mole Fraction, When $g^m$ is a Continuous Function of $X$

(Rowlinson, 1969)

Figure II-1
Thus, at the binary mixture critical point,

\[ \left[ \frac{\partial P}{\partial x_i} \right]_{T, \sigma} = 0 \]  

(II-4)

More meaningfully, Equation II-4 can be written for the case of solid (1) fluid (2) equilibrium by

\[ \left[ \frac{\partial P}{\partial y_1} \right]_{T, \sigma} = 0 \]  

(II-5)

as an equality at the binary critical end points. The differentiation can be conveniently performed along the three-phase locus.
APPENDIX III
DERIVATION OF ENTHALPY CHANGE
OF SOLVATION

The derivation of Equation (6-1.8):

\[
(H_1^F - H_1^S) = -R \left[ \frac{\partial \ln y_1}{\partial \frac{1}{T}} \right]_P \left[ 1 + \left( \frac{\partial \ln \phi_1}{\partial \ln y_1} \right)_{T,P} \right]
\]

is as follows:

With subscript 1 representing the solute, then with equilibrium between a pure solute and a solute dissolved in the supercritical fluid,

\[
d\ln \tilde{F}_1 = d\ln \tilde{F}_1
\]

Expanding Eq. III-1 at constant pressure and assuming that no fluid dissolves in the solute,

\[
- \left( \frac{H_1^F - H_1^S}{RT^2} \right) dT + \left( \frac{\partial \ln \tilde{F}_1}{\partial \ln y_1} \right)_{T,P} d\ln y_1 = - \left( \frac{S_1^F - S_1^F}{RT^2} \right) dT
\]

Using the definition of the fugacity coefficient,

\[
\phi_1^F = \frac{\tilde{F}_1^F}{y_1^F}
\]

then Eq. III-2 can be rearranged to give
\((H_1^F - H_1^S) = -R \left( \frac{\partial \ln y_1}{\partial \frac{1}{T}} \right)_P \left[ 1 + \left( \frac{\partial \ln \phi}{\partial \ln y_1} \right)_{T,P} \right] \) 

(III-4)
APPENDIX IV
FREEZING POINT DATA
FOR MULTICOMPONENT MIXTURES

A Fisher-Johns melting point apparatus (Fisher Scientific, Model 12-144) was used to determine if the solid mixtures used in this research formed solid solutions or an eutectic mixture with the solid phases as pure components. From the freezing point behavior, it can be determined if the solids form a solid solution or an eutectic mixture. Only in the latter case can the activity coefficient of the solid phase be neglected -- see Equation (2-3.3).

In order to test the accuracy of the equipment, a known eutectic mixture was examined: o-chloronitrobenzene with p-chloronitrobenzene (Prigogine and Defay, 1954). As Table IV-1 shows, the agreement between the literature and experimental data for the melting point curve are within ± 0.5 K.

Tables IV-2 through IV-5 give experimental freezing point data for four of the binary systems investigated.* Listed in these tables are both $T_i$ and $T_f$ -- the initial and final freezing points. In each case, since $T_f$ is constant, the formation of a eutectic composition is confirmed. Also listed in Tables IV-2 through IV-5 are the eutectic temperatures predicted from ideal solution theory (Prausnitz,
Table IV-1
Comparison of Melting Point Curve from Literature* vs. Experimental Data for the System o-chloronitrobenzene (1), with p-chloronitrobenzene (2)

<table>
<thead>
<tr>
<th>$X_2$</th>
<th>T(K), Literature*</th>
<th>T(K), Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.035</td>
<td>304.7</td>
<td>304.2</td>
</tr>
<tr>
<td>0.110</td>
<td>301.5</td>
<td>301.2</td>
</tr>
<tr>
<td>0.165</td>
<td>298.5</td>
<td>298.2</td>
</tr>
<tr>
<td>0.210</td>
<td>296.7</td>
<td>297.2</td>
</tr>
<tr>
<td>0.250</td>
<td>294.7</td>
<td>295.2</td>
</tr>
<tr>
<td>0.290</td>
<td>291.5</td>
<td>291.2</td>
</tr>
<tr>
<td>0.330</td>
<td>288.2</td>
<td>288.2</td>
</tr>
<tr>
<td>0.350</td>
<td>292.0</td>
<td>292.2</td>
</tr>
<tr>
<td>0.400</td>
<td>300.0</td>
<td>300.2</td>
</tr>
<tr>
<td>0.450</td>
<td>307.2</td>
<td>307.2</td>
</tr>
<tr>
<td>0.500</td>
<td>315.0</td>
<td>315.2</td>
</tr>
<tr>
<td>0.560</td>
<td>321.2</td>
<td>321.2</td>
</tr>
<tr>
<td>0.620</td>
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<td>326.2</td>
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<tr>
<td>0.670</td>
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</tr>
<tr>
<td>0.720</td>
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<tr>
<td>0.780</td>
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</tr>
<tr>
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<td>345.2</td>
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<tr>
<td>0.900</td>
<td>349.2</td>
<td>349.2</td>
</tr>
<tr>
<td>0.960</td>
<td>352.9</td>
<td>353.2</td>
</tr>
</tbody>
</table>

*Prigogine and Defay (1954)
Table IV-2
Experimental Freezing Curves for Phenanthrene with Naphthalene

<table>
<thead>
<tr>
<th>Mole Fraction Phenanthrene</th>
<th>$T_i$ (K)</th>
<th>$T_f$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>352.2</td>
<td>352.2</td>
</tr>
<tr>
<td>0.1</td>
<td>348.2</td>
<td>326.2</td>
</tr>
<tr>
<td>0.2</td>
<td>342.2</td>
<td>326.2</td>
</tr>
<tr>
<td>0.3</td>
<td>335.2</td>
<td>326.2</td>
</tr>
<tr>
<td>0.4</td>
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<td>326.2</td>
</tr>
<tr>
<td>0.5</td>
<td>335.2</td>
<td>326.2</td>
</tr>
<tr>
<td>0.6</td>
<td>344.2</td>
<td>326.2</td>
</tr>
<tr>
<td>0.7</td>
<td>353.2</td>
<td>326.2</td>
</tr>
<tr>
<td>0.8</td>
<td>360.7</td>
<td>326.2</td>
</tr>
<tr>
<td>0.9</td>
<td>367.2</td>
<td>326.2</td>
</tr>
<tr>
<td>1</td>
<td>369.2</td>
<td>369.2</td>
</tr>
</tbody>
</table>

$T_E$ (ideal solution) = 326.5 K
$T_i$ ≡ liquidus curve
$T_f$ ≡ eutectic line
<table>
<thead>
<tr>
<th>Mole Fraction Phenanthrene</th>
<th>$T_i$(K)</th>
<th>$T_f$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>382.2</td>
<td>382.2</td>
</tr>
<tr>
<td>0.1</td>
<td>378.7</td>
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<td>0.2</td>
<td>374.2</td>
<td>344.2</td>
</tr>
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<td>0.3</td>
<td>367.2</td>
<td>344.2</td>
</tr>
<tr>
<td>0.4</td>
<td>360.2</td>
<td>344.2</td>
</tr>
<tr>
<td>0.5</td>
<td>352.2</td>
<td>344.2</td>
</tr>
<tr>
<td>0.6</td>
<td>344.2</td>
<td>344.2</td>
</tr>
<tr>
<td>0.7</td>
<td>352.2</td>
<td>344.2</td>
</tr>
<tr>
<td>0.8</td>
<td>360.2</td>
<td>344.2</td>
</tr>
<tr>
<td>0.9</td>
<td>367.2</td>
<td>344.2</td>
</tr>
<tr>
<td>1</td>
<td>369.2</td>
<td>369.2</td>
</tr>
</tbody>
</table>

$T_E$(ideal solution) = 343.5K

$T_i$ ≡ liquidus curve

$T_f$ ≡ eutectic line
Table IV-4

Experimental Freezing Curves for Naphthalene with 2,6-DMN

<table>
<thead>
<tr>
<th>Mole Fraction Naphthalene</th>
<th>$T_i (K)$</th>
<th>$T_f (K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>382.2</td>
<td>382.2</td>
</tr>
<tr>
<td>0.1</td>
<td>378.7</td>
<td>334.2</td>
</tr>
<tr>
<td>0.2</td>
<td>374.2</td>
<td>334.2</td>
</tr>
<tr>
<td>0.3</td>
<td>367.2</td>
<td>334.2</td>
</tr>
<tr>
<td>0.4</td>
<td>360.2</td>
<td>334.2</td>
</tr>
<tr>
<td>0.5</td>
<td>353.2</td>
<td>334.2</td>
</tr>
<tr>
<td>0.6</td>
<td>343.7</td>
<td>334.2</td>
</tr>
<tr>
<td>0.7</td>
<td>336.2</td>
<td>334.2</td>
</tr>
<tr>
<td>0.8</td>
<td>343.2</td>
<td>334.2</td>
</tr>
<tr>
<td>0.9</td>
<td>348.7</td>
<td>334.2</td>
</tr>
<tr>
<td>1</td>
<td>352.2</td>
<td>352.2</td>
</tr>
</tbody>
</table>

$T_E$ (ideal solution) = 333.9K

$T_i$ ≡ liquidus curve

$T_f$ ≡ eutectic line
Table IV-5

Experimental Freezing Curves for 2,3-DMN with 2,6-DMN

<table>
<thead>
<tr>
<th>Mole Fraction 2,3-DMN</th>
<th>$T_i$(K)</th>
<th>$T_f$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>382.2</td>
<td>382.2</td>
</tr>
<tr>
<td>0.1</td>
<td>378.2</td>
<td>349.2</td>
</tr>
<tr>
<td>0.2</td>
<td>373.2</td>
<td>349.2</td>
</tr>
<tr>
<td>0.3</td>
<td>367.2</td>
<td>349.2</td>
</tr>
<tr>
<td>0.4</td>
<td>360.7</td>
<td>349.2</td>
</tr>
<tr>
<td>0.5</td>
<td>353.2</td>
<td>349.2</td>
</tr>
<tr>
<td>0.6</td>
<td>354.2</td>
<td>349.2</td>
</tr>
<tr>
<td>0.7</td>
<td>361.2</td>
<td>349.2</td>
</tr>
<tr>
<td>0.8</td>
<td>366.7</td>
<td>349.2</td>
</tr>
<tr>
<td>0.9</td>
<td>371.7</td>
<td>349.2</td>
</tr>
<tr>
<td>1</td>
<td>376.2</td>
<td>376.2</td>
</tr>
</tbody>
</table>

$T_E$(ideal solution) = 349.3K

$T_i$ ≡ liquidus curve

$T_f$ ≡ eutectic line
1969):

\[
\frac{1}{R} \left( \frac{1}{T_1^m} - \frac{1}{T_2^m} \right) = \frac{\ln x_1}{\Delta H_{FUS,1}} - \frac{\ln (1-x_1)}{\Delta H_{FUS,2}}
\]

(IV-2)

where \( T_1^m \) and \( T_2^m \) are the melting points of components 1 and 2 and \( \Delta H_{FUS,1} \) and \( \Delta H_{FUS,2} \) are the enthalpies of fusion of components 1 and 2.

Agreement between experimental eutectic temperatures and eutectic temperatures predicted from ideal solution theory is within one percent error.

Figure IV-1 shows the freezing point diagram for the naphthalene-phenanthrene system and also a comparison with the ideal solution model. In Table IV-6 are listed the melting points and heats of fusion used in the ideal solution model.

*For the systems naphthalene/benzoic acid and phenanthrene/benzoic acid, only the final melting temperature (\( T_f \)) was measured. For both cases, \( T_f \) was constant, and within one percent of the value predicted from ideal solution theory.
Phenanthrene - Naphthalene Freezing Curves

- Experimental First Freezing Point
- Experimental Second Freezing Point
- Ideal Solution Theory

Figure IV-1
Table IV-6
Melting Points and Heats of Fusion

<table>
<thead>
<tr>
<th>Component</th>
<th>$T_{\text{NMP}}$(K)</th>
<th>$\Delta H_{\text{FUS}}$(cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>373.7</td>
<td>4456</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>353.5</td>
<td>4614</td>
</tr>
<tr>
<td>2,3-DMN</td>
<td>376.2</td>
<td>5990</td>
</tr>
<tr>
<td>2,6-DMN</td>
<td>383.3</td>
<td>5990</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>395.6</td>
<td>4140</td>
</tr>
</tbody>
</table>

$T_{\text{NMP}} = \text{normal melting point temperature}$
APPENDIX V

PHYSICAL PROPERTIES OF SOLUTES STUDIED

In Table V-1 are listed physical properties of the supercritical fluids and the solutes studied in this research. Table V-2 lists vapor pressure data for all the solutes.
Table V-1
Physical Properties of Solutes Studied

<table>
<thead>
<tr>
<th>Name</th>
<th>( \omega )</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (bar)</th>
<th>( V^S_{cc} ) (gmol)</th>
<th>Supplier</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Dioxide</td>
<td>0.225(^1)</td>
<td>304.2(^1)</td>
<td>73.8(^1)</td>
<td></td>
<td>Matheson</td>
<td>99.8%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.085(^1)</td>
<td>282.4(^1)</td>
<td>50.36(^1)</td>
<td></td>
<td>Matheson</td>
<td>C.P., 99.5%</td>
</tr>
<tr>
<td>2,3-Dimethylnaphthalene</td>
<td>0.4240(^6)</td>
<td>785(^5)</td>
<td>32.169(^5)</td>
<td>156.36(^4)</td>
<td>Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>2,6-Dimethylnaphthalene</td>
<td>0.4201(^3)</td>
<td>777(^5)</td>
<td>32.217(^5)</td>
<td>156.36(^4)</td>
<td>Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.440(^3)</td>
<td>878(^1)</td>
<td>28.99(^2)</td>
<td>181.9(^4)</td>
<td>Eastman Kodak</td>
<td>98%</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>0.62(^1)</td>
<td>752(^1)</td>
<td>45.6(^1)</td>
<td>96.47(^4)</td>
<td>Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Hexachloroethane</td>
<td>0.255(^7)</td>
<td>698.4(^2)</td>
<td>33.40(^2)</td>
<td>113.22(^4)</td>
<td>Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.302(^1)</td>
<td>748.4(^1)</td>
<td>40.53(^1)</td>
<td>111.943(^4)</td>
<td>Fisher</td>
<td>99.9%</td>
</tr>
</tbody>
</table>

REFERENCES

1. Reid et al. (1977)
2. Estimated by Lydersen's method, see Reid et al. (1977).
3. Reid et al. (1977) for vapor pressures and definition of acentric factor.
4. Weast (1975)
6. Dreisbach (1955) for vapor pressures, and definition of acentric factor.
7. Perry and Chilton (1973) for vapor pressures, and definition of acentric factor.
Table V-2
Vapor Pressures of Solutes Studied

I. Naphthalene

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( P_{vp} ) (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>285.2</td>
<td>3.0701x10(^{-5})</td>
</tr>
<tr>
<td>298.2</td>
<td>1.0943x10(^{-4})</td>
</tr>
<tr>
<td>308.2</td>
<td>2.7966x10(^{-4})</td>
</tr>
</tbody>
</table>

\textbf{Diepen and Scheffer (1948)}

\textbf{Fowler et al. (1968)}

\[
\log_{10} P_{(mm)} = 9.58102 - \frac{2619.91}{(t(°C)+220.651)}
\]

\( 40°C \leq t \leq 80°C \)
II. Benzoic Acid

de Kruif et al. (1975)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>P_{vp}(bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.2</td>
<td>4.49x10^{-7}</td>
</tr>
<tr>
<td>298.2</td>
<td>8.27x10^{-7}</td>
</tr>
<tr>
<td>303.2</td>
<td>1.49x10^{-6}</td>
</tr>
<tr>
<td>308.2</td>
<td>2.64x10^{-6}</td>
</tr>
<tr>
<td>313.2</td>
<td>4.57x10^{-6}</td>
</tr>
<tr>
<td>318.2</td>
<td>7.80x10^{-6}</td>
</tr>
<tr>
<td>323.2</td>
<td>1.31x10^{-5}</td>
</tr>
<tr>
<td>328.2</td>
<td>2.16x10^{-5}</td>
</tr>
</tbody>
</table>
### Table V-2 (cont'd)

#### III. Phenanthrene

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>$P_{vp}$(bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.2</td>
<td>$9.19 \times 10^{-8}$</td>
</tr>
<tr>
<td>298.2</td>
<td>$1.68 \times 10^{-7}$</td>
</tr>
<tr>
<td>303.2</td>
<td>$3.00 \times 10^{-7}$</td>
</tr>
<tr>
<td>308.2</td>
<td>$5.28 \times 10^{-7}$</td>
</tr>
<tr>
<td>313.2</td>
<td>$9.09 \times 10^{-7}$</td>
</tr>
<tr>
<td>318.2</td>
<td>$1.55 \times 10^{-6}$</td>
</tr>
<tr>
<td>323.2</td>
<td>$2.57 \times 10^{-6}$</td>
</tr>
<tr>
<td>328.2</td>
<td>$4.23 \times 10^{-6}$</td>
</tr>
<tr>
<td>333.2</td>
<td>$6.83 \times 10^{-6}$</td>
</tr>
<tr>
<td>338.2</td>
<td>$1.09 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Table V-2 (cont'd)

IV. 2,3-Dimethylnaphthalene

Osborn and Douslin (1975)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>P_{vp}(bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>333.2</td>
<td>1.400x10^{-4}</td>
</tr>
<tr>
<td>338.2</td>
<td>2.200x10^{-4}</td>
</tr>
<tr>
<td>343.2</td>
<td>3.386x10^{-4}</td>
</tr>
<tr>
<td>348.2</td>
<td>5.093x10^{-4}</td>
</tr>
<tr>
<td>353.2</td>
<td>7.653x10^{-4}</td>
</tr>
<tr>
<td>358.2</td>
<td>1.136x10^{-3}</td>
</tr>
<tr>
<td>363.2</td>
<td>1.649x10^{-3}</td>
</tr>
<tr>
<td>368.2</td>
<td>2.376x10^{-3}</td>
</tr>
<tr>
<td>373.2</td>
<td>3.382x10^{-3}</td>
</tr>
</tbody>
</table>
Table V-2 (cont'd)

V. 2,6-Dimethylnaphthalene

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Pvp(bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>348.2</td>
<td>5.360x10^{-4}</td>
</tr>
<tr>
<td>353.2</td>
<td>8.146x10^{-4}</td>
</tr>
<tr>
<td>358.2</td>
<td>1.236x10^{-3}</td>
</tr>
<tr>
<td>363.2</td>
<td>1.823x10^{-3}</td>
</tr>
<tr>
<td>368.2</td>
<td>2.650x10^{-3}</td>
</tr>
<tr>
<td>373.2</td>
<td>3.850x10^{-3}</td>
</tr>
<tr>
<td>378.2</td>
<td>5.488x10^{-3}</td>
</tr>
<tr>
<td>383.2</td>
<td>7.709x10^{-3}</td>
</tr>
</tbody>
</table>
VI. Hexachloroethane

<table>
<thead>
<tr>
<th>Sax (1979)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T(K)</td>
<td>Pvp (mm)</td>
</tr>
<tr>
<td></td>
<td>305.9</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>459.8</td>
<td>760*</td>
</tr>
</tbody>
</table>

*sublimes
APPENDIX VI

SOURCES OF PHYSICAL PROPERTIES OF COMPLEX MOLECULES

Required physical property data for simulating equilibrium solubilities in binary and multicomponent solid-fluid equilibrium systems are: critical temperatures, critical pressures, and acentric factors for solute and solvent and vapor pressure and molar volumes of the solute. Of these properties, those which are usually unknown are solid vapor pressures and solid critical properties. It is the purpose of this appendix to summarize these solid properties. This summary is not meant to be all-inclusive, but it covers physical property data found during the author's work. Table VI-1 lists references containing solid vapor pressures along with the temperature range covered. Sources of critical property data are given by Reid et al. (1977) and Ambrose and Townsend (1978).
Table VI-1
Vapor Pressures of Solid Substances

<table>
<thead>
<tr>
<th>Solid</th>
<th>Temperature Range (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>acenaphthene</td>
<td>338.2-366.4</td>
<td>1</td>
</tr>
<tr>
<td>fluorene</td>
<td>348.2-387.2</td>
<td>1</td>
</tr>
<tr>
<td>1,8-dimethylnaphthalene</td>
<td>328.2-335.7</td>
<td>1</td>
</tr>
<tr>
<td>2,7-dimethylnaphthalene</td>
<td>333.2-368.2</td>
<td>1</td>
</tr>
<tr>
<td>monuron (a herbicide)</td>
<td>303.5-379.1</td>
<td>2</td>
</tr>
<tr>
<td>p-acetophenetidide</td>
<td>312.4-387.8</td>
<td>2</td>
</tr>
<tr>
<td>anthracene</td>
<td>290.1-358.0</td>
<td>2</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>290.4-315.5</td>
<td>2</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>293.2-328.2</td>
<td>3</td>
</tr>
<tr>
<td>α-oxalic acid</td>
<td>293.2-338.2</td>
<td>3</td>
</tr>
<tr>
<td>benzophenone</td>
<td>293.2-318.2</td>
<td>3</td>
</tr>
<tr>
<td>transtilbene</td>
<td>298.2-343.2</td>
<td>3</td>
</tr>
<tr>
<td>anthracene</td>
<td>313.2-343.2</td>
<td>3</td>
</tr>
<tr>
<td>acridine</td>
<td>293.2-338.2</td>
<td>3</td>
</tr>
<tr>
<td>phenazine</td>
<td>293.2-338.2</td>
<td>3</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>293.2-338.2</td>
<td>3</td>
</tr>
<tr>
<td>pyrene</td>
<td>398.2-458.2</td>
<td>4</td>
</tr>
<tr>
<td>2,2-dimethylpropanoic acid</td>
<td>241.62-256.77</td>
<td>5</td>
</tr>
<tr>
<td>nicotine</td>
<td>293.2-323.2</td>
<td>6</td>
</tr>
</tbody>
</table>

References
1. Osborn and Douslin (1975)
2. Wiedemann (1972)
3. de Kruif et al. (1975)
4. Smith et al. (1979)
5. de Kruif and Oonk (1979)
6. Neghbubon (1959)
APPENDIX VII
LISTINGS OF THE PERTINENT COMPUTER PROGRAMS

In this appendix, three computer programs, written in FORTRAN, are listed.

Table VII-1 is the listing of the program PENG. This program is used to calculate the equilibrium solubility of a solid in a fluid for binary systems. The Peng-Robinson equation of state is used.

Table VII-2 lists the program MPR and eight subroutines. This program calculates equilibrium solubilities for multi-component solid-fluid equilibria with the Peng-Robinson equation of state.

Table VII-3 lists the program KIJSP and two subroutines. These programs call a non-linear least squares regression subroutine (GENLSQ) to determine a binary interaction parameter for solid-fluid equilibria. The interaction parameters are those for the Peng-Robinson equation of state.

Table VII-4 gives detailed documentation of the non-linear least squares subroutine GENLSQ that performs the actual regression. This documentation is supplied courtesy of Dr. Herb Britt.

The input parameters for each of these programs are explained in the beginning of the respective programs.
Table VII-1

Computer Program PENG

FILE: PENG FORTRAN A CONVERSATIONAL MONITOR SYSTEM

C**********************************************************************
C C RONALD T. KURNIK
C C MASSACHUSETTS INSTITUTE OF TECHNOLOGY
C C DEPARTMENT OF CHEMICAL ENGINEERING
C C**********************************************************************
C
C THIS PROGRAM CALCULATES THE SOLUBILITY OF A SOLID
C IN THE GAS PHASE USING THE PENG-ROBINSON EQUATION
C
C**********************************************************************
C
C IMPLICIT REAL*8 (A-H,O-Z)
C REAL*8 M, Mw
C INTEGER SS(5), SG(5)
C DIMENSION P(100), VPM(100), VDF(100), CAP(100)
C DIMENSION Y1(100), Y2(100), YA(100), YB(100), YC(100)
C DIMENSION YD(100), YDEIAL(100), CHECK(100,3)
C DIMENSION PENG(4), IR(3), ZI(3)
C REAL*8 K12, IPH, K1, K2
C COMPLEX*16 ZCOM(3)
C NAMELIST /RON/ W1, PC1, TC1, W2, PC2, TC2, V1
C**********************************************************************
C COA, OB, ALE, ABIG, BBIG ARE CONSTANTS IN THE PENG-
C ROBINSON EQUATION OF STATE. R IS THE GAS CONSTANT.
C J IS THE CURRENT COUNTER ON P. J=1,2,3...N.
C WHERE N IS THE NUMBER OF PRESSURE INTERVALS. PENG
C ARE THE COEFFICIENTS OF THE CUBIC POLYNOMIAL OF THE PENG-
C ROBINSON EQUATION OF STATE WRITTEN IN TERMS OF
C COMPRESSIBILITY FACTORS. ZR ARE THE REAL ROOTS OF THIS
C POLYNOMIAL. ZI ARE THE COMPLEX ROOTS OF THIS POLYNOMIAL.
C Y1 IS THE MOLE FRACTION OF THE SOLUTE IN THE GAS PHASE.
C Y2 IS THE MOLE FRACTION OF THE SOLVENT IN THE GAS PHASE.
C YA, YB, YC ARE INTERMEDIATE VALUES OF MOLE
C FRACTIONS USED IN THE WEGSTEIN ACCELERATION METHOD THAT IS
C USED TO CONVERGE MOL FRACTIONS. SG IS THE NAME OF THE
C SOLVENT GAS. SS IS THE NAME OF THE SOLUTE.
C**********************************************************************
C
C READ (5,5) (SG(K), K=1,5)
C 5 FORMAT (54,4)
C READ (5,10) (SS(K), K=1,5)
C 10 FORMAT (54,4)
C READ (5,15) N
C 15 FORMAT (12)
C N IS THE NUMBER OF PRESSURE DATA POINTS.
C DO 25 ILOOP=1,N
C 25 CONTINUE
C P ARE THE PRESSURES IN BARS
C READ (5,30) T
C 30 FORMAT (1F10.5)
C T IS THE TEMPERATURE IN DEGREES K.
C READ (5,40) W1, PC1, TC1
C 40 FORMAT (1F10.5)
FILE: PENG FORTRAN A CONVERSATIONAL MONITOR SYSTEM

```
Table VI-1 (cont.)

Computer Program PENG

READ (5.50) W2, PC2, TC2
50 FORMAT (F10.5) PEN00560
C *************** PEN00570
C d1, PCI, TCI ARE THE ACCENTRIC FACTORS, CRITICAL
C PRESSURES, AND CRITICAL TEMPERATURES. UNITS:
C DEG. K, AND BARS.
C *************** PEN00580
C READ (5.50) PI VAP
60 FORMAT (E11.5) PEN00590
C PI VAP IS THE VAPOR PRESSURE IN BARS.
C READ (5.70) V1
70 FORMAT (F10.5) PEN00600
C V1 IS THE MOLAR VOLUME OF THE SOLUTE IN CC/GMOL.
C READ (5.80) K12
80 FORMAT (F10.5) PEN00610
C K12 IS THE BINARY INTERACTION COEFFICIENT.
DATA CA, CB, R, 0.4572400, 0.0778000, 83.1400/
C END OF DATA INPUT.
C *************** PEN00620
C CALCULATION OF THE CONSTANT PROPERTIES IN THE PENG-
C ROBINSON EQUATION OF STATE.
C *************** PEN00630
B1 = C3 + R*TC1/PC1
B2 = C3 + R*TC2/PC2
T1 = T/TC1
T2 = T/TC2
K1 = 0.3746400 + 1.5422600*W1 - 0.2699200*W1*W1
K2 = 0.3746400 + 1.5422600*W2 - 0.2699200*W2*W2
GAMMA1 = (1.00 - K1*(1.00 - T1**0.5))**2.00
GAMMA2 = (1.00 - K2*(1.00 - T2**0.5))**2.00
ALIE1 = CA + R*TC1 - TC1/PC1
ALIE2 = CA + R*TC2 - TC2/PC2
ALIE1 = ALIE1 + GAMMA1
ALIE2 = ALIE2 + GAMMA2
M = 1
J = 1
L = 1
WRITE (6,90)
90 FORMAT (35X, 'PENG-ROBINSON EQUATION OF STATE')
WRITE (6,100) (SG(K), K=1,5) PEN00940
100 FORMAT (35X, 'SOLVENT GAS:', S4) PEN00950
WRITE (6,110) (SS(K), K=1,5) PEN00960
110 FORMAT (35X, 'SOLUTE:', S4) PEN00970
WRITE (6,120) T PEN00980
120 FORMAT (35X, 'TEMPERATURE=', F6.1, ' K')
WRITE (6,130) PI VAP PEN00990
130 FORMAT (35X, 'VAPOR PRESSURE = ', E10.5, ' BAR')
WRITE (6,131) W PEN01000
131 FORMAT (35X, 'W1=', F10.5) PEN01010
WRITE (6,132) W PEN01020
132 FORMAT (35X, 'W2=', F10.5) PEN01030
WRITE (6,133) TC1 PEN01040
133 FORMAT (35X, 'TC1=', F10.5) PEN01050
WRITE (6,134) TC2 PEN01060
134 FORMAT (35X, 'TC2=', F10.5) PEN01070
```
Table VII-1 (cont.)

Computer Program PENG

FILE: PENG  FORTRAN  A

CONVERSATIONAL MONITOR SYSTEM

WRITE(6,135) PC1
135 FORMAT(26X,'PC1=',F10.5)
WRITE(6,136) PC2
136 FORMAT(26X,'PC2=',F10.5)
WRITE(6,137) V1
137 FORMAT(26X,'V1=',F10.5)
WRITE(6,138) K12
138 FORMAT(35X,'K12=',F10.5)
WRITE(6,139) Y1(K)=0.DO
139 FORMAT(36X,'Y1(K)=0.DO')
WRITE(6,140) Y2(J)=1.DO-Y1(J)
140 FORMAT(25X,'Y2(J)=1.DO-Y1(J)')

---

DO 170 K=1,N
170 Y1(K)=0.DO

---

C TR1,TR2 ARE THE REDUCED TEMPERATURES. K1,K2
C GAMMA1, GAMMA2, ALIE1, ALIE2 ARE THE CONSTANTS
C IN THE PENG-ROBINSON EQUATION OF STATE. L IS A
C COUNTER WHICH IS EITHER 1 OR 2 AND IS USED IN THE
C TWO STEPS OF THE WEIGSTEIN ACCELERATION METHOD OF
C CONVERGING MOL FRACTIONS. M IS A COUNTER ON THE NUMBER OF
C ITERATIONS IN CONVERGING MOL FRACTIONS.

---

CALL ZPOLR(PENG,3,ZCOMP,IER)
IF (IER .EQ. 0) GO TO 200
WRITE (6,150) IER
GO TO 999

---

C THE ABOVE SECTION CALCULATED THE COMPOSITION
C OF THE DEPENDENT PROPERTIES IN THE PENG-ROBINSON EQUATION.
C IN THE NEXT SECTION WILL BE CALCULATED THE MOLAR VOLUME.
C OF THE GAS PHASE BY SOLVING
C THE CUBIC FORM OF THE PENG-ROBINSON EQUATION OF
C STATE AND TAKING THE LARGEST ROOT IN THE CASE OF MULTIPLE
C ROOTS. THE IMSL SUBROUTINE ZPOLR IS REQUIRED

---

CALL ZPOCR(PENG,3,ZCOMP,IER)
IF (IER .EQ. 0) GO TO 200
WRITE (6,150) IER

---

200 ZR(1)=REAL(ZCOMP(1))
ZR(2)=REAL(ZCOMP(2))
ZR(3)=REAL(ZCOMP(3))

---
Table VII-1 (cont.)

Computer Program PENG

FILE: PENG FORTRAN A CONVERSATIONAL MONITOR SYSTEM

ZI(1) = AIMAG(ZCOMP(1))
ZI(2) = AIMAG(ZCOMP(2))
ZI(3) = AIMAG(ZCOMP(3))
DO 220 K = 1, 3
IF (ZI(K) .EQ. 0.00) GO TO 210
ZI(K) = 0.00
GO TO 220
210 ZI(K) = 1.00
220 CONTINUE
DO 230 K = 1, 3
230 ZR(K) = ZR(K) * ZI(K)
CHECK(J, 1) = ZR(1)
CHECK(J, 2) = ZR(2)
CHECK(J, 3) = ZR(3)
VR = T * (CRAX1(ZR(1), ZR(2), ZR(3))/P(J))
C THE FOLLOWING SECTION COMPUTES THE FUGACITY
C COEFFICIENT OF THE SOLID. PHI TO PH6 ARE THE
C COMPONENTS OF THE FUGACITY. PH IS THE LOG OF THE FUGACITY
C COEFFICIENT. PT IS THE POYNTING TERM.
C*****************************************************
Z = P(J)*V*R/T
PH1 = B1*(Z-1.00)/B
PH2 = (-1.00)*DLOG(Z-BBIG)
PH3 = (-1.00)*ABIG*2.00/BBIG/DSORT(2.00)
PH4 = ALIE1=2.00+Y2(J)*(1.00-K12)*
1((ALIE1+ALIE2)=-0.500)/ALIE
PH5 = (-1.00)*B1/B
PH6 = DLOG((Z-2.414 DO*BBIG)/(Z-0.4140*BBIG))
SH1 = PH1 = PH2*PH3*PH4*PH5*PH6
IF = DEXP(PH)
P = DEXP(V1*(P(J)-P1VAP)/R/T)
ENT = PT/1PH
C*****************************************************
C IN THIS SECTION OCCURS THE ACCELERATED WEIGSTEIN
C CONVERGENCE METHOD TO GET CONVERGENCE ON MOL.
C FRACTIONS.
C*****************************************************
IF (L .EQ. 2) GO TO 240
YA(J) = Y1(J)
YB(J) = ENT*P1VAP/P(J)
Y1(J) = YB(J)
L = L + 1
GO TO 180
240 YC(J) = ENT*P1VAP/P(J)
FP = (YC(J)-YB(J))/(YB(J)-YA(J))
ALPHA = 1.00/(1.00-FP)
YD(J) = YB(J)*ALPHA*(YC(J)-YB(J))
ERROR = 1.00*ABS((YC(J)-YB(J))/YC(J))
IF (ERROR .LT. 1.00) GO TO 270
M = M + 1
IF (M .LT. 15) GO TO 250
WRITE (6, 250) M
250 FORMAT (' Y NOT CONVERGED IN ', I2, ' ITERATIONS')
GO TO 888
Table VII-1 (cont.)

Computer Program PENG

FILE: PENG FORTRAN A CONVERSATIONAL MONITOR SYSTEM

260 Y1(J) = YD(J)
L = 1
GO TO 180
270 Y1(J) = YD(J)
Y2(J) = 1.00 - Y1(J)
YIDEAL(J) = P1VAP/P(J)

C IN THIS SECTION OCCURS THE CALCULATIONS FOR THE PARTIAL MOLAR VOLUMES.
C THE DIFFERENCE BETWEEN THE PARTIAL MOLAR VOLUME AND THE SOLID
C VOLUME, AND THE CAPACITY OF THE FLUID PHASE. VPM IS THE
C PARTIAL MOLAR VOLUME(CC/G.MOL). CAP IS THE CAPACITY(G.MOL/CC)
C
Q1 = R*T/(V-B)
Q2 = 1.00 + B1/(V-B)
Q3 = G1 + Q2
Q4 = 2.00*(Y1(J)*ALIE1 + Y2(J)*((ALIE1*ALIE2)/(1.00 - K12)))
Q5 = 2.00*ALIE*B1*(V-B)
Q6 = V*(V+B) + B*(V-B)
Q7 = 05/06
Q8 = Q4 + Q7
Q9 = V*(V+B) + B*(V-B)
Q10 = 08/09
Q11 = 03 - 010
Q12 = R*T/(V-B)/(V-B)
Q13 = 2.00*ALIE*(V-B)
Q14 = V*(V+B) - B*(V-B)**2.00
Q15 = Q12 - Q13/014
Q16 = Q11 + Q15

VPM(J) = Q16

C CAP(J) = Y1(J)/V
WRITE(6,280) P(J), Y1(U), YIDEAL(J), ENT, VZ, IPM, PT
280 FORMAT(8E16.5)
868 J = J + 1
M = 1
L = 1
IF (J .LE. N) GO TO 180
WRITE(6,774)
774 FORMAT(///)
WRITE(6,775)
776 FORMAT(6X,'(P(BAR))',7X,'VPM(CC/G.MOL)',4X,'(VS-VPM)(CC/G.MOL)',
15X,'CAP(G.MOL/CC)')
778 DO 778 I = 1, N
WRITE(6,775) (P(I)), (VPM(I)), (VS - VPM(I))*(CC/G.MOL),
CAP(I)
777 CONTINUE
999 STOP
END
FILE: MPR FORTRAN A CONVERSATIONAL MONITOR SYSTEM

C.................. MPRL0010
C
C RONALD T. KURNIK
C MASSACHUSETTS INSTITUTE OF TECHNOLOGY
C DEPARTMENT OF CHEMICAL ENGINEERING
C
C IMPLICIT REAL*8 (A-H,O-Z)
C
C THIS IS THE PROGRAM THAT CREATES THE CALLING SEQUENCE FOR
C THE MULTICOMPONENT PENG-ROBINSON EOS.
C
DIMENSION PM(100)
DIMENSION X(:,0),Y(10),PT(10)
DIMENSION APHI(10),ERROR(10),AP(10,10),PM(10)
REAL*8 KIJ(10),LIJ(10,10)
INTEGER N,IFLAG,LIJ,IFLAG1
COMMON /Q1/ R,T,TC(10),PC(10),W(10)
COMMON /Q2/ A1(10),B1(10),TR(10)
COMMON /Q3/ KIJ,PVAP(10),VS(10),PHI,AP,SIJ
COMMON /Q4/ N,IFLAG,LIJ,IFLAG1
COMMON /Q5/ VAPHI,Z,YID(10),E(10),PT,Y
COMMON /Q6/ NSOLV,NSOLU
READ(4,10) NP
FORMAT(I2)
NP IS THE NUMBER OF PRESSURE DATA POINTS
READ(4,20) (PM(I),I=1,NP)
FORMAT (F10.5)
P=PM(1)
CALL PENGMR(P)
IF((IFLAG .EQ. 0) .AND. (IFLAG1 .EQ. 0)) GO TO 80
GO TO 999
CONTINUE
CALL PENGFR(W,TC,PC,KIJ,PVAP,VS,NSOLV,NSOLU,N,SIJ)
CALL PENGFR(KIJ,NSOLU,N,T,P,V,Z,YID,E,APHI,PT,SIJ)
WRITE(6,50)
FORMAT(///)
REWIND 5
IF (NP .EQ. 1 ) GO TO 999
DO 30 I=2,NP
P=PM(I)
CALL PENGMR(P)
IF ((IFLAG .EQ. 0) .AND. (IFLAG1 .EQ. 0)) GO TO 70
GO TO 999
CALL PENGFR(KIJ,NSOLU,N,T,P,V,Z,YID,E,APHI,PT,SIJ)
WRITE(6,40)
FORMAT(///)
REWIND 5
CONTINUE
999 STOP
END
FILE: PENGMR FORTRAN

CONVERSATIONAL MONITOR SYSTEM

SUBROUTINE PENGMR(P)
IMPLICIT REAL=8(A-H,O-Z)
DIMENSION X(10),Y(10),PT(10)
DIMENSION APHI(10),ERROR(10),AP(10,10)
DIMENSION PH1(10),PH2(10),PH3(10),PH4(10),PH5(10),PH7(10),
PH8(10),PHI(10)
REAL *8 KIJ(10),LIJ(10,10)
INTEGER NSOLV(5),NSOLU(45)
COMMON /O1/ R,TTC(10),PC(10),W(10)
COMMON /Q3/ KIJ,PVAP(10),VS(10),PHI,AP,SIJ
COMMON /Q7/ PH1,PH2,PH3,PH4,PH5,PH7,PH8
DO 5 I=1,10
ERROR(I)=0.DO
KIJ(I)=0.DO
PVAP(I)=0.DO
VS(I)=0.DO
5 NAMELIST/RON/ PH1,PH2,PH3,PH4,PH5,PH7,PH8,V,Z,A1,B1,TR,PHI,APHI,
PT,LIJ,AP

C 1 IS ALWAYS THE SOLVENT. 2 THRU 10 ARE THE SOLUTES.
C THIS PROGRAM IS THE DRIVER PROGRAM FOR THE MULTICOMPONENT
C EOS SOLID-FLUID EQUILIBRIA CALCULATIONS. AT PRESENT, 2
C SOLUTES AND 1 SOLVENT CAN BE MODELLED, BUT THIS CAN BE EASILY
C EXTENDED. BOTH SOLID-FLUID AND SOLID-SOLID BINARY
C INTERACTIONS CAN BE MODELLED. DIRECT
C ITERATION IS USED FOR CONVERGENCE.
C
READ(5,10) T
10 FORMAT(F14.7)
C T IS THE SYSTEM TEMPERATURE, K
READ(5,20) N
20 FORMAT(I2)
C N IS THE NUMBER OF PHASES, NOW RESTRICTED TO 2 OR 3.
M=N-1
L=1
LM=5*M
R=83.14
READ(5,21) (NSOLV(K),K=1,M)
21 FORMAT(5A4)
C NSOLV IS THE NAME OF THE SOLVENT, 20 CHARACTERS AT MOST.
DO 23 I=1,LM,5
J=I+4
READ(5,22) (NSOLU(K),K=I,J)
22 FORMAT(5A4)
C NSOLU ARE THE NAMES OF THE SOLUTES, 20 CHARACTERS AT MOST.
23 CONTINUE
Table V1-2 (cont.)

Computer Program MPR

FILE: PENGMR FORTRAN A

CONVERSATIONAL MONITOR SYSTEM

DO 210 I=2,N
210  E(I)=Y(I)/YID(I)

Z=P*V/R/T

999  RETURN

END
SUBROUTINE VPSP (ABIG, BBIG, V, IER, IFLAG, T, P, R)  
IMPLICIT REAL*8 (A-H, O-Z)  
FILE: VPSP FORTRAN  
A CONVERSATIONAL MONITOR SYSTEM  
C THIS PROGRAM CALCULATES THE VAPOR ROOT FOR THE PR EOS ONLY.  
C IN THE CASE OF MULTIPLE ROOTS, IFLAG IS SET EQUAL TO 1  
C AND EXECUTION TERMINATED. NOTE: THE IMSL SUBROUTINE ZPOLR  
C IS NEEDED.  
C*************************************************************************  
DIMENSION PENG(4), ZR(3), ZI(3)  
COMPLEX*16 ZCOMP(3)  
IFLAG=0  
PENG(1)=1.D0  
PENG(2)=(-1.DO)*(1.DO-BBIG)  
PENG(3)=(ABIG-3.DO*BBIG*BBIG-2.DO*BBIG)  
PENG(4)=(-1.DO)*(ABIG+BBIG-BBIG*BBIG-BBIG*BBIG)  
CALL ZPOLR (PENG,3,ZCOMP,IER)  
IF (IER .NE. 131) GO TO 5  
WRITE(6,1)  
1 FORMAT(' ROOT FINDING ERROR, IER=131')  
IFLAG=1  
GO TO 999  
5 ZR(1)=REAL(ZCOMP(1))  
ZR(2)=REAL(ZCOMP(2))  
ZR(3)=REAL(ZCOMP(3))  
ZI(1)=AIMAG(ZCOMP(1))  
ZI(2)=AIMAG(ZCOMP(2))  
ZI(3)=AIMAG(ZCOMP(3))  
DO 20 I=1,3  
IF(ZI(I) .EQ. 0.00) GO TO 10  
ZI(I)=0.00  
GO TO 20  
10 CONTINUE  
DO 30 I=1,3  
30 ZR(I)=ZR(I)+ZI(I)  
TOP=DMAX1(ZR(1),ZR(2),ZR(3))  
BOT=DMIN1(ZR(1),ZR(2),ZR(3))  
V=R*T*TOP/P  
999 RETURN  
END
FILE: ES05R FORTRAN A

Computer Program MPR

SUBROUTINE ES05R (P,X,A,ABIG,B,BBIG,APHI,V,Z)

IMPLICIT REAL*8 (A-H,O-Z)

FILE: ESOSR FORTRAN

A CONVERSATIONAL MONITOR SYSTEM

SUBROUTINE ESOSR (P,X,A,ABIG,B,BBIG,APHI,V,Z)

IMPLICIT REAL*8 (A-H,O-Z)

C THIS PROGRAM CALCULATES THE MIXTURE CONSTANTS AND COMPONENT FUGACITIES FOR A N (NOW RESTRICTED TO 10) COMPONENT MIXTURE. THIS IS DONE FOR PR EOS ONLY. COMMONS ARE LINKED WITH PROGRAM ES06R.

C
C
C REAL*8 KIJ(10),LIJ(10,10)
DIMENSION AP(10,10),PHI(10),APHI(10),A2(10),X(10)
DIMENSION PH1(10),PH2(10),PH3(10),PH4(10),PH5(10),PH7(10),PH8(10)
COMMON /01/R,T,TC(I0),PC(10),W(10)
COMMON /Q2/A1(10),B1(10),TR(10)
COMMON /03/KIJ,PVAP(10),VS(10),PHI,AP,SIJ
COMMON /Q4/NIFLAG,LIJ
COMMON /Q7/PH1,PH2,PH3,PH4,PH5,PH7,PH8

=0.00

DO 10 I=1,N
B=B+B1(I)*X(I)

M=N+1
C IN ALL CALCULATIONS, '1' IS THE SOLVENT
C PHASE AND 2 THRU 10 ARE THE SOLUTES
PLUS=0.00
DO 30 I=1,N
DO 30 J=1,N
PLUS=PLUS+(1.0E-LI5(I,J))*DSQRT(A1(I)*Al(J))*X(I)*X(J)

A=PLUS
ABIG=A*P/R/R/T/T
BBIG=B*P/R/T
CALL VPSP(ABIG,BBIGV,IER,IFLAG,T,P,R)

IF (IFLAG EQ. 1 .OR. IER EQ. 131 ) GO TO 999

C CALCULATION OF FUGACITY COEFFICIENTS
Z=P*V/R/T

DO 70 I=2,N
PH1(I)=B1(I)=(Z-1.00)/B
PH2(I)=(-1.00)*DLOG(Z-BBIG)
PH3(I)=(-1.00)*ABIG/2.00/BBIG/DSQRT(2.00)
PLUS=0.00
DO 80 J=1,N
PLUS=PLUS+(1.00-LI5(I,J))*((A1(I)*A(J))**0.5)*X(J)

80 CONTINUE

PH4(I)=2.00*PLUS/A
PH5(I)=(-1.00)*B1(I)/B
PH7(I)=DLOG((Z-2.41400*BBIG)/(Z-0.41400*BBIG))

DO 90 I=2,N
PH(I)=PH1(I)+PH2(I)+PH3(I)*(PH4(I)+PH5(I)+PH7(I))

90 RETURN

END
FILE: ES06R

FORTRAN A

CONVERSATIONAL MONITOR SYSTEM

SUBROUTINE ES06R

C...............................
C THIS PROGRAM INITIALIZES THE PARAMETERS A AND B
C REQUIRED IN PENG-ROBINSON EOS.
C...............................

IMPLICIT REAL*8(A-H,O-Z)
REAL*8 KIJ(10),LIJ(10,10)
DIMENSION PHI(10),AP(10,10)
COMMON /Q1/R.TC(10),PC(10),W(10)
COMMON /Q2/ A1(10),B1(10),TR(10)
COMMON /Q3/ KIJ.PVAP(10),VS(10),PHI,AP,SIJ
COMMON /Q4/ N,IFLAG,LIJ
DIMENSION A2(10),ALPHA(10)
REAL*8 M(10)
DO 10 I=1,N
10 B1(I)=0.07780000*R*TC(I)/PC(I)
DO 20 I=1,N
20 A2(I)=0.45724000*R*/TC(I)*TC(I)/PC(I)
DO 30 I=1,N
30 M(I)=0.37464000+1.54226000*W(I)-0.26992000*W(I)*W(I)
DO 40 I=1,N
40 TR(I)=T/TC(I)
DO 50 I=1,N
50 ALPHA(I)=1.0*1.0-M(I)*(1.0-(TR(I)*1.0))
DO 60 I=1,N
60 ALPHA(I)=ALPHA(I)*ALPHA(I)
DO 70 I=1,N
70 A1(I)=A2(I)*ALPHA(I)
DO 80 I=1,N
80 DO 90 J=1,N
90 LIJ(I,J)=0.0
90 CONTINUE
80 CONTINUE
DO 100 J=2,N
100 LIJ(J,1)=KIJ(J)
LIJ(J,1)=KIJ(J)
CONTINUE
LIJ(2,3)=SIJ
LIJ(3,2)=SIJ
RETURN
END
Table VII-2 (cont.)

Computer Program MPR

FILE: PENGF1 FORTRAN A

SUBROUTINE PENGF1(W,TC,PC,KIJ,PVAP,VS,NSOLV,NSOLU,N,SIJ)
C ........................................................--...............PENO0010
C OUTPUT FORMATTING PROGRAM NO. 1 PEN00020
C ...............................................................-..............PEN00030
IMPLICIT REAL*8 (A-H,O-Z) PEN00040
REAL*8 KIJ(10) PEN00050
INTEGER NSOLU(45),NSOLV(5) PEN00060
DIMENSION W(10),TC(10),PC(10),PVAP(10),VS(10) PEN00070
WRITE(6,10) (NSOLV(K),K=1,5) PEN00080
10 FORMAT(38X,5A4) PEN00090
WRITE(6,20) W(1) PEN00100
20 FORMAT(30X,'W',14X,D10.5) PEN00110
WRITE(6,30) TC(1) PEN00120
30 FORMAT(30X,'TC(K)',10X,D10.5) PEN00130
WRITE(6,40) PC(1) PEN00140
40 FORMAT(30X,'PC(BAR)',8X,D10.5) PEN00150
M=N-1 PEN00160
DO 110 I=2,N PEN00170
LI=(I-1)*5-4 PEN00180
J=LI+4 PEN00190
WRITE(6,50) (NSOLU(K),K=LI,J) PEN00200
50 FORMAT(40X,5A4) PEN00210
WRITE(6,55) KIJ(I) PEN00220
55 FORMAT(30X,'KIJ',11X,D10.5) PEN00230
WRITE(6,60) W(I) PEN00240
60 FORMAT(30X,'W',14X,D10.5) PEN00250
WRITE(6,65) TC(I) PEN00260
65 FORMAT(30X,'TC(K)',10X,D10.5) PEN00270
WRITE(6,70) PC(I) PEN00280
70 FORMAT(30X,'PC(BAR)',8X,D10.5) PEN00290
WRITE(6,75) PVAP(I) PEN00300
75 FORMAT(30X,'PVAP(BAR)',6X,D10.5) PEN00310
WRITE(6,80) VS(I) PEN00320
80 FORMAT(30X,'VS(CC/GR.MOL)',2X,D10.5) PEN00330
CONTINUE PEN00340
110 CONTINUE PEN00350
WRITE(6,120) SIJ PEN00360
120 FORMAT(30X,'SOLUTE=SOLUTE INTERACTION COEFFICIENT= ',F10.5,///) PEN00370
RETURN PEN00380
END PEN00390
FILE: PENGF2 FORTRAN A

SUBROUTINE PENGF2 (KIJ,NSOLU,N,T,P,V,Z,YID,E,APHI,PT,SIJ)

C..............................
C OUTPUT FORMATTING PROGRAM NO. 2
C..............................

IMPLICIT REAL*8 (A-H,O-Z)

REAL*8 KIJ(10)
INTEGER NSOLU(5),NSOLU(45)
DIMENSION W(10),TC(10),PC(10),PVAP(10),VS(10),Y(10),
YID(10),E(10),APHI(10),PT(10)

M=N-1
L=M*5
WRITE(6,120) T
120 FORMAT(40X,' TEMPERATURE=',D10.5,'K')
WRITE(6,130) P
130 FORMAT(40X,' PRESSURE=',D10.5,'BARS')
WRITE(6,140) V
140 FORMAT(40X,' VOLUME=',D10.5,'CC/GR.MOL')
WRITE(6,150) Z
150 FORMAT(40X,' COMPRESSIBILITY=',D10.5,/) 
WRITE(6,160)
160 FORMAT(42X,' Y(PENG)',9X,' Y(Ideal)',6X,' ENHANCEMENT',6X,
1 ' FUGACITY',8X,' POYNTING')
WRITE(6,170)
170 FORMAT(75X,'FACTOR',7X,' COEFFICIENT',8X,' TERM')
DO 200 I=2,N
LI=(I-1)*5-4
J=LI+4
WRITE(6,190) (NSOLU(K),K=LI,J),Y(I),YID(I),E(I),APHI(I),
PT(I)
190 FORMAT(15X,5A4,5D16.5)
200 CONTINUE
RETURN
END
Computer Program MPR

FILE: ERCAL FORTRAN A CONVERSATIONAL MONITOR SYSTEM

FUNCTION ERCAL (ERROR) 
IMPLICIT REALS(A-H,O-Z) 
DIMENSION ERROR(10) 
ERCAL = DMAX1(ERROR(1),ERROR(2),ERROR(3),ERROR(4),ERROR(5), 
ERROR(6),ERROR(7),ERROR(8),ERROR(9),ERROR(10)) 
RETURN 
END 

FILE: SUM FORTRAN A CONVERSATIONAL MONITOR SYSTEM

FUNCTION SUM(X,N) 
IMPLICIT REALS(A-H,O-Z) 
DIMENSION X(10) 
ADD = 0.0 
DO 10 I = 2, N 
ADD = ADD + X(I) 
SUM = ADD 
RETURN 
END
Table VII-3
Computer Program KIJSP

FILE: KIJSP
FORTRAN A
CONVERSATIONAL MONITOR SYSTEM

C.......................... KIU00010
C RONALD T. KURNIK
C MASSACHUSETTS INSTITUTE OF TECHNOLOGY
C DEPARTMENT OF CHEMICAL ENGINEERING
C.......................... KIU00030
C
C IMPLICIT REAL*8 (A-H.O-Z)
C
C THIS PROGRAM PERFORMS A NONLINEAR LEAST SQUARES REGRESSION
C ON (Y,P) DATA TO BACKTRACK OUT AN OPTIMAL BINARY INTERACTION
C PARAMETER. THE FOLLOWING LIBRARIES MUST BE LINKED:
C TESTBED AND PRODCTLB--BOTH AVAILABLE ON PROJECT
C ASPEN. SEE HERB BRITT OF UNION CARBIDE FOR ADDITIONAL
C INFORMATION. THE SUBROUTINES SVEP AND VSVEP ARE ALSO
C REQUIRED.
C
C EXTERNAL SVEP
C COMMON /GLOBAL/ KIU00110
1 KPFLG1 ,KPFLG2 ,KPFLG3 ,LABORT ,NH ,
 1  LDIAG ,NCHAR ,LMISS ,MISSC1 ,MISSC2 ,
 2  LPDIAG ,IEBAL ,IRFLAG ,MXBLKW ,ITYPRN ,
 3  LBCP ,LSBP ,LSDIAG ,MAXNE ,MAXNP1 ,
 4  MAXNP2 ,MAXNP3 ,IUPDAT ,IRSTRT ,LSFLAG ,
 5  LPFLAG ,KBLK1 ,KBLK2 ,KRFLAG ,IRNCLS ,
 6  LSThis
C END COMMON /GLOBAL/ 10-11-79
C
C K IS THE NUMBER OF EXPERIMENTAL DATA POINTS IN Y
C
C READ (3,10) K
C FORMAT (I2)
C
C READ (3,15) T
C FORMAT (F10.5)
C DO 40 I=1,K
C READ(3,30) X(I,I),ZM(I,I)
C FORMAT(F11.5,D11.5)
C DO 35 I=1,K
C
C........................................................... KIU00190
Table VII-3 (cont.)

Computer Program KIJSP

FILE: KIJSP FORTRAN

CONVERSATIONAL MONITOR SYSTEM

35 ZM(1.I)=DLOG(ZM(1.I))
20 READ(5,200) TC1,TC2
200 FORMAT(F10.5)
210 READ(5,210) PC1,PC2
220 FORMAT(F10.5)
230 READ(5,220) T
250 FORMAT(F10.5)

WRITE(6,252)

252 FORMAT('PENG-RADINSON EQUATION OF STATE')

WRITE(6,260) TC1
260 FORMAT('TC1=',F10.5)
WRITE(6,263) TC2
270 FORMAT('TC2=',F10.5)
WRITE(6,266) PC1
280 FORMAT('PC1=',F10.5)
WRITE(6,270) PC2
290 FORMAT('PC2=',F10.5)
WRITE(6,300) W1
300 FORMAT('W1=',F10.5)
WRITE(6,310) W2
310 FORMAT('W2=',F10.5)
WRITE(6,320) VS
320 FORMAT('VS=',F10.5)
WRITE(6,330) PVP
330 FORMAT('PVP=',F10.5)
WRITE(6,350) T
350 FORMAT('T=',F10.5)

WRITE(6,370) K
370 FORMAT('K=',I12)

N=1 M=1
L=1
NC=1 US(1)=0.5 LS(1)=0.3
ITER=50 IDEM=20
ACUT=1
NH=6 IODS=1 SS=0.0001 EFS=1.0-6
NDRIV=1 SSNO=1.0-4
ISV=0
NC=0 ISOUND=1

KIJO560 KIJO570 KIJO580 KIJO590 KIJO600 KIJO610 KIJO620 KIJO630 KIJO640 KIJO650 KIJO660 KIJO670 KIJO680 KIJO690 KIJO700 KIJO710 KIJO720 KIJO730 KIJO740 KIJO750 KIJO760 KIJO770 KIJO780 KIJO790 KIJO800 KIJO810 KIJO820 KIJO830 KIJO840 KIJO850 KIJO860 KIJO870 KIJO880 KIJO890 KIJO900 KIJO910 KIJO920 KIJO930 KIJO940 KIJO950 KIJO960 KIJO970 KIJO980 KIJO990 KIJO100 KIJO101 KIJO102 KIJO103 KIJO104 KIJO105 KIJO106 KIJO107 KIJO108 KIJO109 KIJO110
Computer Program K1JSP

FILE: K1JSP    FORTRAN A  CONVERSATIONAL MONITOR SYSTEM

REWIND 5
 CALL GENLSQ (N,M,MM,LM,NC,NCV,P,ZM,X,RSVEP,ITER,ITERZ, KIJO1110
1 IDEM,ICOD,SS,EP5,KOUT,NOIV,SSND,ISV,WORK,IFWORK,Z,F,DELZ, KIJO1120
2 SUMSO,SIGMA,COVAR,NFEVAL,IER,LBOUND,UB,LM,NIC,O,I)  KIJO1130
 WRITE(6,60) IER  KIJO1140
60 FORMAT (//,'ERROR CODE =',1I1)  KIJO1150
   WRITE(6,70)  KIJO1160
70 FORMAT (//)  KIJO1170
60 FORMAT (///)  KIJO1180
70 FORMAT (///)  KIJO1190
   DO 72 I=1,K  KIJO1200
72 Z(1,I)=DEXP(ZM(1,I))  KIJO1210
   DO 74 I=1,K  KIJO1220
74 PE(I)=DAES(ZM(1,I)-Z(1,I))/ZM(1,I)*100.00  KIJO1230
 WRITE(6,80)  KIJO1240
80 FORMAT (2X,'PRESSURE',6X,'MOL. FRACTION',3X,'MOL. FRACTION', KIJO1250
    16X,'PERCENT')  KIJO1260
   WRITE(6,82)  KIJO1270
82 FORMAT (42X,'(MEASURED)',6X,'(ESTIMATED)',8X,'ERROR')  KIJO1280
   DO 100 I=1,K  KIJO1290
100 WRITE(6,90) (X(1,I),ZM(1,I),Z(1,I),PE(I))  KIJO1300
   CONTINUE  KIJO1310
   STOP  KIJO1320
   END  KIJO1330
Table VII-3 (cont.)

CONVERSATIONAL MONITOR SYSTEM

**Computer Program K1JSP**

**FILE:** SVEP **FORTRAN A**

**SUBROUTINE** SVEP(Z,ZM,X,P,K,M,MV,L,N,NC,NCV,KEY,F)

```fortran
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 M1,M2
DIMENSION ZM(1,100),Z(1,100),P(S),MV(100),NCV(100),F(100)
DIMENSION B(100),A(100),ASIG(100),SSIG(100),
IPH1(100),PH2(100),PH3(100),PH4(100),PHS(100),PS(100),
2PH(100),PV(100),PV1(100),PV2(100),ZC(100),
3V(100),X(1,100)
```

**CASES**

**1** **IS** SOLID, **2** **IS** FLUID

**READ** (5,10) TC1,TC2

```fortran
10 FORMAT(F10.5)
```

**READ** (5,20) PC1,PC2

```fortran
20 FORMAT(F10.5)
```

**READ** (5,30) W1,WZ

```fortran
30 FORMAT(F10.5)
```

**READ** (5,40) VS

```fortran
40 FORMAT(F10.5)
```

**READ** (5,50) PVP

```fortran
50 FORMAT(F10.5)
```

**DATA** RGAS/93.14/

```fortran
DATA OA/0.4572400/
DATA OB/0.0778000/
```

**CALCULATION OF FUGACITY COEFFICIENT OF SOLID**

**DO 70 I=1,K**

```fortran
PS(I)=X(1,I)*VS/RGAS/T+DLOG(PVP)
```

**CALCULATION OF CONSTANT PROPERTIES IN PENG-ROBINSON EOS**

```fortran
B1=OB*RGAS*TC1/PC1
A22=OA*RGAS-PC2
M1=0.3746400+1.54226DO*W1-0.2699200*W1W1
M2=0.3746 4 00+1.54226DO*W2-0.26992DO*W2*W2
TR1=T/TC1
TR2=T/TC2
ALPHA1=1.00+M1*(1.00-TR1**0.5D0))
ALPHA2=1.00+M2*(1.00-TR2**0.5D0))
```

**CALCULATION OF MIXTURE PROPERTIES**

```fortran
Z(1,I)=DEXP(Z(1,I))
```

```fortran
DO 140 I=1,K
Z(1,I)=DEXP(Z(1,I))
DO 150 I=1,K
B(I)=B1+Z(1,I)+B2*(1.00-Z(1,I))
```

**C** 1 IS SOLID, 2 IS FLUID

**READ** (5,10) TC1,TC2

**READ** (5,20) PC1,PC2

**READ** (5,30) W1,WZ

**READ** (5,40) VS

**READ** (5,50) PVP

**DATA** RGAS/93.14/

**DATA** OA/0.4572400/

**DATA** OB/0.0778000/
Computer Program KJESP

FILE: SVEP FORTRAN A CONVERSATIONAL MONITOR SYSTEM

AIJ=((A1*A2)**0.5DO)*(1.DO-P(I))  
DO 165 I=1,K  
165 A(I)=Z(1,I)*Z(I,I)*AIJ+  
12.DO*Z(1,I)*(1.DO-Z(1,I))*AIJ+  
2*(1.DO-Z(1,I))*(1.DO-Z(1,I))*A2  
DO 180 I=1,K  
ABIG(I)=A(I)*X(1,I)/RGAS/RGAS/T/T  
BBIG(I)=B(I)*X(1,I)/RGAS/T  
CALL VSVEP(ABIG,BBIG,V,T,RGAS,KZM,X,Z)  
DO 185 I=1,K  
185 ZC(I)=X(1,I)*V(I)/RGAS/T  
C............................................................ ..........  
C CALCULATION OF FUGACITY COEFFICIENTS.  
C...............................................................................5

DO 190 I=1,K  
PH1(I)=B1*(ZC(I)-1.DO)/B(I)  
PH2(I)=(-1.DO)*DLOG(ZC(I)-BBIG(I))  
PH3(I)=2.DO*(ZC(I)+BBIG(I))/BBIG(I)  
PH4(I)=2.DO* (1.DO-Z(1,I))*AIJ/A(I)  
PH5(I)=(-1.DO)*B1/B(I)  
PH6(I)=DLOG(ZC(I)+2.41400*BBIG(I))/(ZC(I)-0.41400*BBIG(I))  
190 PV1(I)=PH1(I)+PH2(I)+PH3(I)*(PH4(I)+PH5(I))*PH6(I)  
DO 200 I=1,K  
200 PV2(I)=Z(1,I)*X(1,I)*DEXP(PV1(I))  
DO 205 I=1,K  
205 PV(I)=DLOG(PV2(I))  
DO 210 I=1,K  
210 PV(I)=P(I)*S(I)  
DO 220 I=1,K  
220 ZC(I)=DLOG(ZC(I))  
REWIND S  
RETURN  
END  
SVE00680  
SVE00690  
SVE00700  
SVE00710  
SVE00720  
SVE00730  
SVE00740  
SVE00750  
SVE00760  
SVE00770  
SVE00780  
SVE00790  
SVE00800  
SVE00810  
SVE00820  
SVE00830  
SVE00840  
SVE00850  
SVE00860  
SVE00870  
SVE00880  
SVE00890  
SVE00900
Table VII-3 (cont.)

Computer Program KIJS8

**FILE: VSVEP FORTRAN A**

**CONVERSATIONAL MONITOR SYSTEM**

SUBROUTINE VSVEP (ABIG, BBIG, V, T, RGAS, K, ZM, X, Z)

C ....................................................................... VSVO0010
C THIS SUBROUTINE CALCULATES THE SPECIFIC VOLUME OF THE FLUID PHASE. VSVO0020
C THE IMSL SUBROUTINE ZPOLR IS REQUIRED. VSVO0030
C ................................................................................... VSVO0040
IMPLICIT REAL*8 (A-H, O-Z) VSVO0050
DIMENSION PENG(4), V(100), ZR(3), ZI(3), ZM(1, 100), Z(1, 100) VSVO0060
DIMENSION ABIG(100), BBIG(100), X(1, 100) VSVO0070
COMPLEX*16 ZCOMP(3) VSVO0080
RGAS = 83.14 VSVO0090
DO 30 I = 1, K VSVO0100
    PENG(1) = 1.0D0 VSVO0110
    PENG(2) = (-1.0D0) * (1.0D0 - BBIG(I)) VSVO0120
    PENG(3) = ABIG(I) - 3.0D0 * BBIG(I) * BBIG(I) - 2.0D0 * BBIG(I) VSVO0130
    PENG(4) = (-1.0D0) * BBIG(I) * (ABIG(I) - BBIG(I) - BBIG(I) * BBIG(I)) VSVO0140
    CALL ZPOLR(PENG, 3, ZCOMP, IER) VSVO00150
10  DO 20 J = 1, 3 VSVO0160
    ZR(J) = REAL(ZCOMP(J)) VSVO00170
    ZI(J) = AIMAG(ZCOMP(J)) VSVO00180
20  CONTINUE VSVO00190
    IF (ZI(J) .EQ. 0.0D0) GO TO 20 VSVO0200
    ZR(J) = 0.0D0 VSVO00210
DO 30 J = 1, 3 VSVO0220
    IF (ZI(J) .EQ. 0.0D0) GO TO 20 VSVO0230
    ZR(J) = 0.0D0 VSVO0240
30  V(I) = RGAS * T / X(I, 1) * DMAX1(ZR(1), ZR(2), ZR(3)) VSVO0250
RETURN VSVO0260
END VSVO0270
Table VII-4

Documentation of the Subroutine GENLSQ

Purpose

To fit an implicit nonlinear model of the form

\[ f(z_1, \ldots, z_m, x_1, \ldots, x_k, p_1, \ldots, p_n) = 0 \]

to a set of z-x data. The observed z data, zm, is assumed to contain random experimental error while the x data is assumed to be error free. This subroutine may be thought of as an extension of ordinary least squares to the case where some of independent variables, as well as the dependent variable, are subject to error.

An alternative interpretation is to think of GENLSQ as a routine for simultaneous data adjustment and model fitting.

Method

The generalized least squares algorithm of Britt and Luecke. The values of \( p_1, \ldots, p_n \) are found that minimize

\[
\sum_{i=1}^{k} \sum_{j=1}^{m} \frac{(z_{m_{j_i}} - z_{j_i})^2}{r_{j_i}^2}
\]

subject to the constraints

\[ f(z_{l_i}, \ldots, z_{m_i}, x_{l_i}, \ldots, p_{l_i}, p_1, \ldots, p_n) = 0, \quad i=1, \ldots, k \]
269

where \( r_{ji} \) is the standard deviation of the error in \( zm_{ji} \) and \( k \) is the number of data points to be fit. The values of \( z \) are the estimates of the true values of the model variables whose observed values \( zm \) were assumed to be subject to error. The Deming approximate algorithm is used to generate starting values for the Britt-Luecke algorithm. For reference, see Britt, H.I., and Luecke, R.H., "The Estimation of Parameters in Non Linear, Implicit Models," Technometrics, 15,2, 233 (1975), and Deming, W.E., "Statistical Adjustment of Data," Wiley, New York, 1943.

**Usage**

The subroutine is called by the following statement:

```
CALL GENLSQ (N,M,MV,L,K,NC,NCV,P,ZM,X,R,SVEP,ITER,ITERZ,
IDEM,IØDS,SS,EPS,KØUT,NDRIV,SSND,ISV,WORK,INWORK,Z,F,DELZ,
SUMSQ,SIGMA,CØVAR,NFEVAL,IER,IBØUND,LB,UB,LM,NIC,C,D)
```

**Description of Parameters**

**Input:**

This is a double precision program. All floating point variables must be declared REAL*8 in the calling program.

- \( N \) - Number of unknown model parameters to be estimated.
- \( K \) - Number of data points to be fit \((K > N)\)
- \( L \) - Number of model independent variables \((L > 1)\)
**Vector of length N** containing the initial guesses of the unknown model parameters.

**ZM** - Vector of length K containing the observed values of the model dependent variable, one per data point.

**X** - Array of dimension L*K containing the values of the model independent variables, L per data point.

**R** - Vector of length K containing the standard deviations of YM. These values may be thought of as the inverse of the weighing factor for each data point. For unweighted least squares, set all elements of R equal to 1.0.

**MODEL** - Name of user supplied model subroutine described below. Must be declared EXTERNAL in the calling program.

**ITER** - Maximum number of iterations allowed. A good choice is 50.

**IDEM** - Deming method parameter

**IDEM<ITER** - Deming's method is used until convergence is obtained or until IDEM iterations have been made. The program will then switch to the Britt-Luecke method.

**IDEM = -1** - Deming's method is used for all iterations. The exact least squares solution is obtained in
only certain special cases.

IØDS   - Key for one dimensional search during Deming iterations. See Remark 2.

1ØDS=0 No one dimensional search. Take SS times the predicted Gauss-Newton step on each iteration.

1ØDS=1 Search for the minimum in the Gauss-Newton direction on each iteration. On the 1st iteration, begin the search by taking SS times the predicted Gauss-Newton step. On subsequent iterations, begin the search with the optimum value of SS from the previous iteration.

1ØDS=2 Search for the minimum in the Gauss-Newton direction on each iteration. Begin the search on each iteration by taking SS times the predicted Gauss-Newton step.

SS    - Step size parameter. See 1ØDS above and Remark 2.

EPS   - Convergence tolerance. Convergence is declared if the root mean square fractional change in P is less than EPS. A good choice is 1.D-6.

KØUT  - Print output key.

0     No printed output.

1     Final results only.
Minimum amount of information per iteration and final results.

Relatively more output per iteration. Used for debugging purposes.

NDRIV - Derivative key.

0 User supplied model subroutine evaluates model and its first derivatives with respect to P and Z.

1 User supplied model subroutine evaluates model only. Derivatives are calculated numerically by GENLSQ.

SSND - Step size to be used in calculating numerical derivatives. Applies only if NDRIV=1. A good choice is 1.D-4.

ISV - Variance-covariance matrix computation key.

See Remark 4.

ISV=0 It is assumed that the input values \( R \) of the standard deviations of ZM are proportional to the correct values. The constant of proportionality is estimated by the standard error of curve fit (SIGMA) and \( R \) is adjusted accordingly before the variance-covariance matrix \( (C\overline{O}\overline{V}AR) \) of the parameter estimates is computed.

ISV=1 It is assumed that the input values \( R \) of the standard deviations of ZM
are correct. Their values are not adjusted by the standard error of curve fit (SIGMA) before the variance-covariance matrix (CØVAR) of the parameter estimates is computed.

It is suggested that ISV=0 be used unless R is known with a high degree of certainty.

**WØRK** - Work vector of length \(2N + 3K + MK + NK + \max(N,M)K + \frac{3}{2}N(N+1)\)

**IWØRK** - Integer work vector of length \(N\).

**Z** - Array of dimension \((M,K)\).

**F** - Vector of length \(K\).

**DELZ** - Array of dimension \((M,K)\).

**CØVAR** - Vector of length \(N(N+1)/2\).

**Output**

**P** - Vector containing the least squares parameter estimates if converged or most recent values if not converged.

**ITER** - Number of iterations used.

**Z** - Array containing the estimates of the true values of the model variables whose observed values (ZM) were assumed to be subject to random experimental error.

**SUMSQ** - Weighted sum of squares of residuals at \(P\), i.e., the minimized sum of squares value.

**SIGMA** - Standard error of curve fit.
CØVAR - Vector representing the lower triangular part of the (symmetric) variance-covariance matrix of the parameter estimates, stored by columns. For example, the order of storage is

1
2 4
3 5 6

for N=3. Parameter estimate standard deviations are obtained by taking the square root of the diagonal elements of this matrix.

NFEVAL - Number of times the user supplied subroutine was called by GENLSQ.

IER - Error code.

0 - No error.
1 - Minimum not found in ITER iterations.
2 - Steps taken to overcome matrix singularity have caused CØVAR to be modified. It is no longer the variance-covariance matrix. This problem is caused by highly correlated model parameters. Reformulation of the model with fewer, less dependent parameters may help.
3 - Program stopped because of matrix inversion problems. Comments for IER=2 apply.
**Subroutines Required**

GENLSQ calls a user supplied routine to evaluate the model and, optionally, its first derivatives with respect to the model parameters \( P \). The form for \( \text{NDRIV}=0 \) is:

```fortran
SUBROUTINE MODEL (ZZMX, P, K, M, L, N, KEY, F)
IMPLICIT REAL*8 (A-H,0-Z)
DIMENSION Z (M,K),ZM(M,K),X(L,K),P(N),F(K),FZ(M,K),
FP(N,K)
DO 3 l=1,K
  F(1)=f(Z(1,1),...,Z(M,1),X(1,1),...,X(L,1),P(1),...,P(N))
C IF KEY=1 DERIVATIVES ARE NOT REQUIRED
IF (KEY.EQ.1) GO TO 3
DO 1 J=1,N
  FP(J,1)= \( \partial f(Z(1,1),...,Z(M,1),X(1,1),...,X(L,1),P(1),...,P(N))/\partial P(J) \)
  DØ 2 J=1,M
2 FZ(J,1)= \( \partial f(Z(1,1),...,Z(M,1),X(1,1),...,X(L,1),P(1),...,P(N))/\partial Z(J,1) \)
3 CONTINUE
RETURN
END
```

The form for \( \text{NDRIV}=1 \) is

```fortran
SUBROUTINE MODEL(Z,ZM,X,P,K,M,L,N,KEY,F)
IMPLICIT REAL*8 (A-H,0-Z)
DIMENSION Z(M,K),ZM(M,K),X(L,K),P(N),F(K)
DØ 1 I=1,K
```
\begin{verbatim}

1 \text{F}(l) = f(Z(l,1), \ldots, Z(M,1), X(1,1), \ldots, X(L,1), P(1),
   \ldots, P(N))
RETURN
END

NOTE: It is permissible for the model function to change with \text{l}.

The subroutine name (not necessarily \text{MODEL}) must appear in the argument list of \text{GENLSQ} at the proper position and must also appear in an \text{EXTERNAL} statement in the program which invokes \text{GENLSQ}.

A subroutine \text{LUEBRI}, supplied by the catalogued procedure, is called by \text{GENLSQ} to do the actual calculations.

Space Requirement

? decimal bytes.

Remarks

1. For explicit models with significant error in only the dependent variable, use subroutine \text{NLLSQ}.
2. The Deming approximate algorithm is an excellent initialization method for the Britt-Luecke algorithm since it usually produces estimates very close to the exact Britt-Luecke estimates and is less prone to convergence problems. The Britt-Luecke algorithm almost always converges rapidly from a converged Deming solution. Both algorithms are of the Gauss-Newton type; that is they are based on model linearization.
\end{verbatim}
When convergence problems do arise during the Deming initialization, they can often be overcome by step size (SS) adjustment. GENLSQ uses the unmodified Deming method when lØDS=0 and SS=1.0. Setting SS=1.0 damps the search and is often helpful. Setting lØDS=1 or 2 causes a one-dimensional search to be made in the Gauss-Newton direction on each iteration to find a near-optimum value of SS. The following strategy is recommended:

(a) Make sure you are providing the program with the best initial guesses of $P_1 \ldots P_N$ you can come up with.

(b) Try using lØDS=0, SS=1.0. This should result in rapid convergence for most problems.

(c) If (b) fails, try damping the search. A range of .1 to .5 is recommended for SS. Leave lØDS=0.

(d) If (c) fails, try lØDS=1, SS=.1.

(e) If (d) fails, contact H. l. Britt, Applied Mathematics and Computing Group.

The significance of Step (a) depends greatly on the particular model and data. In the event that you are having convergence problems that appear to be due to poor starting values, and you are unable to come up with better ones, a randomized start is recommended. A procedure for doing this is described on page 15 of the UCC R&D Report "SIDEWINDER IV" by C.D. Hendrix, File No. 18454, dated June 11, 1973. This tactic also provides some protection against converging to a local minimum rather than the global
minimum.

There is no one dimensional search during the Britt-Luecke iterations, however the step size is adjusted by the SS parameter.

3. The X array is not used by GENLSQ. It is only a vehicle for passing data to the user supplied model subroutine. As a result, it can be dimensioned any way the user pleases, although X(L,K) is the normal case.

5. The weighing factors in the least squares criteria have been denoted $1/r_i^2$, rather than the more typical $w_i$, to emphasize the statistical aspects of the curve fitting problem. If the errors in measuring the y's are independent of each other and normally distributed with zero mean and variance $\sigma^2 r_i^2$, then GENLSQ produces the maximum likelihood estimate of $p_1, \ldots, p_n$. The factor $\sigma^2$ need not be known. In other words, it is only the ratios of the standard deviations that need be known. For example, it is often assumed that the error in measuring pressure is proportional to the pressure (constant relative error). Therefore, if pressure were the dependent variable in a curve fitting problem, it would be appropriate to set $R_i = Z_{M_i}$, $i=1, \ldots, k$. The output variable SIGMA would then be the estimated constant of proportionality.

Example

Suppose it is desired to fit the Antoine equation

$$\ln P = A - \frac{B}{T + C}$$
to 100 data points using unweighted least squares with
$\ln P$ as the independent variable. Input to GENLSQ would be
as follows:

- **N=3**
  - A, B, and C are the unknown parameters

- **K=100**
  - There are 100 sets of $T-\ln P$ data.

- **K=1**
  - $T$ is the single independent variable.

- **P(1, P(2), P(3)**
  - Are initial guesses of A, B, & C, respectively.

- **ZM(1,1)-ZM(1,100)**
  - Are the 100 measured values of $P$.

- **ZM(2,1)-ZM(2,100)**
  - Are the corresponding 100 measured values of $T$.

- **X**
  - Not used since there are no model variables whose values are assumed to be known exactly.

- **R(1,1)-R(1,100)**
  - Are set equal to 0.01P for the corresponding 100 pressures.

- **R(2,1)-R(2,100)**
  - Are all set equal to 0.01.

- **ANT0IN**
  - Is the name of the user supplied subroutine.

- **ITER=50**
  - A maximum of 50 iterations will be allowed, including Deming iterations.

- **IDEM=20**
  - A maximum of 20 Deming iterations will be made before switching to the Britt-Luecke algorithm.

- **I0DS=0, SS=1.0**
  - The unmodified search will be tried.

- **EPS=1.D-6**
  - Convergence tolerance.

- **K0UT=1**
  - The program is to print the final
results.

NDRIV=1      Numerical derivatives.
SSND=1.D-4    Numerical derivative step size.

The main program would include the following statements:

EXTERNAL ANTØIN

DIMENSIØN P(3), ZM(2,100), R(2,100), WØRK(1124),
IWØRK(3), Z(2,100), F(100), DELZ(2,100), CØVAR(6)

The user supplied subroutine would be:

SUBROUTINE ANTØIN(Z,ZM,X,P,K,M,L,N,KEY,F)

IMPLICIT REAL*8(A-H,O-Z)

DIMENSIØN Z(M,K),ZM(M,K),P(N),F(K)

DO 1 I=1, K

1 F(I)=DLØG(Z(1,I))-P(1)+P(2)/(Z(2,I)+P(3))

RETURN

END
APPENDIX VIII
DETAILS EQUIPMENT SPECIFICATIONS
AND OPERATING PROCEDURES

Extractor

The extractor used in this thesis consists of an Autoclave CNLX16012 medium pressure tube, 30.48 cm in length and 1.75 cm in diameter. Attached to the extractor inlet are openings for the thermocouple assembly and for the fluid inlet stream. Details of the extractor are shown in Figure VIII-1.

Temperature Control of Extractor

The extraction temperature was controlled by use of a heating tape (Fisher 11-463-55D) wrapped around the extractor and connected to a LFE 238 PID temperature controller with a 20 AMP integral power pack. The temperature sensor was an iron-constantan thermocouple (Omega SH48-ICSS-116U-15) housed inside the extractor.

Optimal temperature control ($\pm 0.5 \text{ K}$) was obtained with the following settings on the temperature controller:

- proportional control: proportional band = 10
- integral control: 16 minutes
- derivative control: off
- cycle time: minimum
EXTRACTOR DESIGN

Fluid Exit

Autoclave Coupling (20F41666)

Autoclave 1"OD Nipple (CNLX16012)

Wood Supports

Autoclave Coupling (20F41666)

30 cm

Fluid Inlet

Autoclave Tee (CTX 440)

Special 1/16" Ferrule Required (Autoclave 1010-6850)

Omega Thermocouple (SH 48-1CSS-116U-15)

To Temperature Controller

(not drawn to scale)

Figure VIII-1
With these controller values, the digital set point should be put at a temperature 2 K below the desired extraction temperature. Electronic reference junctions for the thermocouples were standard with the controller and digital temperature readout.

**Pressure Control of Extractor**

Pressure was controlled in the extractor by an on/off controller (Autoclave P481-P713) located at the surge tank outlet. Control action was directly to the compressor. As the system was configured, the controller was in the high limit off mode. Positioning the set point at the desired pressure (making use of the more accurate calibration from the Heise gauge CM,400, with thermal compensation and slotted link protection) enables the pressure to be controlled to \(\pm 1\) bar.

**Surge Tank**

A two liter magnedrive packless autoclave was used as the surge tank. As the system is configured, there were three Autoclave SW 2072 valves connected to the autoclave -- one at the inlet, one at the outlet, and one for venting purposes. The purpose of the inlet and outlet valves were to enable the autoclave to be isolated from the rest of the system. Isolation was necessary when changing gas cylinders, depressurizing the extractor, and venting the autoclave.
In addition to its use as a surge tank, the autoclave is also useful as a device to pre-saturate the supercritical fluid with a liquid solvent before the fluid contacts the solute species. When used in this mode, the autoclave must be preheated to the desired temperature. For this purpose a LFE 232 10 Amp proportional controller was used to control the power input to heating tape wrapped around the autoclave. Also, the connecting tubing between the autoclave and the extractor must be heated to prevent condensation of the liquid species. A variac was conveniently located for connection to heating tapes for this purpose.

Start up Procedure

After the extractor is charged with the solute species to be extracted, the outlet valve of the surge tank was cracked open so that the pressure in the extractor was slowly increased to the autoclave pressure. When the pressures of the two vessels were equal (but below the desired extraction pressure), the set point on the pressure controller was adjusted to the desired value and the compressor switch turned on.

Simultaneously, the temperature controller switch was turned on. It takes about one-half hour for the system to stabilize at the desired operating temperature and pressure. After the system had stabilized, the extraction could be started by opening the exist regulating valve until a steady
flow rate of about 0.4 standard liters per minute was achieved.

**Shut Down Procedure**

To shut down the extraction system, the compressor and temperature controller switches were turned off (but the thermocouple switch left on since this switch also turns the heating tape on the exit regulating valve on and off).

Then, the exit value on the autoclave was completely shut off so as to isolate the autoclave from the rest of the system. After attaching the tygon tube vent pipe (connected to the hood) to the regulating valve outlet, the regulating valve was slowly opened until the extractor was depressurized. Finally, the thermocouple switch was turned off and the entire system disassembled and cleaned.
APPENDIX IX
OPERATING CONDITIONS AND CALIBRATIONS
FOR THE GAS CHROMATOGRAPH

To analyze the composition of the solid mixture precipitated from the U-tube, a Perkin-Elmer Sigma 2/Sigma 10 gas chromatograph equipped with a flame ionization detector (FID) was used. In the FID configuration, three gas cylinders are required at the following delivery pressures:

- **Air**: 45 psig
- **N₂**: 85 psig
- **H₂**: 30 psig

Pressures for these gases on the gas chromatograph should be set at

- **Air**: 30 psig
- **N₂**: 69 psig, inlet A
- **H₂**: 20 psig

Analysis of the solid systems was done under the temperature program conditions and with the response factors shown in Table IX-1. The response factors are for use with an area normalization calibration as specified by

\[ C_i = \left( \frac{A_i f_i}{\sum A_i f_i} \right) \times 100 \quad \text{(IX-1)} \]
#### Table IX-1

**Temperature Programmed Conditions and Response Factors for Chromatography**

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Final Temperature (°C)</th>
<th>Final Temperature (°C)</th>
<th>Ramp Rate (°C/min)</th>
<th>Initial Hold (min)</th>
<th>Final Hold (min)</th>
<th>Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-DMN / 2,3-DMN</td>
<td>160</td>
<td>182</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>1/1.034</td>
</tr>
<tr>
<td>Naphthalene / Phenanthrene</td>
<td>150</td>
<td>250</td>
<td>10</td>
<td>0</td>
<td>5</td>
<td>1/1.029</td>
</tr>
<tr>
<td>2,3-DMN / Phenanthrene</td>
<td>150</td>
<td>250</td>
<td>10</td>
<td>0</td>
<td>5</td>
<td>1/0.998</td>
</tr>
<tr>
<td>2,6-DMN / Phenanthrene</td>
<td>150</td>
<td>250</td>
<td>10</td>
<td>0</td>
<td>5</td>
<td>1/1.043</td>
</tr>
<tr>
<td>Phenanthrene / Benzoic Acid*</td>
<td>150</td>
<td>250</td>
<td>10</td>
<td>3.5</td>
<td>3.5</td>
<td>1/0.097</td>
</tr>
<tr>
<td>2,3-DMN / Naphthalene</td>
<td>150</td>
<td>250</td>
<td>10</td>
<td>0</td>
<td>5</td>
<td>1.038/1</td>
</tr>
<tr>
<td>Naphthalene / Benzoic Acid*</td>
<td>140</td>
<td>140</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1/1.071</td>
</tr>
</tbody>
</table>

**Injector & Detector Temperature = 300°C**

*Reacted with silyl reagent n-o-bis(trimethylsilyl)acetamide*
where \( f_i \) is the response factor

\( A_i \) is the peak area

\( C_i \) is the concentration in weight %.

**Solid Preparation**

The precipitated solid in all cases was dissolved in methylene chloride at a concentration of about 0.5 weight percent. This dilute solution was satisfactory for injection into the GC system. In the case of mixtures containing benzoic acid, however, a silyl reagent had to be added to the solution in a 10\% weight ratio to prevent severe tailing of the acid peak. The reagent used was N,0-bis (trimethylsilyl) acetamide, purchased from Supelco.

**Gas Chromatograph Column and Septa**

The column used for all separations was a 10\% SP-2100 methyl silicone stationary phase on a 100/120 Supelcoport support with the following dimensions:

- length: 10 ft
- O.D.: 1/8"
- material: 316 SS

This column is a stock column from Supelco Inc. In all cases, nitrogen was the carrier gas at a flow rate of 30 ml/min.

For the injection conditions used in this thesis, the best septa was Supelco Thermogreen, LB-1, 11mm.
Data Station Operating Methods

The Sigma 10 data station requires operating software for each sample. Software for each of the solid systems investigated are shown in Tables IX-2 through IX-3.

Detector Linearity and Response Factors

Calibration curves for each of the mixture species studied were examined to determine the range of linearity and the response factors of the detector. These curves are shown in Figures IX-1 through IX-7.

In all cases, the detector was linear over the range studied. Response factors are given in Table IX-1.
Table 1X-2
Sigma 10 Software for 2,6-DMN/2,3-DMN Analysis

**ANALYZER CONTROL**

<table>
<thead>
<tr>
<th>INJ TEMP</th>
<th>DET ZONE</th>
<th>FLOW A,B</th>
<th>INIT OVEN TEMP, TIME</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1,2</td>
<td>5,5</td>
<td>76, 999</td>
</tr>
</tbody>
</table>

**DATA PROC**

<table>
<thead>
<tr>
<th>STD WT, SMP WT</th>
<th>FACTOR, SCALE</th>
<th>TIMES</th>
<th>SENS-DET RANGE</th>
<th>UNK, AIR</th>
<th>TOL</th>
<th>REF PK</th>
<th>STD NAME</th>
<th>RT</th>
<th>RF</th>
<th>CONC</th>
<th>NAME</th>
</tr>
</thead>
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<tr>
<td>0.0000</td>
<td>1.0000</td>
<td>15.00</td>
<td>75</td>
<td>0.0000</td>
<td>0.050</td>
<td>8.25</td>
<td>2-6-DMN</td>
<td>8.35</td>
<td>1.00</td>
<td>47.2688</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0000</td>
<td>0.050</td>
<td>8.45</td>
<td>2-3-DMN</td>
<td>9.29</td>
<td>1.034</td>
<td>52.7296</td>
<td>2-3-DMN</td>
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</table>

**EVENT CONTROL**

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<tr>
<th>ATTN-CHART-DELAY</th>
<th>TIME</th>
<th>DEVICE</th>
<th>FUNCTION</th>
<th>NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>10, 10, 0.01</td>
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<td></td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>TIME</th>
<th>DEVICE</th>
<th>FUNCTION</th>
<th>NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>ATTN A</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>2.10</td>
<td>CHART C</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
Table I X-3
Sigma 10 Software for
Naphthalene/Phenanthrene Analysis

**ANALYZER CONTROL**

INJ TEMP  25
DET ZONE 1,2  65  25
AUX TEMP  25
FLOW A,B  5  5
INIT OVEN TEMP,TIME  76  999

**DATA PROC**

STD WT,SMP WT  0.0000  1.0000  0
FACTOR,SCALE  1  0
TIMES  15.00  1.90  327.67  327.67  327.67  327.67
SENS-DET RANGE  75  4  5.00  2  0  0
UNK,AIR  0.000  0.00
TOL  0.0000  0.050  1.0
REF PK  1.000  3.86  4.06  3.96
STD NAME NAPHTHALENE

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<th>RT</th>
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<th>CONC</th>
<th>NAME</th>
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<tr>
<td>3.96</td>
<td>1.000</td>
<td>16.2800</td>
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<tr>
<td>10.52</td>
<td>1.029</td>
<td>83.7184</td>
<td>PHENANTHRENE</td>
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**EVENT CONTROL**

ATTN-CHART-DELAY  10  10  0.01

<table>
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<tr>
<th>TIME</th>
<th>DEVICE</th>
<th>FUNCTION</th>
<th>NAME</th>
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<tbody>
<tr>
<td>2.10</td>
<td>CHART</td>
<td>C</td>
<td>4</td>
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<tr>
<td>6.00</td>
<td>ATTN</td>
<td>A</td>
<td>4</td>
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</table>
Table 1X-4
Sigma 10 Software for 2,3-DMN/Phenanthrene Analysis

ANALYZER CONTROL

INJ TEMP 25
DET ZONE 1,2 65 25
AUX TEMP 25
FLOW A,B 5 5
INIT OVEN TEMP,TIME 76 999

DATA PROC

STD WT, SMP WT 0.0000 1.0000 0
FACTOR, SCALE 1.0
TIMES 15.00 1.90 327.67 327.67 327.67 327.67
SENS-DET RANGE 75 4 5.00 2 0 0
UNK, AIR 0.000 0.00
TOL 0.0000 0.050 1.0
REF PK 1.000 6.68 6.78 6.73
STD NAME 2 3-DMN

RT RF CONC NAME
6.73 1.000 79.4976 2 3-DMN
10.52 0.998 20.5000 PHENANTHRENE

EVENT CONTROL

ATTN-CHART-DELAY 10 10 0.01

TIME DEVICE FUNCTION NAME
2.00 ATTN A 6
2.18 CHART C 4
8.50 ATTN A 4
Table IX-5
Sigma 10 Software for
2,6-DMN/Phenanthrene Analysis

ANALYZER CONTROL

INJ TEMP 25
DET ZONE 1,2 65 25
AUX TEMP 25
FLOW A, B 5 5
INIT OVEN TEMP, TIME 76 999

DATA PROC

STD WT, SMP WT 0.0000 1.0000 0
FACTOR, SCALE 1 0
TIMES 15.00 1.90 327.67 327.67 327.67 327.67
SENS-DET RANGE 75 4 5.00 2 0 0
UNK, AIR 0.000 0.00
TOL 0.0000 0.050 1.0
REF PK 1.000 6.00 6.40 6.22
STD NAME 2 6-DMN

RT RF CONC NAME
6.22 1.000 50.0000 2 6-DMN
10.43 1.043 50.0000 PHENANTHRENE

EVENT CONTROL

ATTN-CHART-DELAY 10 10 0.01

TIME DEVICE FUNCTION NAME
2.00 ATTN A 6
2.10 CHART C 4
8.50 ATTN A 4
Table IX-6
Sigma 10 Software for
Benzoic Acid/Phenanthrene Analysis

ANALYZER CONTROL

INJ TEMP 25
DET ZONE 1,2 65 25
AUX TEMP 25
FLOW A,B 5 5
INIT OVEN TEMP, TIME 76 999

DATA PROC

STD WT,SMP WT 0.0000 1.0000 0
FACTOR, SCALE 1 0
TIMES 17.00 4.19 327.67 327.67 327.67 327.67
SENS-DET RANGE 75 4 5.00 2 0 0
UNK, AIR 0.000 0.00
TOL 0.0000 0.050 1.0
REF PK 1.000 5.80 6.20 6.03
STD NAME BENZOIC ACID

RT RF CONC NAME
6.03 1.000 50.0000 BENZOIC ACID
13.71 0.971 50.0000 PHENANTHRENE

EVENT CONTROL

ATTN-CHART-DELAY 10 10 0.01

TIME DEVICE FUNCTION NAME
4.20 ATTN A 4
4.30 CHART C 4
Table 1X-7
Sigma 10 Software for
Naphthalene/2,3-DMN Analysis

### Analyzer Control

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<tr>
<td>DET ZONE 1,2</td>
<td>65, 25</td>
</tr>
<tr>
<td>AUX TEMP</td>
<td>25</td>
</tr>
<tr>
<td>FLOW A,B</td>
<td>5, 5</td>
</tr>
<tr>
<td>INIT OVEN TEMP</td>
<td>76, 999</td>
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### Data Proc

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<tr>
<td>TIMES</td>
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</tr>
<tr>
<td>SENS-DET RANGE</td>
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<tr>
<td>UNK, AIR</td>
<td>0.0000, 0.00</td>
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<tr>
<td>TOL</td>
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<tr>
<td>REF PK</td>
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<td>STD NAME NAPHTHALENE</td>
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<th>CONC</th>
<th>NAME</th>
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<td>1.000</td>
<td>50.000</td>
<td>NAPHTHALENE</td>
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<td>6.60</td>
<td>1.038</td>
<td>50.000</td>
<td>2 3-DMN</td>
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### Event Control

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<td>10, 10, 0.01</td>
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<th>TIME</th>
<th>DEVICE</th>
<th>FUNCTION</th>
<th>NAME</th>
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<tbody>
<tr>
<td>2.00</td>
<td>ATTN A</td>
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</tr>
<tr>
<td>2.10</td>
<td>CHART C</td>
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<td>6.00</td>
<td>ATTN A</td>
<td>4</td>
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</table>
Table 1X-3
Sigma 10 Software for Naphthalene/Benzoic Acid Analysis

**ANALYZER CONTROL**

INJ TEMP 25
DET ZONE 1,2 65 25
AUX TEMP 25
FLOW A, B 5 5
INIT OVEN TEMP, TIME 76 999

**DATA PROC**

STD WT, SMP WT 0.0000 1.0000 0
FACTOR, SCALE 1 0
TIMES 15.00 4.00 327.67 327.67 327.67 327.67
SENS-DET RANGE 75 4 5.00 2 0 0
UNK, AIR 0.000 0.00
TOL 0.0000 0.050 1.0
REF PK 1.000 7.18 7.30 7.18
STD NAME NAPHTHALENE

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<th>RF</th>
<th>CONC</th>
<th>NAME</th>
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<tr>
<td>7.18</td>
<td>1.00</td>
<td>50.000</td>
<td>NAPHTHALENE</td>
</tr>
<tr>
<td>8.93</td>
<td>1.07</td>
<td>50.000</td>
<td>BENZOIC ACID</td>
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</table>

**EVENT CONTROL**

ATTN-CHART-DELAY 10 10 0.01

<table>
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<th>TIME</th>
<th>DEVICE</th>
<th>FUNCTION</th>
<th>NAME</th>
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</thead>
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<td>ATTN A</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>4.01</td>
<td>CHART C</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>8.00</td>
<td>ATTN A</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
Gas Chromatograph Calibration Curve For Phenanthrene / Benzoic Acid* Mixture

* Reacted with Silyl Reagent
N,O-bis (trimethylsilyl) acetamide

Figure IX-1
Gas Chromatograph Calibration Curve for Naphthalene / Benzoic Acid* Mixture

* Reacted with Silyl Reagent NO-bis (trimethyl silyl) acetamide
Gas Chromatograph Calibration Curve for 2,3-DMN / Phenanthrene Mixture

Figure IX-3
Gas Chromatograph Calibration Curve for 2,6-DMN / 2,3-DMN Mixture

Figure IX-4
Gas Chromatograph Calibration Curve for Naphthalene / Phenanthrene Mixture

Figure IX-5
Gas Chromatograph Calibration Curve for Phenanthrene / 2,6 DMN Mixture

Figure IX-6

- 2,6-DMN
- Phenanthrene
Gas Chromatograph Calibration Curve
for Naphthalene / 2,3 - Dimethylnaphthalene

Figure IX-7
APPENDIX X
SAMPLE CALCULATIONS

Sample calculations for converting raw experimental data for binary and ternary systems into equilibrium solubility data are shown below.

**Binary Systems**

Raw Data for Run R280.
System: Phenanthrene-Ethylene
Barometric Pressure = 1.0168 BAR
Weight of Sample Collected in First U-tube = 1.17 gm
Weight of Sample Collected in Second U-tube = 0.00 gm
Temperature of Extraction = 318 K
Pressure of Extraction = 280 BAR
Temperature of Gas Leaving Dry Test Meter = 297.4 K
Pressure of Gas Leaving Dry Test Meter = 0 BAR (guage)
Total Volume of Ethylene Passed = 34.84 l
Molecular Weight of Phenanthrene = 178.23

**Calculations**

Moles of Ethylene Passed \((n_2)\):

\[
    n_2 = \frac{(1.0168)(34.84)}{(0.08314(297.4)} = 1.4327 \text{ g mol}
\]
Moles of Phenanthrene Collected (n₁):

\[ n₁ = \frac{1.17}{173.2} = 6.5645 \times 10^{-3} \text{ gmol} \]

\[ \therefore Y₁ = \frac{n₁}{n₁ + n₂} = 4.561 \times 10^{-3} \]

Ternary Systems

Raw Data for Run M58

System: Carbon Dioxide; 2,6-DMN; 2,3-DMN

Barometric Pressure = 1.0141 BAR

Weight of Sample Collected in First U-tube = 1.40 gm

Weight of Sample Collected in Second U-tube = 0.00 gm

Temperature of Extraction = 308 K

Pressure of Extraction = 260 BAR

Temperature of Gas Leaving Dry Test Meter = 296.8 K

Pressure of Gas Leaving Dry Test Meter = 0 BAR (gauge)

Total Volume of Ethylene Passed = 20.00 \( \ell \)

Molecular Weight of 2,6-DMN = 156.23

Molecular Weight of 2,3-DMN = 156.23

Composition of Mixture by Gas Chromatography:

- 42.87 wt. % 2,6-DMN
- 57.13 wt. % 2,3-DMN

Calculations

Moles of Carbon Dioxide Passed (n₁):

\[ n₁ = \frac{(1.0141)(20)}{(0.08314)(296.8)} = 0.8219 \text{ gmol} \]
Moles of 2,6-DMN Collected ($n_2$):

$$n_2 = \frac{(0.4287)(1.40)}{(156.23)} = 3.8405 \times 10^{-3} \text{ gmol}$$

Moles of 2,3-DMN Collected ($n_3$):

$$n_3 = \frac{(0.5713)(1.40)}{(156.23)} = 5.1206 \times 10^{-3} \text{ gmol}$$

\[ \therefore \quad \gamma_2 = \frac{n_2}{n_1 + n_2 + n_3} = 4.622 \times 10^{-3} \]

\[ \gamma_3 = \frac{n_3}{n_1 + n_2 + n_3} = 6.163 \times 10^{-3} \]
APPENDIX XI

EQUIPMENT STANDARDIZATION AND ERROR ANALYSIS

Equipment standardization and error analysis consists of verifying that the extraction was (within experimental error): isothermal, isobaric, and at equilibrium. As discussed in Appendix VIII the extraction is kept isothermal by means of a PID temperature controller and isobaric by means of an on/off pressure controller. The maximum deviation of the extraction temperature from the set point was 0.5 K. The on/off pressure controller kept the extraction isobaric to within ±1 bar.

Since a flow system is used to obtain solubility data, there are several key points to check to verify that the data obtained are equilibrium data. First, solubility has to be independent of flow rate. After showing this, the data has to reproduce accepted equilibrium data from the literature. Finally, comparisons of the system residence time to the extraction residence time must be made and shown not to matter.

Examining the first question of independence of flow rate, shown in Table XI-1 is the solubility of naphthalene in supercritical carbon dioxide at 191 bar and 308 K as a function of flow rate (and charge to the extractor). As the average deviation from the maximum solubility is low
<table>
<thead>
<tr>
<th>Extractor Charge (gm)</th>
<th>Flow Rate* (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>28</td>
<td>1.623</td>
</tr>
<tr>
<td>20</td>
<td>1.625</td>
</tr>
</tbody>
</table>

Experimental Value of Tsekhanskaya (1964): $y=1.701 \times 10^{-2}$

*at 1 atm and 294K.
(2.8%), it is confirmed that the solubility is independent of flow rate. At the same conditions of temperature and pressure Tsekhanskaya (1964) reports and equilibrium solubility of $1.701 \times 10^{-2}$ mole fraction. The average deviation of the experimental data from that obtained from Tsekhanskaya is 2.07%. As all the experimental data taken in this thesis was at a flow rate of 0.4 liters per minute* or less, and at a reactor charge of at least 28 grams, equilibrium can be assured.

To further check the agreement between experimental data and that published in the literature, additional data on the system naphthalene-carbon dioxide were taken at 328 K and for various pressures as shown in Table XI-2. The average percent error of 1.28% confirms that equilibrium was achieved in the extractor.

Additional Isothermal Calibration

At the extraction conditions of 197 bar and 328 K, additional checks were performed on the isothermality of the extractor as follows. Transverses of the thermocouple inside the extractor (the set point thermocouple) were made. Equilibrium solubilities obtained by positioning the thermocouple at the top or bottom of the extractor (the usual position was the middle) were within 2% of the data of Tsekhanskaya (1964).

*At 1 atm and 294 K.
Table XI-2

Solubility of Naphthalene in Carbon Dioxide at 328K
(Experimental Values vs. Literature)

<table>
<thead>
<tr>
<th>P(bar)</th>
<th>(y_{(exp.)})</th>
<th>(y_{(Tsekhan skaya)}^*)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>1.41x10^{-2}</td>
<td>1.42x10^{-2}</td>
<td>0.70</td>
</tr>
<tr>
<td>162</td>
<td>2.92x10^{-2}</td>
<td>3.00x10^{-2}</td>
<td>2.67</td>
</tr>
<tr>
<td>197</td>
<td>4.01x10^{-2}</td>
<td>3.99x10^{-2}</td>
<td>0.50</td>
</tr>
<tr>
<td>253</td>
<td>4.79x10^{-2}</td>
<td>4.85x10^{-2}</td>
<td>1.24</td>
</tr>
</tbody>
</table>

*Data of Tsekhan skaya (1964).*
In addition, the solid naphthalene was congregated in just the uppermost and lowermost portion of the extractor (usually it is spread evenly throughout the extractor) -- see Figure XI-1. Taking experimental data of the system carbon dioxide-naphthalene at 197 bar and 328 K with the naphthalene in the upper and lower configurations gave equilibrium solubilities no more than 0.4% different from the data of Tsekhanskaya. Thus, the isothermality of the extractor was confirmed.

Extractor Residence Time

A simple calculation on the extractor for carbon dioxide at 170 bar and 308 K shows that the superficial velocity was $7.8 \times 10^{-3}$ cm/s and that the mean residence time was 64 minutes. As extractions for naphthalene-carbon dioxide may only last 20 minutes,* it was necessary to examine the consequences of the residence time. The solubility data comparisons just examined were for a maximum experimental residence time of 20 minutes. Thus, it was apparent that equilibrium was rapidly achieved in order for the extraction time to be less than the mean residence time and still achieve equilibrium.

As expected, experiments with naphthalene-carbon dioxide at 197 bar and 308 K at very low flow rates -- giving a residence time of over two hours -- show the

*Experiments with other solids (e.g. phenanthrene) last up to 4 hours.
Positions of Solid in Extractor for Test of Isothermality

(a) Solid at Bottom of Extractor

(b) Solid at Top of Extractor

(c) Normal Position: Solid Evenly Distributed

(not drawn to scale)

Figure XI-1
experimental data to agree to within one percent of the data of Tsekhanskaya.
APPENDIX XII
LOCATION OF ORIGINAL DATA, COMPUTER PROGRAMS, AND OUTPUT

The original binary and ternary data obtained during this thesis are in the possession of the author. Duplicate copies of these data can be obtained from Professor Robert C. Reid. Card decks for the computer programs can be obtained from the author, or Professor Robert C. Reid. Computer outputs are in the possession of the author.
NOTATION

\(a_i, a_{ij}, A\) parameters in Peng-Robinson Equation of State
\(A_{vv}, A_{v1}, A_{ll}\) derivatives of Helmholtz Free Energy
\(b_i, B\) parameters in Peng-Robinson Equation of State
\(B_{M}, B_{11}, B_{12}, B_{22}\) second virial coefficients
\(C_M\) third virial coefficient
\(C_P\) heat capacity (cal/gmol K)
\(E\) eutectic point; enhancement factor
\(f\) fugacity (bar)
\(G\) gas phase
\(H\) enthalpy (cal/mole)
\(K_1, K_1', K_2, K_2'\) binary critical end points
\(K_A, K_B, K_C\) critical points
\(k_{12}\) Peng-Robinson binary interaction parameter
\(L\) liquid phase
\(L_1\) stability matrix
\(M_1\) stability matrix
\(N\) moles
\(P\) pressure (bar)
\(Q\) heat (cal/mole)
\(R\) gas constant
\(S_B, S_C\) solid B, C
\(T\) temperature (K)
\(U\) internal energy (cal/mole)
$V$ volume (cm$^3$/mole)

$y$ mole fraction, Legendre Transform

$z$ compressibility factor
SUPERSCRIPTS

C  critical point
E  experimental
F  fluid
FUS fusion
ID  ideal gas
L  liquid phase
M  melting point
R  reduced property
S  solid phase
SUB sublimation
t  triple point
vp  vapor pressure

^  component property
-  partial molar property
∞  at infinite dilution
SUBSCRIPTS

1, 2, i  component 1, 2, i
12  mixture property of components 1 and 2
p  lower critical end point
q  upper critical end point
GREEK LETTERS

α  parameter in Peng-Robinson Equation of State
γ  activity coefficient
κ  parameter in Peng-Robinson Equation of State
ξ  dimensionless density (b/V)
σ  property to be evaluated at saturation
φ  fugacity coefficient
ω  acentric factor
Ω_a', Ω_b  constants in the Peng-Robinson Equation of State
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