

BINARY VAPOR-LIQUID PHASE EQUILIBRIUM
FOR CARBON MONOXIDE + HYDROCARBONS

By

XIAOHUA YI

Bachelor of Engineering

Tianjin University

Tianjin, P. R. China

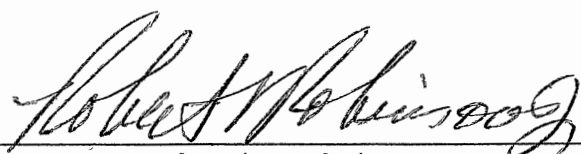
1984

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 1992

Sheldon
1993
Y505b

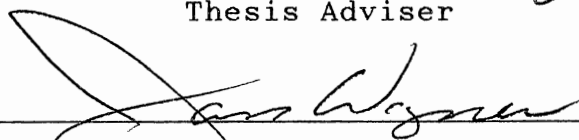
BINARY VAPOR-LIQUID PHASE EQUILIBRIUM
FOR CARBON MONOXIDE + HYDROCARBONS

Thesis Approved:



Robert Robinson


Thesis Adviser



Jan Wynn



KAM BASON



Thomas C. Collins

Dean of the Graduate College

PREFACE

This study deals the binary vapor-liquid phase equilibrium for carbon monoxide in selected hydrocarbons. The solubilities of carbon monoxide in these hydrocarbons were measured at temperatures from 50°C to 160°C and pressures to 102 bar. Binary interaction parameters in the Soave-Redlich-Kwong equation and the Peng-Robinson equation were regressed from the experimental results for each of the systems studied; these equations provided excellent representation of the data.

I extend my sincere thanks and gratitude to my adviser, Dr. Robert L. Robinson, Jr.. His intelligent guidance, authoritative knowledge and depth of experience have contributed significantly to the completion of this work.

I would like to thank Dr. K. A. M. Gasem for his direction and supervision in all stages of this work.

Thanks are also extended to Dr. Jan Wagner for his help and encouragement during the course of this work. His service as member of my committee is greatly appreciated.

I would also like to express my thanks to Dr. Zhiqiang Zhu, my previous adviser in Zhejiang University, for his teaching and introducing me into the field of thermodynamics and fluid phase equilibrium.

Dr. Naif Abdelaziz Darwish and Mr. Srinivasa Srivatsan

deserve special thanks for patiently explaining to me the operation of the equipment and the software packages used in this research.

Finally, I would like to acknowledge the financial support received from the United States Department of Energy.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.....	1
II. FUNDAMENTAL PRINCIPLES OF VAPOR-LIQUID EQUILIBRIUM.....	2
III. LITERATURE REVIEW	6
Experimental Data.....	6
Correlation Method.....	6
IV. EXPERIMENTAL APPARATUS AND OPERATING PROCEDURE.....	14
Experimental Apparatus.....	14
Operating Procedure.....	17
V. EXPERIMENT RESULTS AND ERROR ANALYSIS.....	24
Experimental Results.....	24
Error Analysis.....	36
VI. CORRELATION OF EXPERIMENTAL DATA.....	43
SRK and PR Equation Representations.....	43
Representations.....	43
Parameter Generalization.....	54
Krichevsky-Kasaronvsky Equation Representation.....	61
VII. CONCLUSIONS AND RECOMMENDATIONS.....	66
Conclusions.....	66
Recommendation.....	67
BIBLIOGRAPHY.....	68
APPENDIX - SRK AND PR EQUATION OF STATE REPRESENTATIONS OF CARBON MONOXIDE + HYDROCARBONS.....	71

LIST OF TABLES

Table	Page
I. Available Literature Data for Systems Studied in This Work.....	7
II. Purities and Sources of Chemicals Used in This Study.....	18
III. Compressibility Test of the Solvent Injection Pump.....	23
IV. Solubility Data for Carbon Monoxide + n-Hexane...	25
V. Solubility Data for Carbon Monoxide + Benzene....	26
VI. Solubility Data for Carbon Monoxide + n-Decane...	27
VII. Solubility Data for Carbon Monoxide + n-Octacosane.....	28
VIII. Solubility Data for Carbon Monoxide + n-Hexatriacontane.....	29
IX. Empirical Correlation of Experimental Data.....	35
X. Solubility Data for Methane + n-Decane.....	38
XI. Maximum Experimental Uncertainties in Solubility and Bubble Point Pressure.....	41
XII. Critical Properties and Acentric Factors Used in the SRK and PR Equation of State.....	44
XIII. Summary of Correlation Results by Using the SRK Equation.....	45
XIV. Summary of Interaction Parameters in the SRK Equation.....	46
XV. Specific Cases for Generalization of Interaction Parameters of SRK Equation.....	58
XVI. Summary of Results of Parameter Generalization...	59
XVII. Comparison of Interaction Parameters and Corresponding Deviations.....	60

Table	Page
XVIII. Parameters of Krichevsky-Kasarnovsky Correlation.....	65

LIST OF FIGURES

Figure	Page
1. Schematic Diagram of Experimental Apparatus.....	15
2. Determination of Bubble Point Pressure.....	20
3. Removing Non-Condensable Gas Bubbles.....	22
4. Bubble Point Pressure for Carbon Monoxide + n-Hexane.....	30
5. Bubble Point Pressure for Carbon Monoxide + Benzene.....	31
6. Bubble Point Pressure for Carbon Monoxide + n-Decane.....	32
7. Bubble Point Pressure for Carbon Monoxide + n-Octacosane.....	33
8. Bubble Point Pressure for Carbon Monoxide + n-Hexatriacontane.....	34
9. Comparison of Solubilities of Methane + n-Decane.....	39
10. Comparison of Solubilities of Carbon Monoxide + n-Hexane.....	49
11. Comparison of Solubilities of Carbon Monoxide + Benzene.....	50
12. Comparison of Solubilities of Carbon Monoxide + n-Decane.....	51
13. Comparison of Solubilities of Carbon Monoxide + n-Octacosane.....	52
14. Comparison of Solubilities of Carbon Monoxide + n-Hexatriacontane.....	53
15. Effect of k_{ij} and l_{ij} on SRK Bubble Point Pressure Prediction.....	55

Figure	Page
16. Effect of k_{ij} and l_{ij} on SRK Solubility Prediction.....	56
17. Comparison of Fugacity of Carbon Monoxide Predicted by PR Equation and Goodwin's Correlation.....	63

NOMENCLATURE

a	energy parameter in cubic equation of state
b	co-volume parameter in cubic equation of state
B	second virial coefficient
C	constants
F	freedom of a system
f	fugacity
G	Gibbs free energy
$H_{i,j}$	Henry's constant for solute i in solvent j
I	number of solute injections
k,l	interaction parameters in equation of state.
n	number of moles
N	number of components
c,d,o,p	constants used to correlate the temperature and density dependence of interaction parameters
max	maximum
min	minimum
P	pressure
q	constants in mixing rule
R	ideal gas constant
T	temperature
v	molar volume
x	liquid composition
y	vapor composition

z compressibility factor or independent variables

Greek Symbols

γ activity coefficient
 ϕ fugacity coefficient
 ρ density
 ω acentric factor
 Λ constant in Vidal's mixing rule
 μ chemical potential
 ϵ instrumental error
 σ standard variance
 a ratio of parameter a to parameter b in cubic equation of state
 Δ change in property
 π number of phases

Subscripts

i,j,k component or data point or solute injection index
b property at bubble point
c critical state
cal calculated value
exp experimental value
m property of mixture
t total property
 ∞ infinite dilution or infinite pressure

Superscripts

l liquid phase

s saturated state
v vapor phase
• standard state
E excess property
^ property of component in a mixture
- partial molar property
★ asymmetric property used in solution model

CHAPTER I

INTRODUCTION

A knowledge of the phase behavior of carbon monoxide + hydrocarbons is useful in the design and optimization of processes for the conversion of coal to fluid fuel. Limited experimental data on these mixtures have been reported.

The equation-of-state method has proved an effective means to describe the phase behavior of mixtures containing supercritical components at high pressures if an appropriate equation of state and corresponding mixing rule are applied. Thus, the purpose of this work was to determine the solubilities of carbon monoxide in n-hexane, benzene, n-decane, n-octacosane and n-hexatriacontane and to correlate the data using the Peng-Robinson (PR) and the Soave-Redlich-Kwong (SRK) equations of state.

CHAPTER II

FUNDAMENTAL PRINCIPLES OF VAPOR-LIQUID EQUILIBRIUM

For a closed equilibrium system composed of a vapor and a liquid phase, the temperature and pressure of both phases are identical. The chemical potential of a given component i in the two phases is also identical; this condition results from applying the first and the second laws of thermodynamics to the system. Therefore the following equations describe the equilibrium of such a system:

$$T^v = T^l \quad (1)$$

$$P^v = P^l \quad (2)$$

$$\mu_i^v = \mu_i^l \quad (i=1, 2, \dots, N) \quad (3)$$

The equal chemical potential criterion can be expressed in terms of fugacity which is defined as follows.

For a pure component at constant temperature,

$$d\mu_i = RT d \ln f_i \quad (4)$$

$$\lim_{P \rightarrow 0} \frac{f_i}{P} = 1 \quad (5)$$

For a component in a mixture at constant temperature and composition,

$$d\hat{\mu}_i = RT d \ln \hat{f}_i \quad (6)$$

$$\lim_{P \rightarrow 0} \frac{\hat{f}_i}{P x_i} = 1 \quad (7)$$

Equation 1-3 can be reexpressed as:

$$T^v = T^l \quad (8)$$

$$P^v = P^l \quad (9)$$

$$\hat{f}_i^v = \hat{f}_i^l \quad (i=1, 2, \dots, N) \quad (10)$$

Equation 8-10 are the starting equations to solve problems of vapor-liquid equilibrium.

Component fugacity is a function of temperature, pressure and composition. To obtain the relation between fugacity and these measurable variables, two approaches are generally used. The first is the equation-of-state method, as described by the following relation (1):

$$\ln \frac{\hat{f}_i}{x_i P} = \int_0^{\infty} \left(\left(\frac{\partial p}{\partial n_i} \right)_{T, v, n_{j \neq i}} - \frac{RT}{v} \right) dv - RT \ln Z \quad (11)$$

To apply this equation, knowledge of the P-v-T-x behavior of the mixture is required.

The second method, which is called the activity coefficient method, is based on the following definition:

$$\hat{f}_i = \gamma_i x_i \hat{f}_i^0 \quad (12)$$

or

$$\hat{f}_i = \gamma_i^* X_i H_{i,m} \quad (13)$$

Where f° is fugacity of pure specie i at a specified "standard state", e.g, the pure species i at the system temperature and pressure. $H_{i,m}$ is the Henry's constant for solute i in mixture. The activity coefficient γ_i itself is also a function of temperature, composition and pressure (although the pressure dependence at low and medium pressures is negligible). Classical thermodynamics use another property of mixtures, the excess Gibbs free energy, to express γ_i :

$$\frac{G^E}{RT} = \sum_i X_i \ln \gamma_i \quad (14)$$

Or equivalently,

$$\ln \gamma_i = \left(\frac{\partial (n_t G^E / RT)}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (15)$$

Unfortunately, classical thermodynamics does not provide either the P-v-T-x behavior of the mixture or an analytical expression for the Gibbs free energy of the mixture. Statistical thermodynamics can give some guidance but still cannot yet give a perfect model for P-v-T-x or Gibbs free energy. Therefore semi-empirical methods are widely used to study both equations of state and Gibbs free energy models.

By using the so-called semi-empirical method, numerous equations of state have been developed, such as the equations of Van der Waals, Viral, BWR, Martin-Hou, Redlich-

Kwong, and more recently SRK and PR equation. Numerous mixing rules (which are required when applying an equation of state to mixtures) have been proposed, such as the classic quadratic mixing rule, Vidal type mixing rules and the density dependent local composition (DDLC) mixing rules (2).

Many Gibbs free energy models have also been established such as the model of Van Laar, Wilson, NRTL, and group contribution models such as ASOG and UNIFAC. An interesting review of the historical development of the modeling of fluid phase equilibrium has been given by Knapp (3).

CHAPTER III

LITERATURE REVIEW

Experimental Data

An extensive literature survey concerning the vapor-liquid equilibrium of mixtures containing carbon monoxide was conducted. The sources searched include Chemical Abstracts, a solubility data compilation (4), a vapor-liquid equilibrium data compilation (5) and specialized journals. The available literature data for carbon monoxide + n-hexane, benzene, n-decane, n-octacosane, and n-hexatriacontane are presented in Table I.

Correlation Methods

As described in Chapter II, there are two main methods for phase equilibrium calculations, the activity coefficient method and equation-of-state method. Each has advantages and disadvantages, and a clear comparison has been made by Prausnitz et al.(6). In general, the equation-of-state method is preferred for high pressure problems, especially when the system contains supercritical components.

Much of the work regarding the equation-of-state method focuses on the development and modification of mixing rules for equations of state, which are required when applying an

TABLE I
 AVAILABLE LITERATURE DATA FOR SYSTEMS
 STUDIED IN THIS WORK

SYSTEM	TEMPERATURE RANGE, K	PRESSURE RANGE, atm	REFERENCE NUMBER
CH ₄ + n-C ₁₀	310.9 - 410.9	1.5 - 340	36
	310.9 - 410.9	10 - 87	37
CO + n-C ₆	298.2	1	39
CO + Benzene	433.2 - 533.2	7 - 68	40
CO + n-C ₁₀	283.2 - 313.4	1	39
CO + n-C ₂₈	373.2 - 573.2	10 - 50	41
CO + n-C ₃₆	373.2 - 573.2	10 - 50	41

equation of state to multicomponent systems. The following section is devoted to a brief review and discussion of mixing rules for cubic equations of state.

The most common and also the most widely used mixing rule is the classic quadratic mixing rule, in which there is a second order dependence of the parameters of upon compositions. It can be written as following (7):

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (16)$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (17)$$

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{\frac{1}{2}} \quad (18)$$

$$b_{ij} = (1 - l_{ij}) \frac{b_i + b_j}{2} \quad (19)$$

Where $k_{i,j}$ and $l_{i,j}$ are binary parameters used to account for deviations from the simple rules suggested by Van der Waals (8). If both $k_{i,j}$ and $l_{i,j}$ are set to be zero, the above equations can be reduced to:

$$a = \sum_i x_i a_i^{\frac{1}{2}} \quad (20)$$

$$b = \sum_i x_i b_i \quad (21)$$

The quadratic mixing rule is strongly supported by statistical thermodynamics, since there exists a simple relation between the second virial coefficient and the parameters of cubic equations,

$$B = a - \frac{b}{RT} \quad (22)$$

and the quadratic dependence of B on composition has been derived theoretically from statistical mechanics (9).

Interaction parameters $k_{i,j}$ and $l_{i,j}$ are generally considered to be temperature dependent. Some researchers have studied the generalized relations for $k_{i,j}$, $l_{i,j}$ as function of temperature and characteristic properties such as acentric factor and carbon number of hydrocarbons (10-12).

The quadratic mixing rule has been shown to give good results for systems consisting of components which are similar both in size and chemical nature. But for mixtures of components which are dissimilar in size or in chemical nature, the correlation results are not as satisfactory.

Some investigators have modified the quadratic mixing rule to make it applicable to polar and asymmetric systems. For example, Panagiotopoulos and Reid (13) proposed the following mixing rule:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{\frac{1}{2}} (1 - k_{ij} + (k_{ij} - k_{ji}) x_i) \quad (23)$$

$$b = \sum_i x_i b_i \quad (24)$$

where $k_{i,j}$ does not equal $k_{j,i}$. By applying this mixing rule along with a new method of estimating pure component parameters in the equation of state from vapor pressure information (14), they achieved improved results for some

binary mixtures containing polar compounds such as water + ethanol. The predictions of vapor-liquid equilibrium of carbon dioxide + ethanol + water and carbon dioxide + acetone + water (15) using binary parameters regressed from binary experimental data are quite acceptable. One of its disadvantages is that it does not reduce to the classic quadratic form at low densities, which has been proved theoretically correct. But the authors show that the deviation from quadratic behavior is not significant. Similar work has also been done by Stryjek (16), Adachi (17), and others.

In 1978 Vidal (18) published his new method to obtain mixing rules from solution models. It is done simply by matching the excess Gibbs free energy derived from an equation of state to that obtained from a solution model at infinite pressure. In fact, a similar idea had been used to obtain the first solution model from Van der Waals equation by Van Laar and Van der Waals in 1910 (19). For cubic equations, Vidal's mixing rule for parameter a can be written as follows if a linear mixing rule for b is assumed,

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{G_{\infty}^E}{\Lambda} \quad (25)$$

Where Λ is a constant for a given cubic equation. For example, Λ equal $\ln 2$ for the SRK equation.

Huron and Vidal (20) applied this new mixing rule, incorporating the one-parameter Redlich-Kister model and a modified NRTL model for G^E , to correlate vapor-liquid

equilibrium data of some binary mixtures containing polar components. Remarkable improvements were obtained (even at low pressures) compared to the results given by the quadratic mixing rule. After that, many investigators used this mixing rule for polar and asymmetric systems by using different excess Gibbs free energy models such as the Wilson, NRTL, UNIQUAC models and group contribution models such as UNIFAC and ASOG.

Strictly speaking, Vidal's mixing rule is valid only at infinite pressure. Therefore the parameters in a solution model regressed from low pressure data can not be used directly to get the parameters for an equation of state at either high or low pressures. To overcome this shortcoming, Mollerup (21) suggested a modification of Vidal's method by matching the excess Gibbs free energy given by an equation of state and solution model at zero pressure. Following the proposed procedure of Mollerup, Michelsen (22) obtained the following mixing rule:

$$q_1 \left(\alpha - \sum_i x_i \alpha_i \right) + q_2 \left(\alpha^2 - \sum_i x_i \alpha_i^2 \right) = \frac{G^E}{RT} + \sum_i x_i \ln \left(\frac{b_i}{b} \right) \quad (26)$$

Where α and α_i is defined as following:

$$\alpha = \frac{a}{bRT} \quad (27)$$

$$\alpha_i = \frac{a_i}{b_i RT} \quad (28)$$

q_1 and q_2 are constants having values of -0.478 and 0.0047

respectively (for the SRK equation). This mixing rule, along with the modified UNIFAC model (23) has been applied to predict vapor-liquid equilibrium (24) and gas solubilities (25) for some polar and asymmetric systems at both low and high pressures by using UNIFAC parameters regressed from low pressure data; quite satisfactory results were obtained for the mixtures investigated.

Vidal's mixing rule still has the deficiency that it does not reduce to the quadratic form at low density conditions, as faced by Panagiotopoulos's modified quadratic mixing rule. Therefore another type of mixing rule was developed which can avoid this shortcoming. It is called the density dependent local composition (DDLC) mixing rule. Molleup (26) originally proposed the idea for such consideration, but it should be ascribed to Whiting (27) who developed the first DDLC mixing rule. The advantage of a DDLC mixing rule is that it reduces to the quadratic form at low densities. For example, Panagiotopoulos and Reid (28) proposed the following DDLC mixing rule:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{\frac{1}{2}} (1 - k_{ij}) + \frac{b}{VRT} \sum_i \sum_j x_i x_j (x_i \lambda_{ij} + x_j \lambda_{ji}) \quad (29)$$

Obviously, the quadratic dependence on composition is satisfied at low densities. But the calculated results do not improve very much compared to the Vidal's mixing rule. Luedecke (29) and Sandler (30) also proposed different DDLC mixing rules. A review of DDLC mixing rules has been given by Danner (31).

Although Vidal's mixing rule and the DDLC mixing rule generally give better results than the classic quadratic mixing rule for some polar and asymmetric systems, for simpler system such as nitrogen + n-butane the classic quadratic mixing rule proves superior to the Vidal's mixing rules and the DDLC mixing rules according to Shibate (2). Adachi (32) considers that the DDLC mixing rules as unnecessary from a practical point of view. In fact, the quadratic mixing rule is still attractive due to the following advantages:

1. theoretical background.
2. simplicity.
3. flexibility in form for further modification.

The last point has been partially demonstrated by Panagiotopoulos and Reid (13,28) and also by De Leeuw (33). In the approach of De Leeuw and et al., the temperature and density effect on the interaction parameters is assumed to have the following forms:

$$k_{ij} = k_{ij}^0 + c_{ij}T + d_{ij}/v \quad (30)$$

$$l_{ij} = l_{ij}^0 + o_{ij}T + p_{ij}/v \quad (31)$$

Good fitting results are achieved for some nitrogen-containing mixtures at pressures as high as 2,000 bars. Based on considerations described above, the classic quadratic mixing rule is adopted as being adequate for the purposes of the present work.

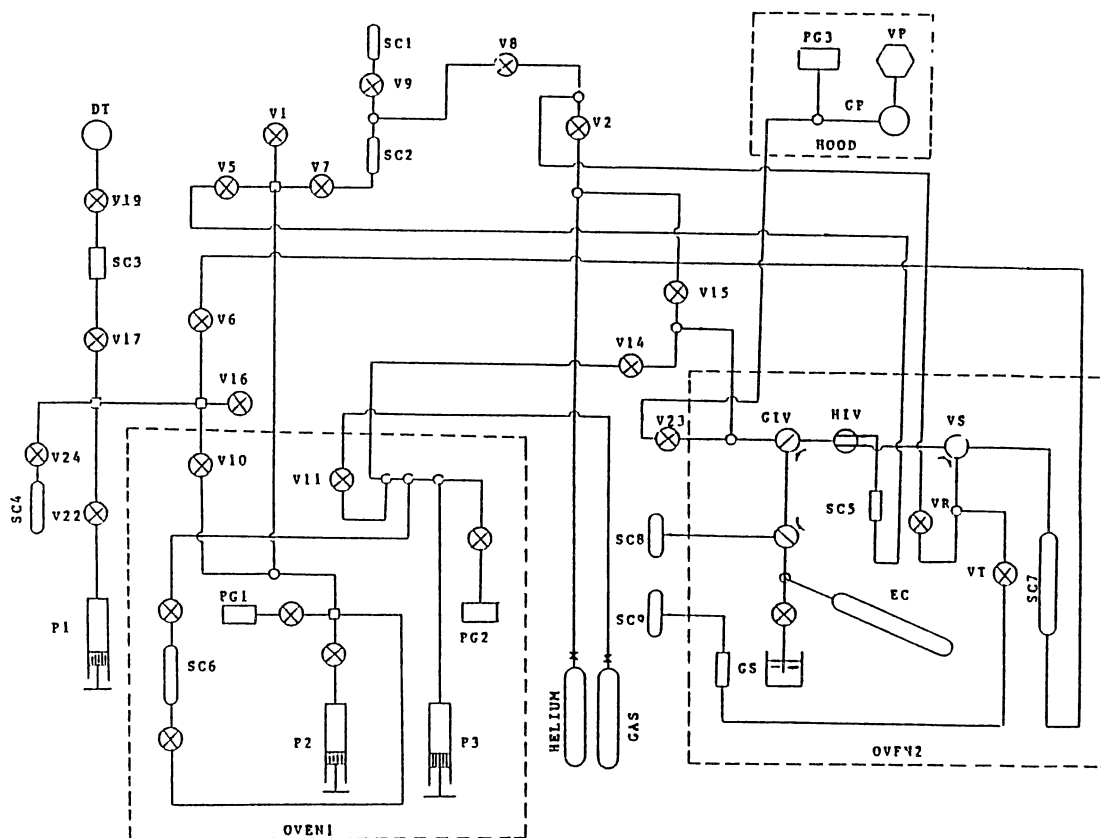
CHAPTER IV
EXPERIMENTAL APPARATUS AND
OPERATING PROCEDURES

Experimental Apparatus

The experimental apparatus used in this study was originally set by Gasem (12) in 1984 and has been extensively modified by Bufkin (34), Barrick (35) and Darwish (37) since then. A detailed description of the apparatus is given by Darwish (37). Following is a brief description of the main components of the apparatus, which is illustrated in Figure 1.

A 316ss high pressure tubular reactor (High Pressure Equipment Company, Catalog Number: MS-14) is used as the equilibrium cell (EC). One end of the equilibrium cell is plugged and connected to a drive wheel, which is driven by a 1/50 HP variable speed motor to rock the cell. The another end of the cell is connected to the gas injection valve. Five steel balls are placed inside the cell to promote mixing of the solvent and solute.

Three pumps are used in this apparatus. The first one is a 10 cc positive displacement pump (TEMCO Company, Catalog Number: 10-1-12-H) used mainly for solvent injection and cleaning of the equilibrium cell (P1). The second one is



SC1	Cleaner Storage Cell
SC2	Inter-Storage Cell of Cleaner
SC4	Mercury Storage Cell
SC5	Inter-Storage Cell of Mercury
SC7	Solvent Storage Cell
SC8, SC9	Trash Cell
DT	Dead Weight Tester
PG1, PG2	Pressure Transducer
PG3	Vacuum Gauge
VP	Vacuum Pump
GP	Gas Trap
P1	Cleaning Pump
P2	Solvent Injection Pump
P3	Solute Injection Pump
GS	Slight Glass
EC	Equilibrium Cell

Figure 1. Schematic Diagram of Experimental Apparatus

a 25 cc positive displacement pump (TEMCO Company, Catalog Number: 25-1-10-HAT) used mainly for solute injection (P2). The third one is a 500 cc positive displacement pump (Ruska Company, Catalog Number: 2210-801) mainly used for cleaning of the solvent storage cell (P3).

Two constant temperature ovens are used in this apparatus. One is used to house the solvent injection pump and the solute injection pump, and the temperature is generally set at 50°C. The another is used to house the equilibrium cell as well as the solvent storage cell, the temperature can be adjusted according to requirement.

Two pressure transducers (Sensotec Company, Catalog Number: TJE/743-03) are used to measure the pressure inside the equilibrium cell and the pressure inside the solute injection pump, respectively. These two traducers are calibrated periodically using a dead weight tester (Ruska Instrument Company, Catalog Number: 2426.1-M288).

A high pressure reactor (High Pressure Equipment Company, Catalog number: OC-1) is used as the solvent storage cell (SC7). Another high pressure reactor (High Pressure Equipment Company, Catalog Number: MS-12) is used as the interstorage cell of mercury (SC5), which is connected to the equilibrium cell.

All fittings, tubings and valves used in this study were supplied by High Pressure Equipment Company. All chemicals used in this study were provided by commercial suppliers. No further purification of the chemicals was

attempted. The suppliers and the claimed purities are presented in Table II.

Experimental Procedure

The experimental procedure is quite simple theoretically. A known amount of solvent and a known amount of solute are injected into the equilibrium cell. Then the phase transition from vapor-liquid mixture to liquid mixture is realized by the introduction of mercury and the equilibrium pressure (or bubble point pressure) is determined from a plot of pressure versus volume of mercury injected.

According to the Gibbs phase law, the freedom of a two-phase binary system is

$$F = N - \pi + 2 = 2 - 2 + 2 = 2 \quad (32)$$

Therefore at least three variables need to be measured to set up a model describing the phase behavior of such system if the model has adjustable parameters which need to be regressed from experimental data. In the experiment of this work, temperature, liquid composition and equilibrium pressure are measured and only isothermal data is acquired in this work (this means that bubble point pressure is observed as a function of liquid composition at fixed temperature). A brief description of the conceptual steps is given below. A step-by-step operating procedure is also given by Darwish (37). There were no significant modifications during the course of this work.

TABLE II
CHEMICALS AND PURITIES USED IN THIS WORK

Chemicals	Source	Purity(mol%)
Methane	Big 3 Industries, Inc.	99.97+
Carbon Monoxide	Matheson Gas Products	99.99+
n-Hexane	Aldrich Chemical Company	99+
n-Decane	Aldrich Chemical Company	99+
Benzene	Aldrich Chemical Company	99+
n-Octacosane	Aldrich Chemical Company	98+
n-Hexatriacontane	Aldrich Chemical Company	98+

1. The solvent and solute inside the equilibrium cell are emptied from the cell and then the cell is cleaned. Vacuum is applied to the equilibrium cell after cleaning to remove any residual solvent or other volatile components.

2. Known amounts of solvent and solute are injected into the equilibrium cell using the solvent injection pump and the solute injection pump.

3. A specific amount of mercury, Δv (0.01 cc or 0.005 cc) is injected into the equilibrium cell and the equilibrium pressure is recorded. This is done repeatedly and the bubble point pressure is interpreted from the P- Δv curve. A typical P- Δv curve is shown in Figure 2.

By subsequent solute injections, 2 to 4 data points are measured in each run of a isotherm. Each isotherm is measured at least two times to confirm the observations.

At the beginning of the study of a new system, the solvent storage cell is cleaned and vacuumed. Then solvent is transferred into the storage cell and degassed.

As described previously, the operating procedure is quite simple theoretically, but several problems were encountered during this work. One serious problem is the presence of non-condensable gas bubbles in the solvent injection pump, which makes the mercury "compressible" and thus affects the accuracy of bubble point pressure determination. Following is a brief description of the procedures used to remove gas bubbles.

1. Isolate the solvent injection pump and the cleaning

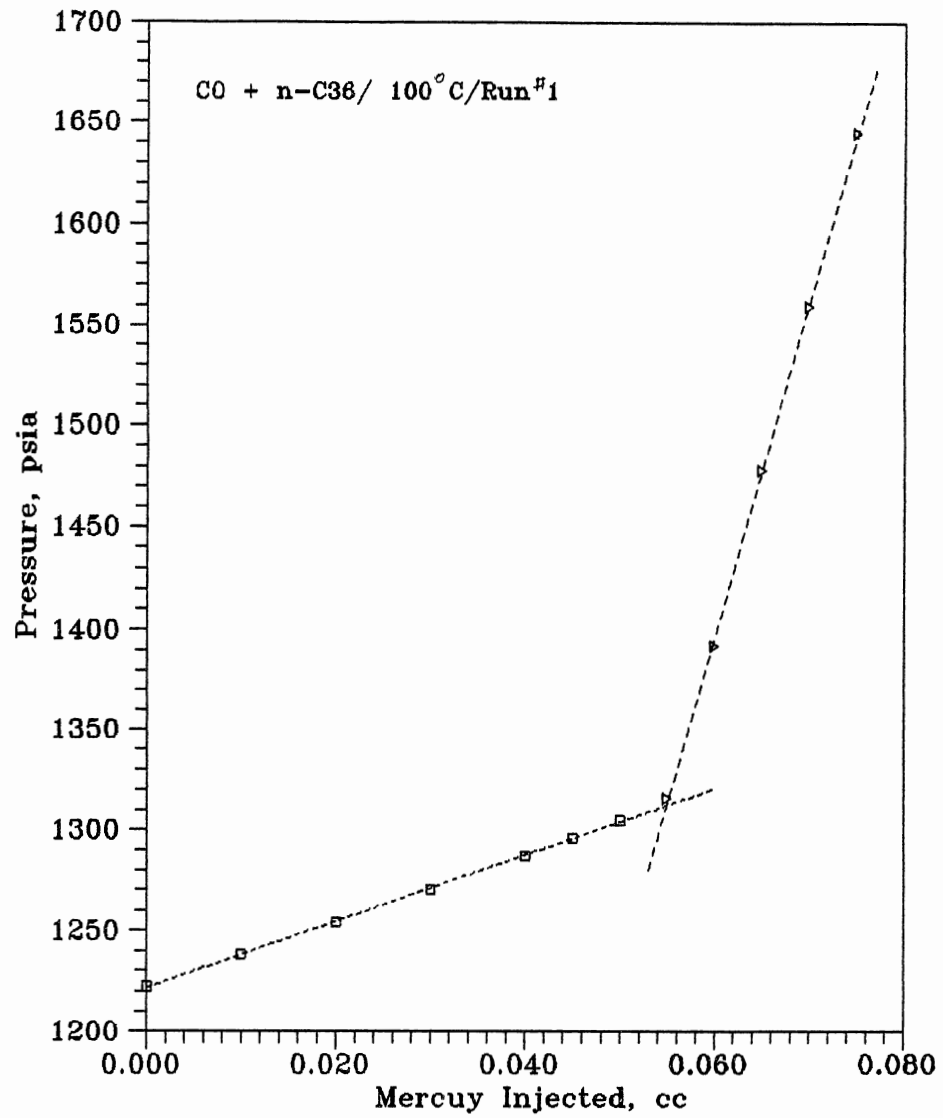


Figure 2. Determination of Bubble Point Pressure

pump by closing V_{13} , V_1 , V_7 , V_6 , V_{16} , V_{24} , V_{17} as shown in Figure 3.

2. Back off the cleaning pump approximately 100 cc and incline the solvent injection pump to remove the mercury inside it into the cleaning pump.

3. Push all mercury between $ISC \rightarrow V_5 \rightarrow V_{10}$ into the cleaning pump using helium at about 200 psia.

4. Close V_{10} and apply vacuum to the cleaning pump about 4 to 8 hours through V_{27} . Then forward the cleaning pump until the pump is filled with mercury. Close V_{27} .

5. Apply vacuum to the solvent injection pump for 2 to 4 hours through V_{26} . Then open V_{10} and forward the cleaning pump very slowly until the solvent injection pump is filled with mercury till V_{26} . Close V_{26} .

6. Test the compressibility of mercury inside the solvent injection pump. A typical result is presented in Table III when the pump is gas-free.

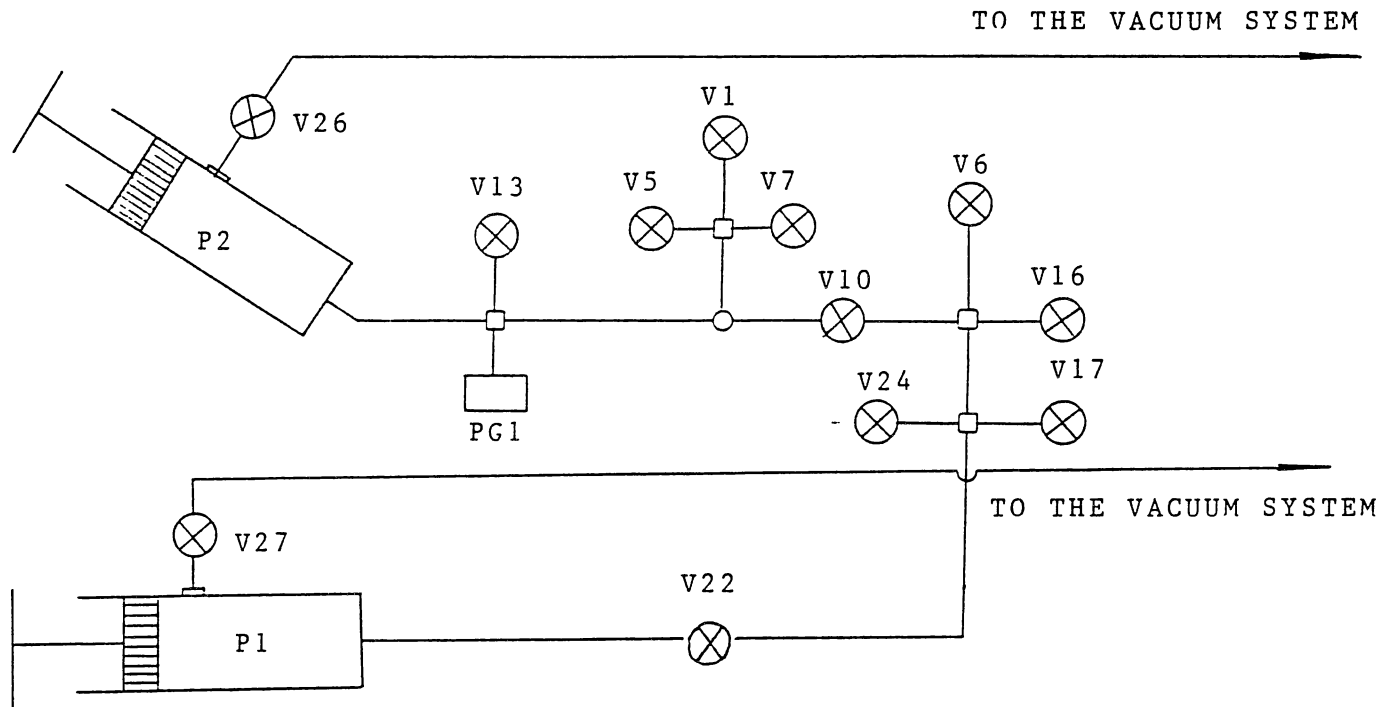


Figure 3. Removing Non-Condensable Gas Bubbles

TABLE III
COMPRESSIBILITY TEST OF THE
SOLVENT INJECTION PUMP

Pump Position	6.05	6.06	6.07	6.08
Pressure, psia	38	228	900	>1600

CHAPTER V

EXPERIMENTAL RESULTS AND ERROR ANALYSIS

Experimental Results

In this work, the solubilities of carbon monoxide in n-hexane, n-decane, benzene, n-octacosane and n-hexatriacontane were measured at temperatures from 50°C to 160°C and pressures to 1500 psia. The experimental data are presented in Tables IV - VIII.

These experimental data and available literature data appear in Figures 4 - 8, which show $(P_b - P_s)/x$ as a function of x . The experimental data are plotted in this form since any internal scatter or disagreement with literature data are magnified in such plots. The vapor pressures, P_s were taken from the literature (42).

As the figures show, the experimental data can be represented simply by a linear expression for each isotherm studied of the form:

$$\frac{P_b - P_s}{x_2} = c_1 + c_2 x_2 \quad (33)$$

Values of c_1 and c_2 and the maximum deviation between correlated and experimental bubble point pressures of each system at each temperature are listed in Table IX. This

TABLE IV
 SOLUBILITY DATA FOR CARBON MONOXIDE + n- HEXANE

Mole Fraction CO	Bubble Point Pressure	
	bar	(psia)
----- 323.2K (50.0°C, 122.0°F) -----		
0.0310	17.5	(254)
0.0549	31.4	(456)
0.0800	46.2	(670)
0.1000	58.8	(852)
0.1346	80.4	(1166)
0.1439	86.9	(1260)
-----373.2K (100.0°C, 212.0°F)-----		
0.0296	17.2	(250)
0.0474	27.4	(398)
0.0807	44.3	(643)
0.1009	55.0	(798)
0.1144	62.6	(909)
0.1408	77.3	(1121)
-----423.2K (150°C, 302°F)-----		
0.0099	11.8	(171)
0.0538	31.2	(453)
0.0799	43.1	(625)
0.0758	40.8	(592)
0.1260	63.9	(927)
0.1466	73.6	(1068)

TABLE V
SOLUBILITY DATA FOR CARBON MONOXIDE + BENZENE

Mole Fraction CO	Bubble Point bar	Pressure (psia)
----- 323.2K (50.0°C, 122.0°F) -----		
0.0099	14.7	(213)
0.0197	29.4	(426)
0.0296	44.5	(645)
0.0398	60.4	(876)
0.0478	73.3	(1063)
0.0546	84.2	(1221)
0.0597	92.6	(1343)
-----373.2K (100.0°C, 212.0°F)-----		
0.0103	14.1	(205)
0.0150	19.8	(287)
0.0212	27.1	(394)
0.0340	42.9	(622)
0.0371	47.0	(681)
0.0450	56.8	(824)
0.0516	65.1	(945)
0.0637	80.5	(1167)
----- 433.2K (160.0°C, 320.0°F) -----		
0.0148	21.2	(308)
0.0252	31.3	(445)
0.0398	45.6	(662)
0.0428	48.6	(704)
0.0548	60.5	(877)
0.0590	64.6	(937)

TABLE VI
 SOLUBILITY DATA FOR CARBON MONOXIDE + n-DECANE

Mole Fraction CO	Bubble Point bar	Pressure (psia)
----- 377.6K (104.4°C, 220.0°F) -----		
0.0388	22.2	(323)
0.0619	36.2	(526)
0.0895	53.9	(782)
0.1197	73.7	(1070)
0.1400	88.1	(1278)
0.1599	102.0	(1480)
-----310.9K (37.8°C, 100.0°F)-----		
0.0448	28.4	(412)
0.0873	58.1	(842)
0.0953	64.5	(936)
0.1097	75.7	(1097)
0.1247	87.8	(1273)
0.1399	100.0	(1451)
-----344.3K (71.1°C, 160.0°F)-----		
0.0385	23.6	(342)
0.0538	33.0	(479)
0.0770	48.5	(704)
0.0883	56.4	(818)
0.1171	76.9	(1115)
0.1363	91.5	(1327)

TABLE VII
SOLUBILITY DATA FOR CARBON MONOXIDE + n-OCTACOSANE

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
----- 373.2K (100.0°C, 212.0°F) -----		
0.0463	20.1	(291)
0.0577	24.2	(351)
0.1005	44.2	(641)
0.1131	50.2	(728)
0.1463	68.0	(986)
-----424.2K (150.0°C, 302.0°F)-----		
0.0551	21.9	(317)
0.1027	41.8	(606)
0.1315	55.9	(811)
0.1623	70.8	(1017)
0.1853	84.1	(1220)

TABLE VIII
 SOLUBILITY DATA FOR CARBON MONOXIDE + n-HEXATRIACONTANE

Mole Fraction Methane	Bubble Point bar	Pressure (psia)
----- 373.2K (100.0°C, 212.0°F) -----		
0.0494	18.0	(261)
0.0638	23.4	(340)
0.0900	34.4	(499)
0.1192	47.5	(689)
0.1603	67.6	(980)
0.2002	89.5	(1299)
-----423.2K (150.0°C, 302.0°F)-----		
0.0568	18.5	(269)
0.0705	23.7	(344)
0.1040	36.0	(522)
0.1289	46.6	(676)
0.1742	66.1	(958)
0.2099	84.0	(1218)

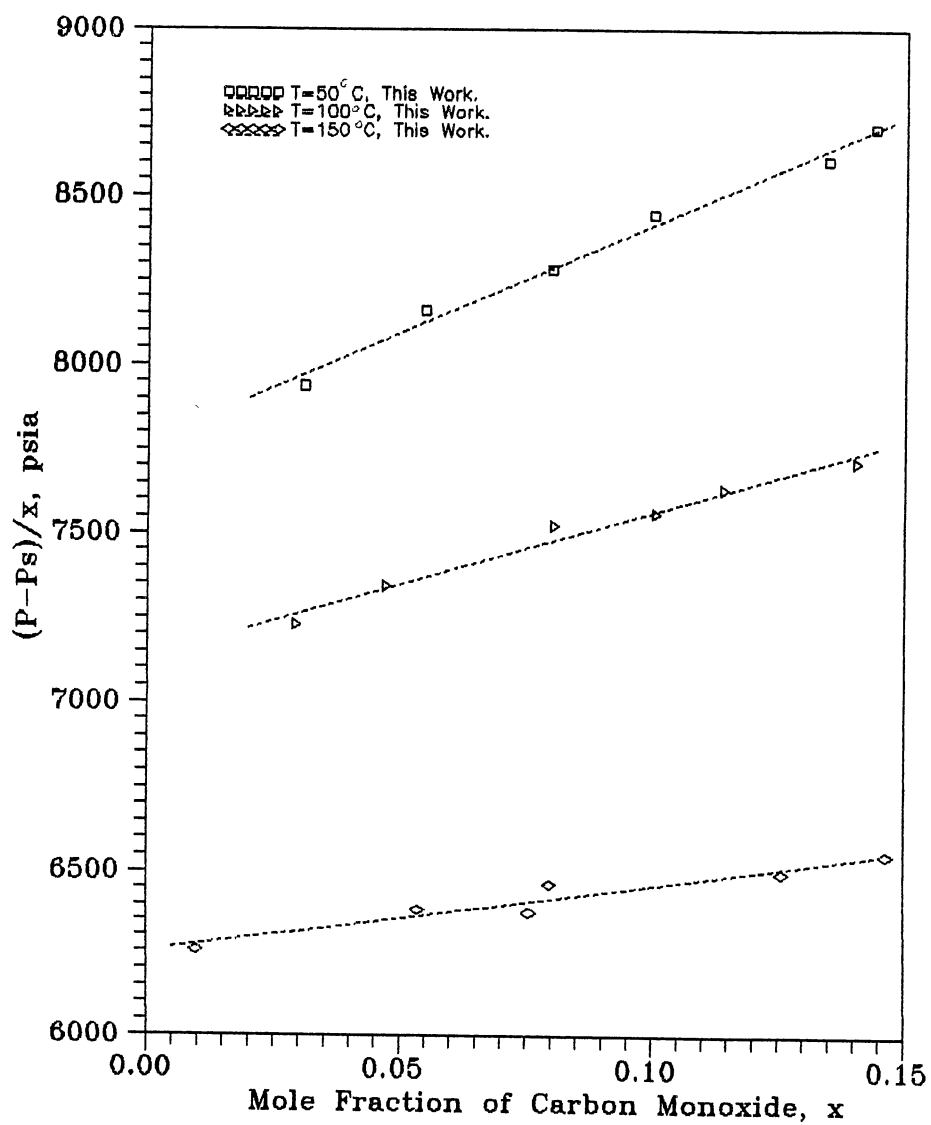


Figure 4. Bubble Point Pressure for Carbon Monoxide + n-Hexane

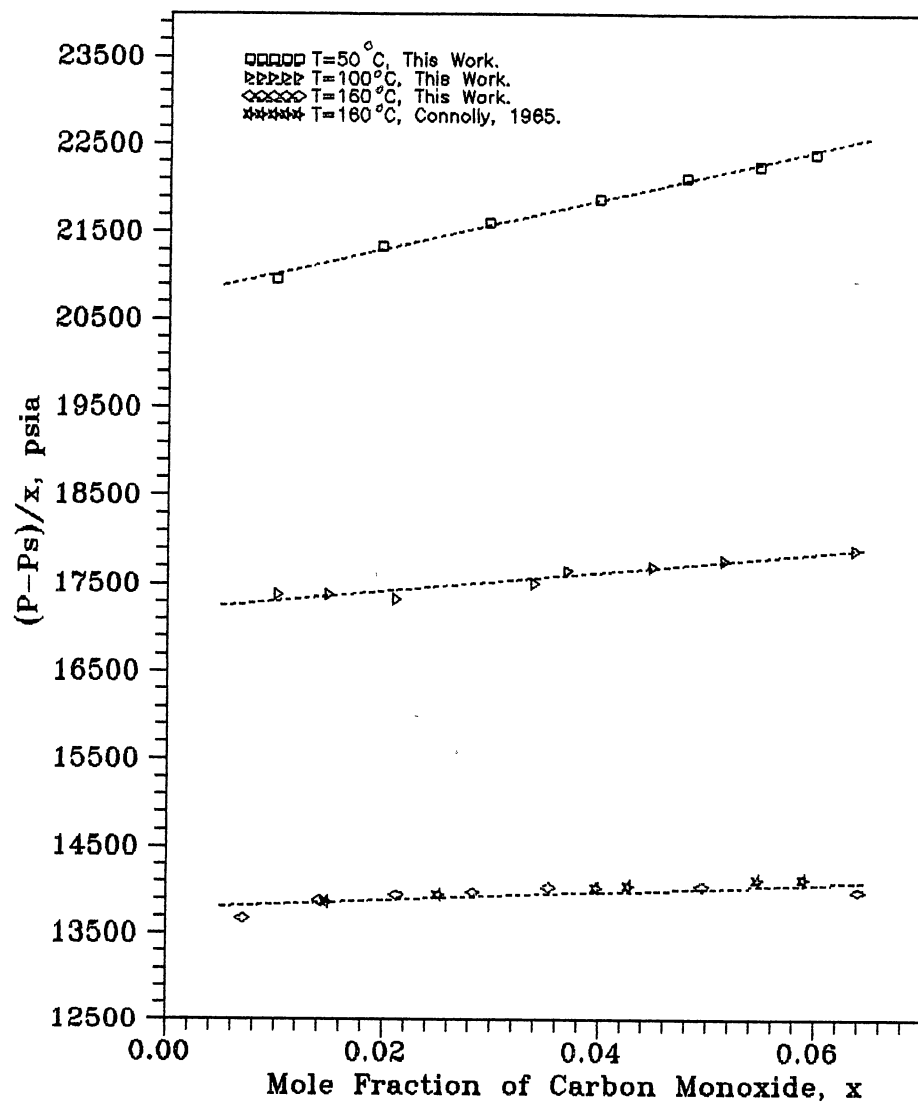


Figure 5. Bubble Point Pressure for Carbon Monoxide + Benzene

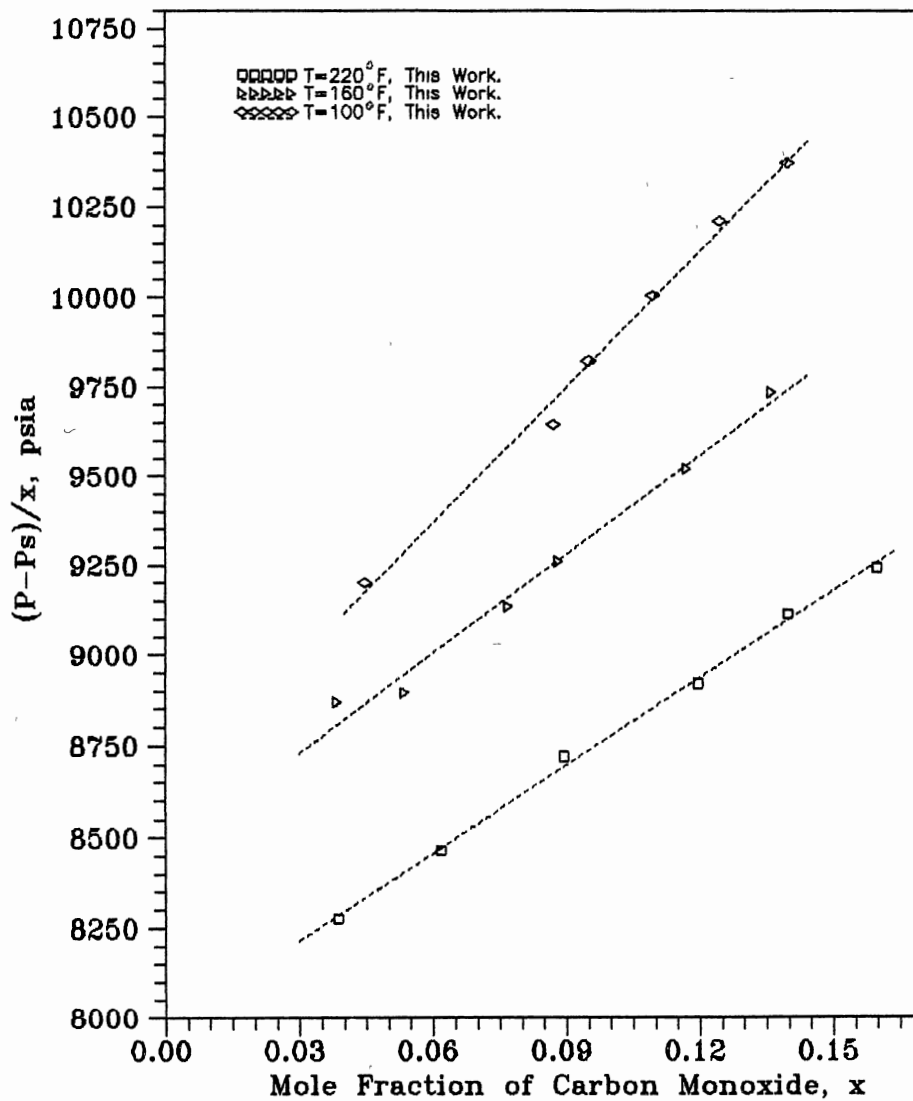


Figure 6. Bubble Point Pressure for Carbon Monoxide + n-Decane

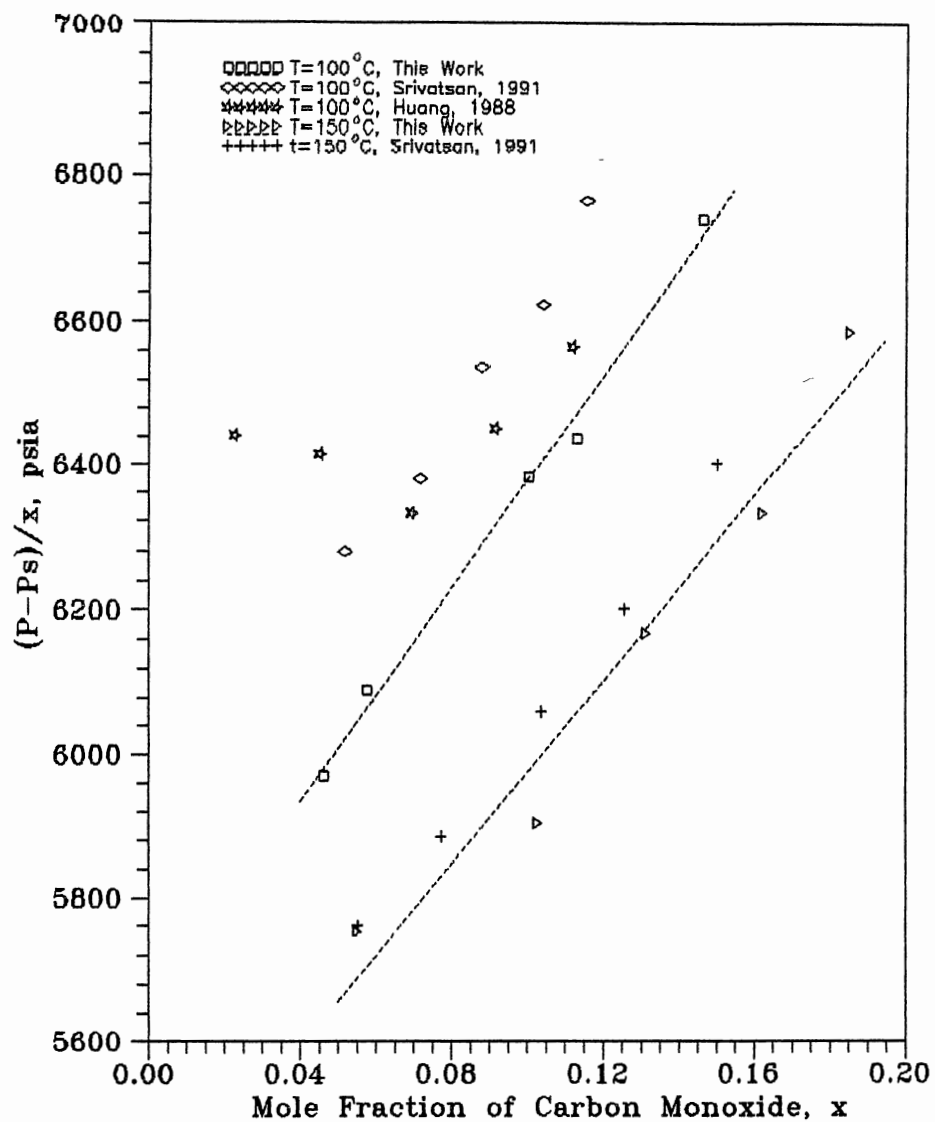


Figure 7. Bubble Point Pressures for Carbon Monoxide + n-Octacosane

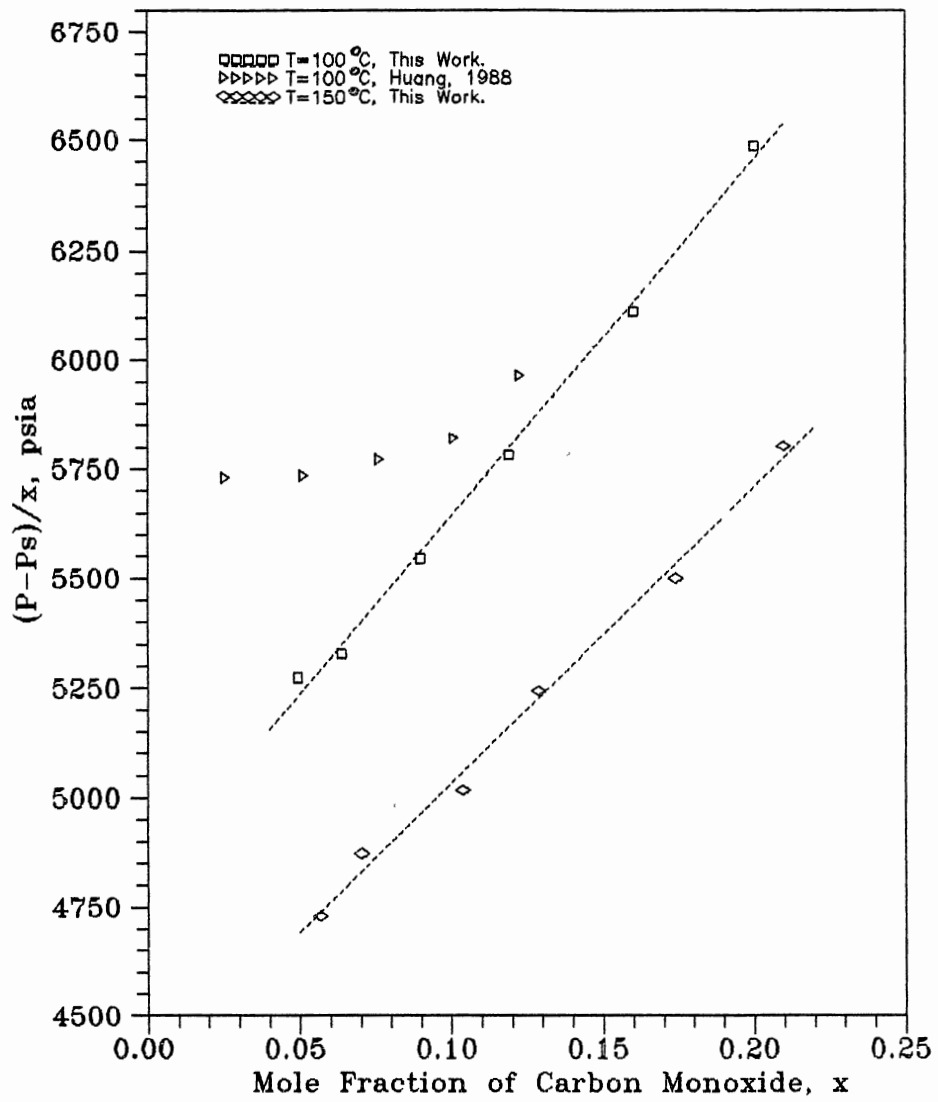


Figure 8. Bubble Point Pressures for Carbon Monoxide + Hexatriacontane

TABLE IX
EMPIRICAL CORRELATION OF SOLUBILITY DATA

SOLVENT	TEMPERATURE °C	C ₁ (psia)	C ₂ (psia)	P _{cal} -P _{exp} _{max} (psia)
n-C ₆	50.0	6426	7769	4
	100.0	4343	7137	4
	150.0	1987	6252	4
C ₆ H ₆	50.0	26894	20827	3
	100.0	11441	17186	2
	160.0	6677	13760	6
n-C ₁₀	37.3	12568	8619	6
	71.1	9250	8442	4
	104.4	8056	7973	3
n-C ₂₈	100.0	7365	5640	6
	150.0	6341	5340	4
n-C ₃₆	100.0	7991	4855	7
	150.0	6743	4359	6

correlation is purely empirical and is required when evaluating the experimental uncertainties of bubble point pressures as described later, which is equivalent to using a second order polynomial to describe the relation between bubble point pressure and solubility:

$$P_b = c_0 + c_1 x_2 + c_2 x_2^2 \quad (34)$$

Obviously c_0 should equal P_s in the above equation.

Error Analysis

Two types of errors generally occur in experiments, systematic and random error. Systematic errors are those that have direct relation with the experimental apparatus, operating procedures and other causes that result in consistent deviations of observations from the "true value". Random errors are usually attributed to a combination of disturbances which result in deviations of observations from the "true value". In general, systematic errors affect the accuracy of measurement and random errors affect the precision of measurement.

To eliminate systematic errors in the present work, several efforts were made. One of them was to calibrate the pressure and temperature transducers periodically. The calibration of pressure transducers was done by using a dead weight tester as described in Chapter IV. The calibration of temperature transducers was checked by measuring the ice-point of pure water.

To evaluate the apparatus and procedures used in this

work, initial measurements were made for methane + n-decane and compared with the results given by Reamer (36) and Darwish (37). The experimental data are presented in Table X and the comparison between the results of this work and those of Reamer and Darwish are shown in Figure 9. In the figure, the deviation in solubility predicted by the SRK equation (with the parameters of equation of state regressed from the data of this work) are plotted as a function of bubble point pressure. It shows that the results of this work are in good agreement with those of Darwish (maximum deviation is less than 0.002) and in reasonable agreement with these of Reamer (absolute maximum deviation is less than 0.004).

Random errors can be estimated by error propagation. In general, if y is a variable calculated from a set of measurable variables z_i ($i=1,2,\dots,N$), i.e:

$$y = f(z_1, z_2, \dots, z_N) \quad (35)$$

The variance of y can be estimated by the following equation provided that z_i ($i=1,2,\dots,N$) are independent variables (38):

$$\sigma_y^2 = \sum_{i=1}^N \left(\frac{\partial f}{\partial z_i} \right)^2 \sigma_{z_i}^2 + \epsilon_y^2 \quad (36)$$

Where σ_z is the standard derivation of z_i , ϵ_y is instrumental error in y (if y itself is also a measured variable). In this experiment, both bubble point pressure and solubility are determined. For solubility,

TABLE X
 SOLUBILITY DATA FOR METHANE IN n-DECANE

Mole Fraction Methane	Bubble Point Pressure	
	bar	(psia)
----- 344.3K (71.1°C, 160.0°F) -----		
0.0521	12.5	(181)
0.1152	28.6	(415)
0.1602	41.5	(602)
0.2000	53.2	(772)
0.2325	64.2	(931)
0.2590	72.8	(1055)
-----377.6K (104.4°C, 220°F)-----		
0.0466	12.2	(176)
0.0801	21.0	(305)
0.1161	31.4	(455)
0.1498	41.4	(601)
0.2000	57.6	(835)
0.2252	66.1	(958)
0.2502	74.3	(1078)

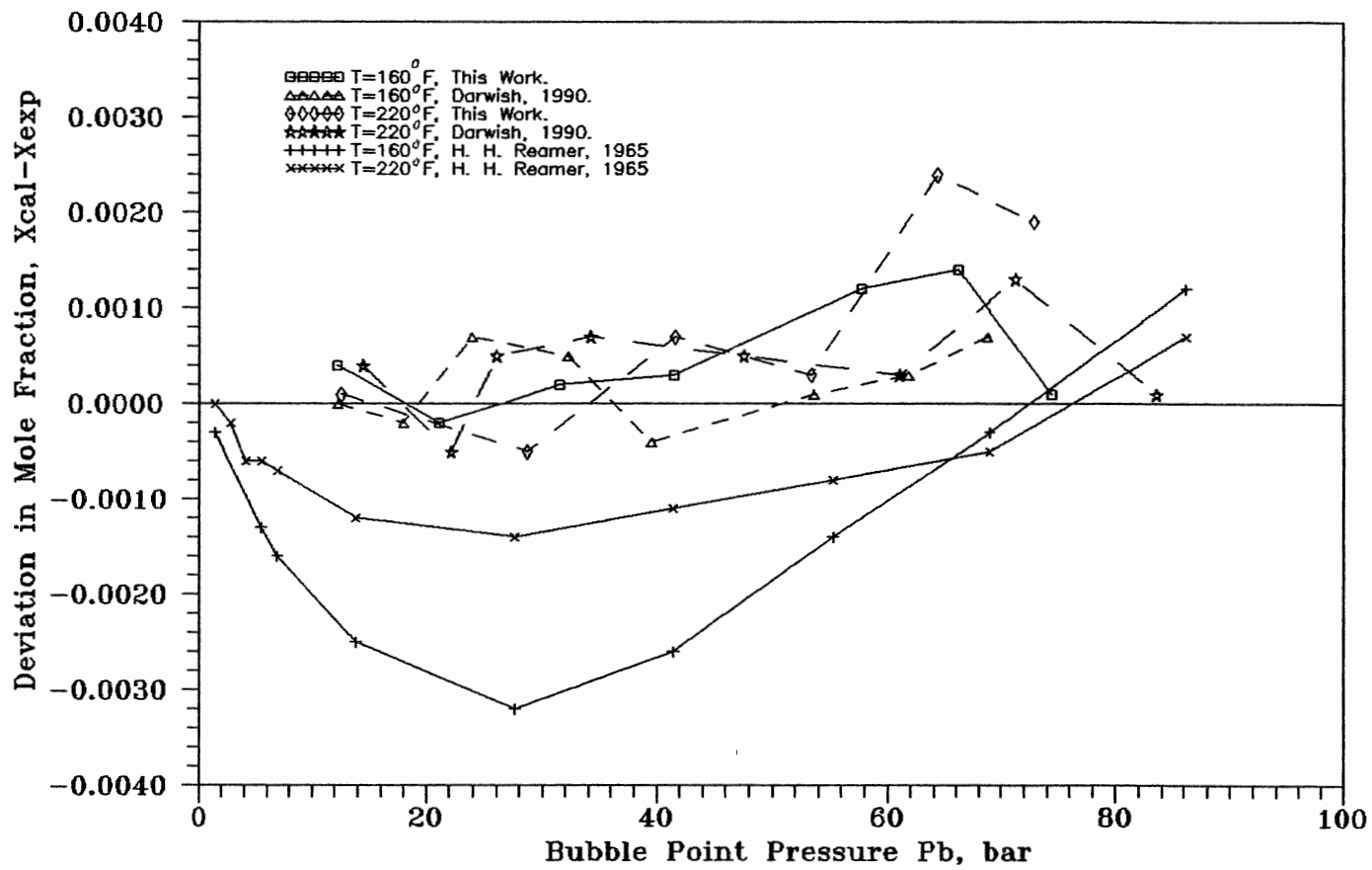


Figure 9. Comparison of Solubilities of Methane in n-Decane

$$x_1 = \frac{n_1}{n_1 + n_2} \quad (37)$$

Where n_1 and n_2 are the number of moles of solvent and solute injected which are determined by the following relations:

$$n_1 = \rho_1 v_{11} \quad (38)$$

$$n_2 = \rho_2 \sum_{j=1}^I v_{2j} \quad (39)$$

Combining Equations 35-39 gives

$$x_1 = \frac{\rho_1 v_{11}}{\rho_1 v_{11} + \rho_2 \sum_{j=1}^I v_{2j}} \quad (40)$$

$$x_2 = 1 - x_1 \quad (41)$$

Applying Equation 36 to the above equation, we obtain

$$\sigma_{x_2}^2 = x_2^2 (1 - x_2)^2 \left(\left(\frac{\sigma_{\rho_1}}{\rho_1} \right)^2 + \left(\frac{\sigma_{\rho_2}}{\rho_2} \right)^2 + \left(\frac{\sigma_{v_{11}}}{v_{11}} \right)^2 + I \sum_j \left(\frac{\sigma_{v_{2j}}}{v_{2j}} \right)^2 \right) \quad (42)$$

Where I is the number of solute injections. The maximum uncertainty in solubility for each isotherm is listed in Table XI by using Equation 42 along with the following specifications:

$$\sigma_{\rho_1} / \rho_1 = 0.0015 \quad (43)$$

$$\sigma_{\rho_2} / \rho_2 = 0.0015 \quad (44)$$

$$\sigma_{v_{11}} = \sigma_{v_{2j}} = 0.005cc \quad (45)$$

The uncertainties in bubble point pressure as a

TABLE XI
 MAXIMUM UNCERTAINTIES IN SOLUBILITY
 AND BUBBLE POINT PRESSURE

System	Temperature (K)	x_{\max}	$\sigma_{p,\max}$ (psia)	$\sigma_{x,\max}$
CO + n-C ₆	323.2	0.1439	5	0.0004
	373.2	0.1408	4	0.0004
	423.2	0.1466	4	0.0005
CO + C ₆ H ₆	323.2	0.0597	4	0.0003
	373.2	0.0637	5	0.0002
	423.2	0.0548	4	0.0002
CO + n-C ₁₀	310.9	0.1399	6	0.0005
	344.3	0.1172	6	0.0005
	377.6	0.1400	6	0.0005
CO + n-C ₂₈	373.2	0.1463	6	0.0007
	423.2	0.1623	5	0.0006
CO + n-C ₃₆	373.2	0.2002	8	0.0009
	423.2	0.2099	7	0.0008

function of temperature and solubility can be obtained from the following equation:

$$\sigma_{p_b}^2 = \epsilon_{p_b}^2 + \left(\frac{\partial p_b}{\partial x_2}\right)^2 \sigma_{x_2}^2 + \left(\frac{\partial p_b}{\partial T}\right)^2 \sigma_T^2 \quad (46)$$

The temperature effect is generally neglected since it is quite small compared with the first two terms. The partial derivative of pressure with solubility is obtained directly from Equation 34:

$$\frac{\partial p_b}{\partial x_2} = c_1 + 2c_2 x_2 \quad (47)$$

The instrumental error in pressure is expressed as follows according to Darwish (37):

$$\epsilon_p = 0.004p \quad (48)$$

The maximum uncertainties in bubble point pressures for each isotherm are also presented in Table XI. These estimates are in excellent agreement with the actual experimental results given in Table IX for the error in calculated bubble points.

CHAPTER VI

CORRELATION OF EXPERIMENTAL DATA

SRK and PR Equation Representations

Representation

All experimental data were correlated using the SRK and PR equations. The critical properties of the pure components were taken from the literature (43) for those components for which experimental values are available. For those that lacked experimental critical properties, Gasem's method (12) was adopted to obtain the required properties. All parameters used in the correlation are presented in Table XII. Detailed procedures for data reduction are given by Gasem (12).

Table XIII is a summary of correlation results and the regressed binary parameters are summarized in Table XIV. Detailed correlation results are presented in Tables A.1-A.6 in Appendix. Binary interaction parameters k_{ij} and l_{ij} , root mean square errors in solubilities

$$RMSE = \left\{ \frac{1}{N} \sum_{i=1}^N (x_{cal} - x_{exp})^2 \right\}^{\frac{1}{2}} \quad (49)$$

and maximum deviations between experimental and calculated solubilities are listed in these tables. Each table contains

TABLE XII
CRITICAL PROPERTIES AND ACENTRIC FACTORS
USED IN THE SRK AND PR EQUATIONS OF STATE

Component	Pressure bar	Temperature K	Acentric Factor	Reference
CH ₄	46.60	190.5	0.0110	(43)
CO	34.94	132.9	0.0490	(43)
n-C ₆	30.30	507.9	0.2980	(43)
C ₆ H ₆	48.94	562.1	0.2120	(43)
n-C ₁₀	21.08	617.6	0.4900	(43)
n-C ₂₈	8.26	845.4	1.1073	(12)
n-C ₃₆	6.91	901.1	1.2847	(12)

TABLE XIII
SUMMARY OF CORRELATION RESULTS BY USING SRK EQUATION

Solvent	Temperature K	RMSE in Solubility, Mole Fraction			
		Case 1	Case 2	Case 3	Case 4
n-C ₆	323.2	0.0002	0.0002	0.0019	0.0019
	373.2	0.0002	0.0003		
	423.2	0.0003	0.0005		
Benzene	323.2	0.0000	0.0002	0.0008	0.0008
	373.2	0.0001	0.0002		
	433.2	0.0000	0.0001		
n-C ₁₀	310.9	0.0003	0.0003	0.0014	0.0014
	344.3	0.0002	0.0002		
	377.6	0.0002	0.0003		
n-C ₂₈	373.2	0.0002	0.0008	0.0029	0.0029
	423.2	0.0008	0.0012		
n-C ₃₆	373.2	0.0002	0.0025	0.0069	0.0084
	423.2	0.0005	0.0026		

TABLE XIV
SUMMARY OF BINARY PARAMETERS IN THE SRK EQUATION

Solvent	T (K)	Case 1		Case 2	Case 3		Case 4
		k_{ij}	l_{ij}	k_{ij}	k_{ij}	l_{ij}	k_{ij}
n-C ₆	323.2	0.0608	0.0006	0.0626			
	373.2	0.0297	0.0115	0.0633	0.0850	-0.0065	0.0657
	423.2	0.0146	0.0329	0.1072			
Benzene	323.2	-0.0122	0.0326	0.0953			
	373.2	-0.0321	0.0306	0.0700	0.1646	-0.0230	0.0884
	423.2	-0.0316	0.0332	0.0803			
n-C ₁₀	310.9	0.1356	-0.0031	0.1204			
	344.3	0.1115	-0.0004	0.1094	0.1104	0.0007	0.1136
	377.6	0.0800	0.0043	0.1006			
n-C ₂₀ (*)	323.2	0.2772	-0.0113	0.1602			
	373.2	0.2257	-0.0105	0.1166	0.1439	-0.0018	0.1253
	423.2	0.2292	-0.0140	0.0873			
n-C ₂₈	373.2	0.1498	-0.0071	0.0438	0.0427	-0.0013	0.0246
	423.2	0.1413	0.0100	0.0031			
n-C ₃₆	373.2	0.1937	-0.0122	-0.0045	0.3063	-0.0219	-0.0542
	423.2	0.1218	-0.0151	-0.1299			

*: Experimental data is given by Srivatsan (44).

results for the following four cases:

1. Two interaction parameters, k_{ij} and l_{ij} are determined from the experimental data for each system at each temperature.

2. One interaction parameter, k_{ij} , is determined from the experimental data for each system at each temperature ($l_{ij}=0$).

3. Two interaction parameters, k_{ij} and l_{ij} are determined from the experimental data for each system, independent of temperature.

4. One interaction parameter, k_{ij} , is determined from experimental data for each system, independent of temperature ($l_{ij}=0$).

Table XIII shows that when two temperature dependent binary interaction parameters are used for each isotherm (Case 1), the SRK or PR equation is capable of describing the solubilities with RMSE no more than 0.0008 in mole fraction for each system studied.

When only one temperature dependent interaction parameter k_{ij} is used for each isotherm (Case 2), nearly the same RMSE is achieved as in Case 1 for carbon monoxide + n-hexane, benzene, and n-decane systems. For carbon monoxide + n-octacosane, n-hexatriacontane systems, however, the RMSE obtained are larger than for Case 1. This may be explained briefly from the meaning of the second interaction parameter l_{ij} , which is used to correct the so called co-volume of the mixture. When l_{ij} is set to be zero, Equation 17 and

Equation 19 reduces to:

$$b = \sum_i x_i b_i \quad (50)$$

For carbon monoxide + n-hexane, benzene, n-decane system, this simplification does not introduce as much error as for carbon monoxide + n-octacosane, n-hexatriacontane systems, since the differences between the solvent and solute in molecular sizes are less than for the later systems.

The RMSE is larger than the experimental uncertainties when lumped k_{ij} and l_{ij} (or lumped k_{ij}) is used (Case 3 and Case 4) for all systems under study. This suggests that the temperature effect on the interaction parameters should be considered if better correlation results are required.

Correlation results for Case 1 are also plotted in Figures 10- 14. The comparisons of our results with those of other investigators are also shown in these figures by predicting the solubilities using the binary interaction parameters regressed from our data at each temperature.

Figure 11 shows that for carbon monoxide + benzene system our results are in good agreement with those of Connolly (40) at 160.0°C. The maximum deviation between prediction and measurement is 0.0006. For carbon monoxide + n-octacosane, n-hexatriacontane systems, our solubilities are slightly higher than those reported by Huang et al. (41) at 100.0°C and 150.0°C respectively as indicated by Figure 13 and Figure 14.

There exists correlation between the two interaction

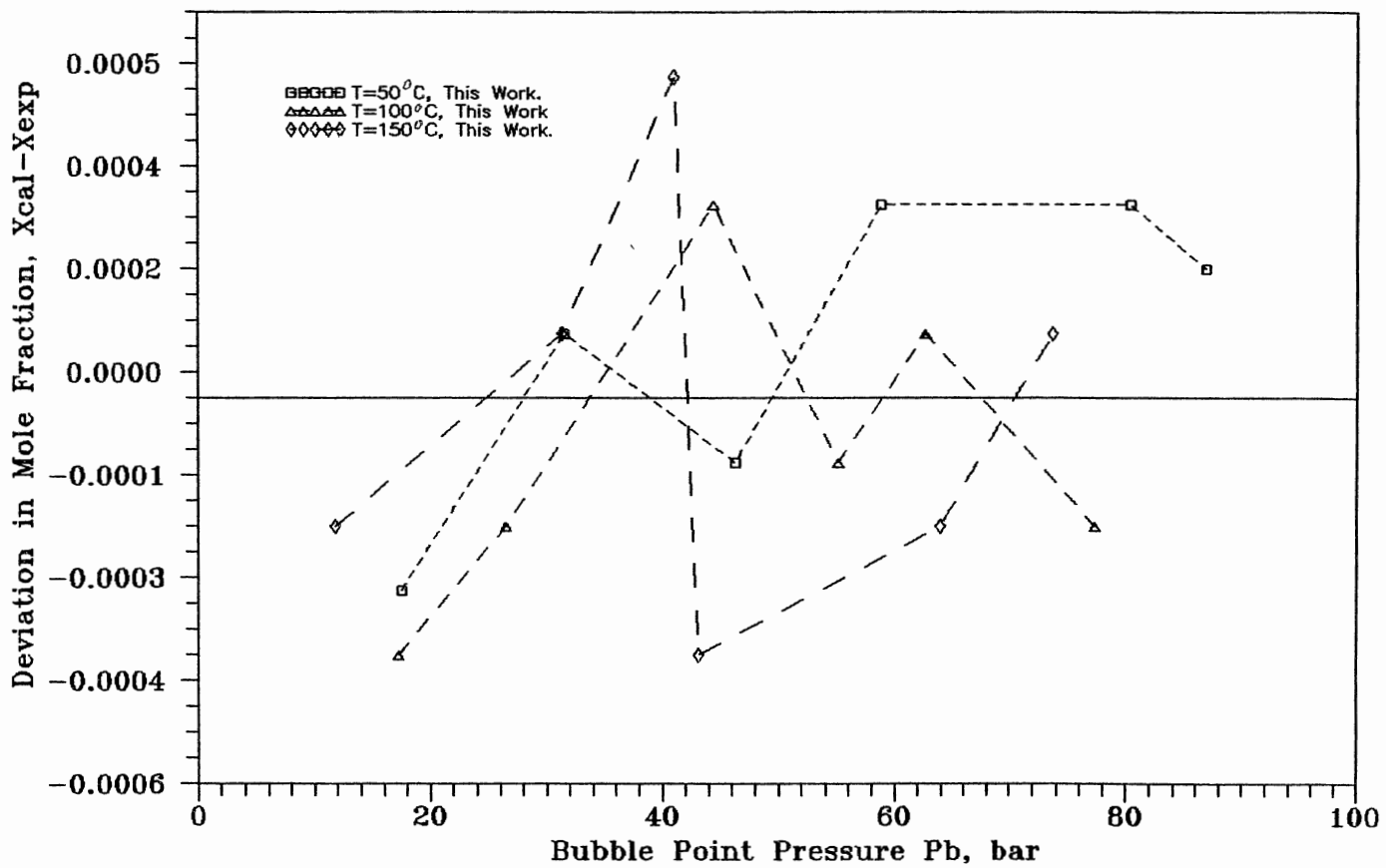


Figure 10. Comparison of Solubilities of Carbon Monoxide in n-Hexane

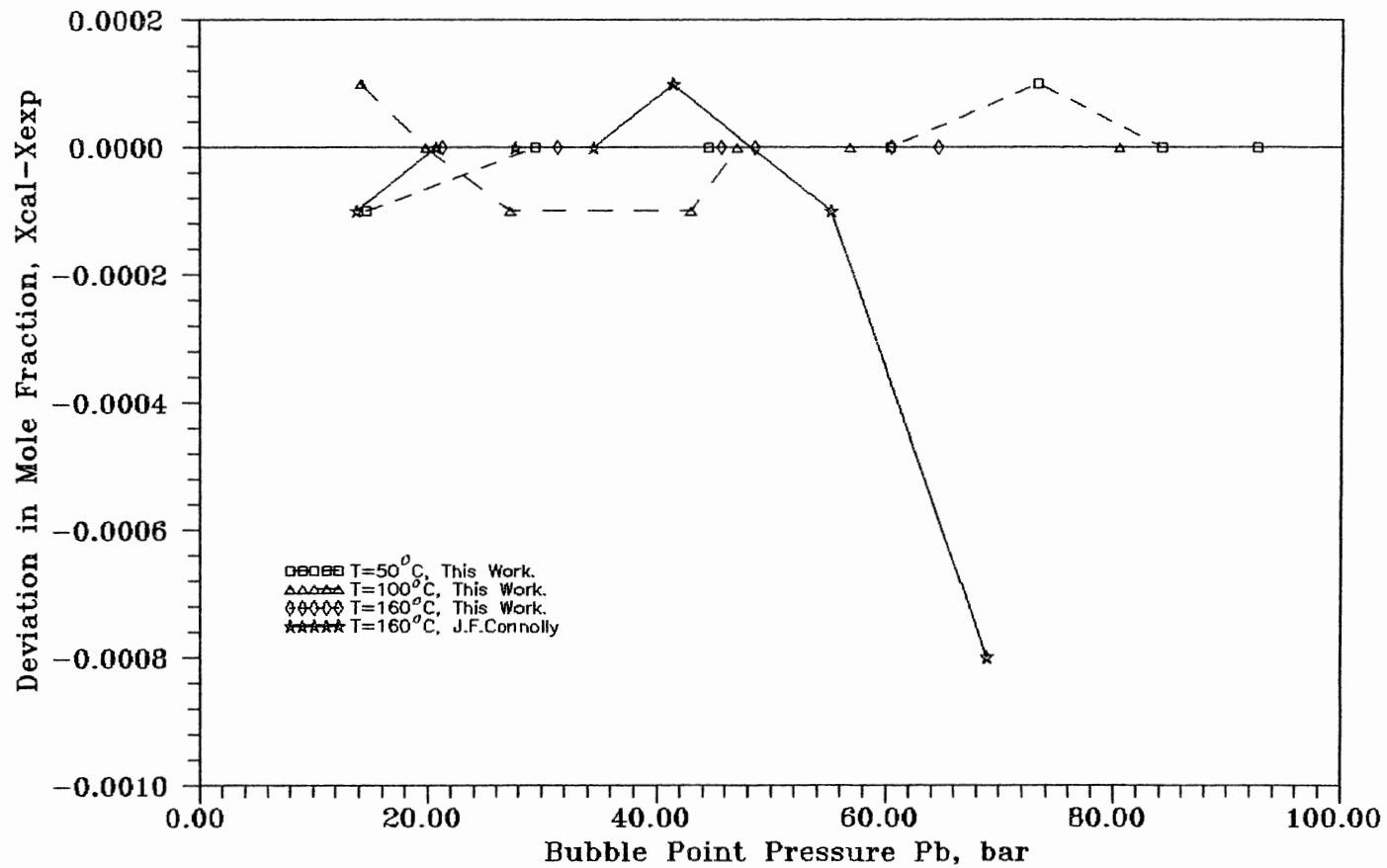


Figure 11. Comparison of Solubilities of Carbon Monoxide in Benzene

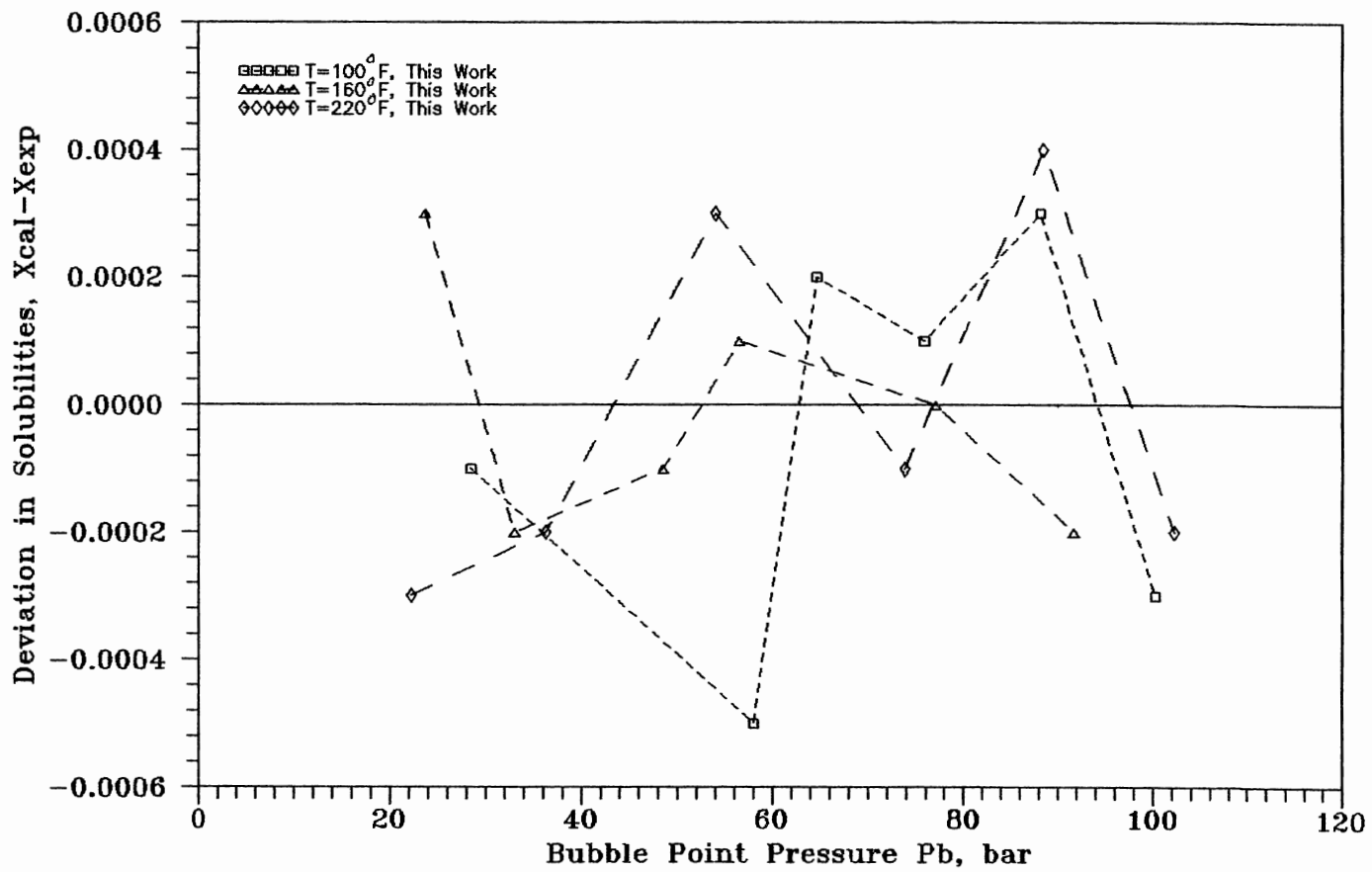


Figure 12. Comparison of Solubilities for Carbon Monoxide in n-Decane

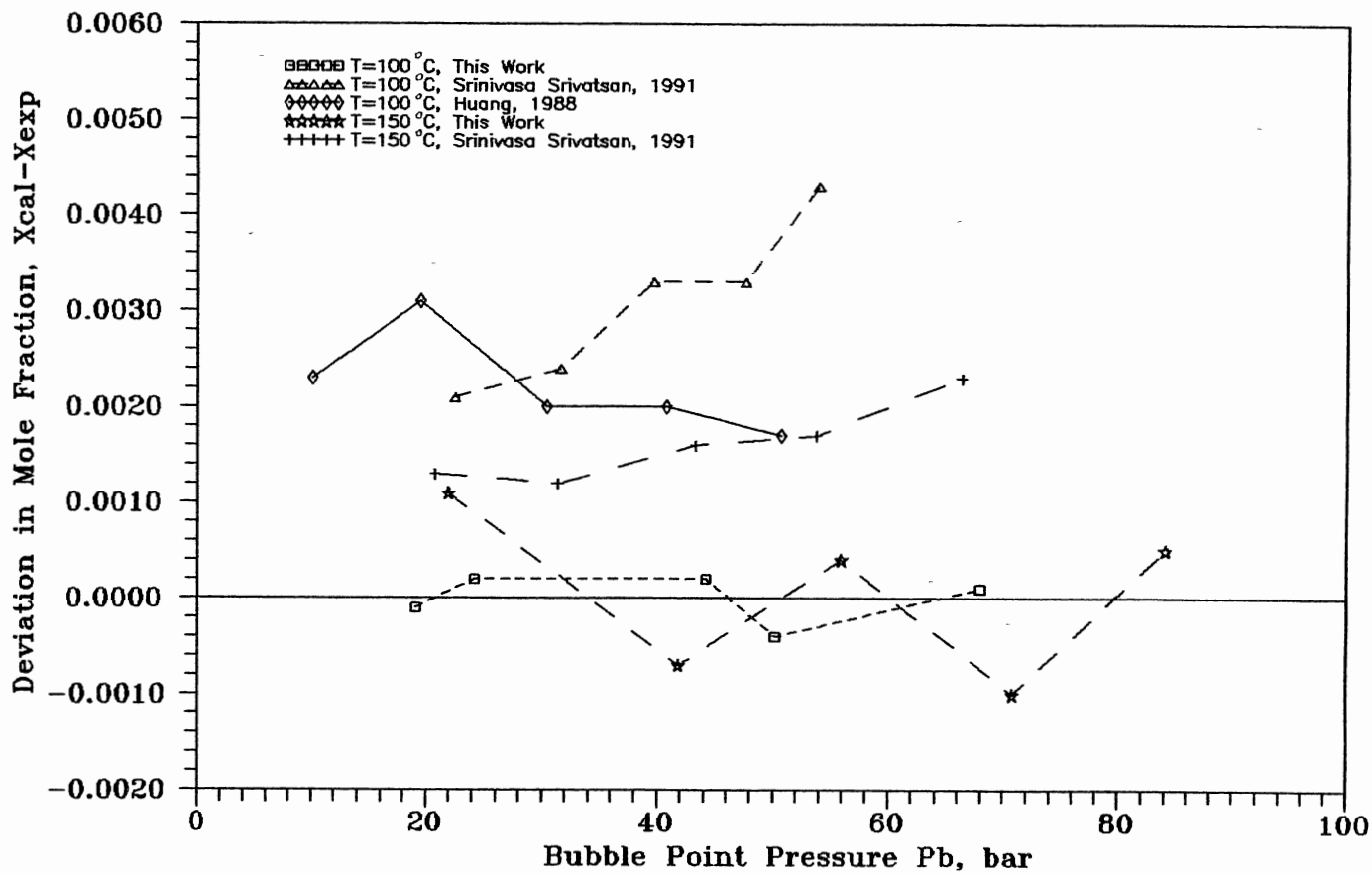


Figure 13. Comparison of Solubilities of Carbon Monoxide in n-Octacosane

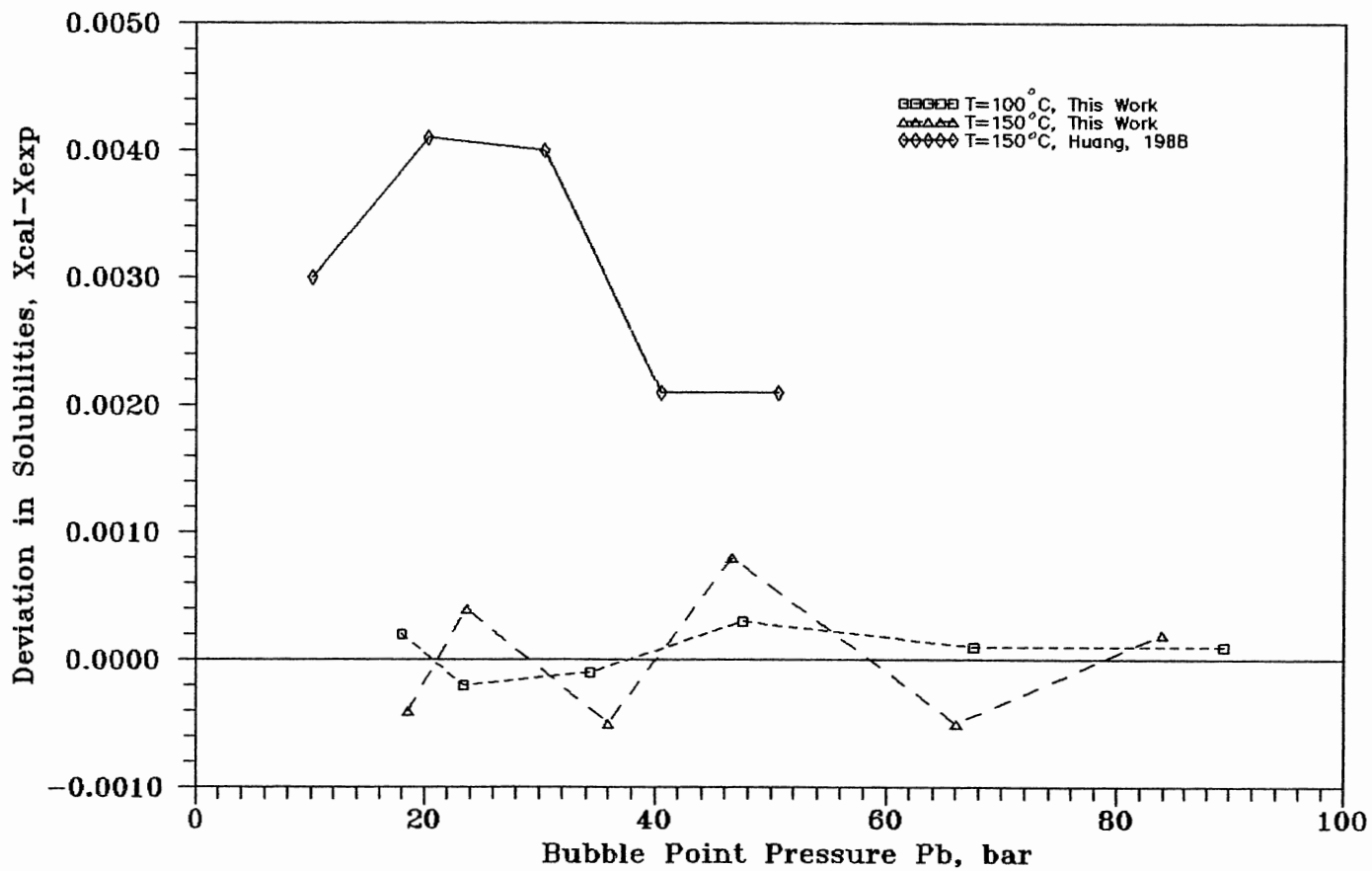


Figure 14. Comparison of Solubilities for Carbon Monoxide in n-Hexatriacontane

parameters k_{ij} and l_{ij} (the correlation coefficients are close to -1 for all isotherms/ systems studied). Although this does not mean that two interaction parameters are not necessary to describe the phase behavior of the systems, it is obvious that for paraffins with carbon numbers less than 10, the improvement in prediction is marginal after the introduction of the second interaction parameter l_{ij} as clearly indicated by Figure 15. Here the optimized interaction parameter k_{ij} corresponds to a specified interaction parameter l_{ij} , and the predicted bubble point pressure in the form of a "reduced" RMSE (the ratio of RMSE in bubble point pressure prediction to that of Case 1) are presented as a function of specified l_{ij} .

For n-C₆, the reduced RMSE is not greatly affected by changes in l_{ij} if k_{ij} is optimized for a given value of l_{ij} . For n-C₃₆, however, the prediction results become increasingly sensitive to the second interaction parameter l_{ij} as the carbon number of solvent increases as is also shown in Figure 15. In Figure 16, the effects of k_{ij} and l_{ij} on solubility prediction show the same pattern as in bubble-point pressure predictions presented in Figure 15.

Parameter Generalization

To facilitate the interpolation and extrapolation to conditions or systems for which no experimental data exist, parameter generalizations were considered on the basis of the experimental data obtained in this work. Temperature is

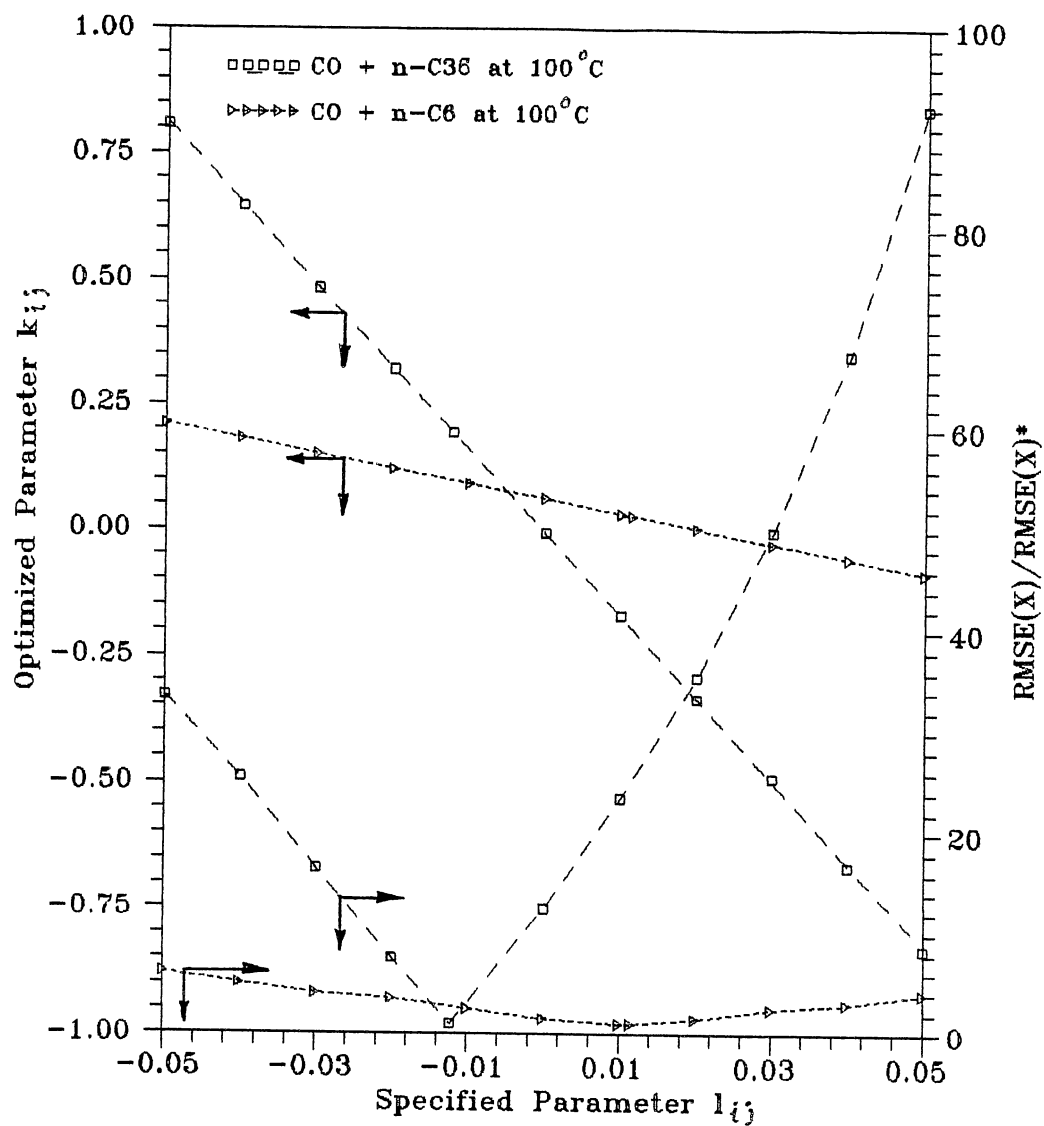


Figure 16. Effects of k_{ij} and l_{ij} on SRK solubility Prediction

chosen as one of the correlation variables since the temperature dependence is significant, as shown in Table XIII. Another correlation variable chosen is the carbon number of solvent. The acentric factor of the solvent, which is frequently used as a correlation variable in parameter generalization by some investigators (10) (12), is deliberately avoided since the experimental information on critical properties of heavy normal paraffins (and thus acentric factor) is lacking.

The interaction parameters are (simply) expressed as a linear function of both temperature and carbon number of solvent as following:

$$k_{ij} = A_1 + A_2 CN + (A_3 + A_4 CN) T \quad (51)$$

$$l_{ij} = B_1 + B_2 CN + (B_3 + B_4 CN) T \quad (52)$$

It should be mentioned that it is the residual in bubble point pressure between prediction and experimentation (not the obtained interaction parameters) that was used as the criterion for the optimization. Several cases were studied; the detailed descriptions of the cases are listed in Table XV. The summary of the prediction results by different generalization approaches and the optimized parameter constant are presented in Table XVI. In Table XVIII, the calculation results of Case 1 in the previous section are compared with the results corresponding to Case 10 in this section.

TABLE XV
 SPECIFIC CASES FOR GENERALIZATION OF
 INTERACTION PARAMETERS OF SRK EQUATION

Case Number	Description
1	$k_{ij}=0$ $l_{ij}=0$
2	$k_{ij}=\text{Constant}$ $l_{ij}=0$ <p>Constant k_{ij} is used for application to all binary systems.</p>
3	$k_{ij}=\text{Constant}$ $l_{ij}=\text{Constant}$ <p>Constant k_{ij} and l_{ij} are used for application to all binary systems.</p>
4	$k_{ij}=k_{ij}(\text{CN})$ $l_{ij}=0$ <p>k_{ij} is correlated as a function of carbon number.</p>
5	$k_{ij}=k_{ij}(\text{CN})$ $l_{ij}=\text{constant}$ <p>k_{ij} is correlated as a function of carbon number and constant l_{ij} is used for all systems.</p>
6	$k_{ij}=k_{ij}(\text{CN}, T)$ $l_{ij}=0$ <p>k_{ij} is correlated as a function of both carbon number and temperature.</p>
7	$k_{ij}=k_{ij}(\text{CN}, T)$ $l_{ij}=\text{constant}$ <p>k_{ij} is correlated as a function of both carbon number and temperature and constant l_{ij} is used for all systems.</p>
8	$k_{ij}=k_{ij}(\text{CN})$ $l_{ij}=l_{ij}(\text{CN})$ <p>Both k_{ij} and l_{ij} are correlated as functions of carbon number.</p>
9	$k_{ij}=\text{Constant}$ $l_{ij}=l_{ij}(\text{CN}, T)$ <p>Constant k_{ij} is used for all systems and l_{ij} is correlated as a function of temperature and carbon number.</p>
10	$k_{ij}=k_{ij}(\text{CN}, T)$ $l_{ij}=l_{ij}(\text{CN}, T)$ <p>Both k_{ij} and l_{ij} are correlated as functions of carbon number and temperatures.</p>

TABLE XVI
SUMMARY OF RESULTS OF PARAMETER GENERALIZATION

Case	1	2	3	4	5	6	7	8	9	10
-----PRESSURE-----										
RMSE bar	8.96	5.62	5.04	4.92	4.68	3.62	3.40	2.30	1.49	1.23
BIAS bar	-5.79	0.24	-0.27	-0.20	0.31	-0.09	0.31	-0.01	0.19	-0.04
AAD	7.02	4.19	3.62	3.51	3.50	2.84	2.68	1.60	1.16	0.93
AAD%	13.08	8.44	7.15	7.04	7.46	5.60	5.73	3.22	2.46	1.86
NRMSE ^a	7.28	4.57	4.10	4.00	3.80	2.94	2.76	1.87	1.21	1.00
-----CONSTANTS-----										
A ₁	0	0.0832	0.1312	0.1343	0.1301	-0.4136	-0.3710	-0.0664	-0.0207	-0.1604
A ₂	0	0	0	-0.0032	-0.0160	0.0474	0.0338	0.0112	0	0.0393
A ₃	0	0	0	0	0	0.0015	0.0013	0	0	3.09E-4
A ₄	0	0	0	0	0	-1.3E-4	-1.2E-4	0	0	-7.90E-5
B ₁	0	0	-0.0061	0	0.0269	0	2.2E-2	0.0300	0.0217	-0.0202
B ₂	0	0	0	0	0	0	0	0.0015	9.42E-4	-5.48E-5
B ₃	0	0	0	0	0	0	0	0	4.27E-5	1.22E-4
B ₄	0	0	0	0	0	0	0	0	-5.32E-6	-3.20E-6

NRMSE^a=RMSE/RMSE for Case 10

TABLE XVII
COMPARISON OF INTERACTION PARAMETERS AND
CORRESPONDING DEVIATIONS

T(K)	k_{1j}	k_{1j}^g	l_{ij}	l_{ij}^g	$ \Delta P %$	$ \Delta P ^g%$	NP
CO + n-C ₆							
323.2	0.0608	0.0218	0.0006	0.0128	0.3	0.7	6
373.2	0.0297	0.0135	0.0115	0.0179	0.4	0.9	6
423.2	0.0146	0.0052	0.0329	0.0231	0.3	2.5	6
CO +n-C ₁₀							
310.9	0.1356	0.0826	-0.0031	0.0073	0.3	0.7	6
344.3	0.1115	0.0665	-0.0004	0.0103	0.3	1.9	6
377.6	0.0800	0.0505	0.0043	0.0133	0.3	2.5	6
CO +n-C ₂₀							
323.2	0.2772	0.2193	-0.0113	-0.0025	0.2	1.4	6
373.2	0.2257	0.1503	-0.0105	0.0004	0.1	0.7	6
423.2	0.2292	0.0867	-0.0140	0.0034	0.1	1.9	8
CO + n-C ₂₈							
373.2	0.1498	0.2285	-0.0071	-0.0096	0.1	5.5	5
423.2	0.1413	0.1333	-0.0100	-0.0079	0.3	2.1	5
CO +n-C ₃₆							
373.2	0.1937	0.3067	-0.0122	-0.0196	0.2	2.4	6
423.2	0.1218	0.1798	-0.0151	-0.0192	0.4	1.6	6
					0.2	1.8	88

g: The properties corresponding to the generalized parameters.

Krichevsky-Kasarnovsky Equation

Representation

The Krichevsky-Kasarnovsky (K-K) equation was also used to analyze the solubility data of carbon monoxide + n-eicosane, n-octacosane and n-hexatriacontane to get the Henry's constants of carbon monoxide in these solvents. The procedure for deriving the K-K equation is described below.

From the pressure dependence of component fugacity in a mixture

$$\left(\frac{\partial \ln f}{\partial p}\right)_{T,x} = \frac{\bar{V}_1}{RT} \quad (53)$$

we can get:

$$\left(\frac{\partial \ln (f_i/x_i)}{\partial p}\right)_{T,x} = \frac{\bar{V}_i}{RT} \quad (54)$$

Combining the definition of Henry's constant

$$H_{i,s} = \lim_{x_i \rightarrow 0} f_i/x_i \quad (55)$$

and Equation 54 gives the pressure dependence of Henry's constant:

$$\left(\frac{\partial \ln H_{i,s}}{\partial p}\right)_T = \frac{\bar{V}_i^\infty}{RT} \quad (56)$$

Integrating the above equation with the assumption that the infinite dilute partial molar volume of the solute does not change with pressure gives:

$$\ln H_{i,s}(T, P) = \ln H_{i,s}(T, P^r) + \frac{\bar{V}_i^\infty (P - P^r)}{RT} \quad (57)$$

Where P^r is a arbitrary reference pressure and $H_{i,s}(T, P^r)$ is the Henry's constant at system temperature and reference

pressure.

Assuming that the solute obeys Henry's law:

$$\hat{f}_i = H_{i,s}(T, P) x_i \quad (58)$$

Choosing the saturation pressure of the solvent as the reference pressure and substituting Equation 58 into Equation 57 gives:

$$\ln \frac{\hat{f}_i}{x_i} = \ln H_{i,s}(T, P^s) + \frac{\bar{v}_i^\infty (P - P^s)}{RT} \quad (59)$$

This equation is called the K-K equation.

To apply the K-K equation, the fugacity of the solute in the vapor mixture is needed. For carbon monoxide + n-eicosane, n-octacosane and n-hexatriacontane, no significant errors will result if the fugacity of pure solute at system temperature and pressure is substituted with the assumption that the vapor phase is composed of pure solute. For carbon monoxide + n-hexane, benzene, n-decane, however, errors introduced by such a simplification are not negligible. Therefore Krichevsky-Kasarnovsky analysis has been applied only for carbon monoxide + n-eicosane, n-octacosane and n-hexatriacontane.

Goodwin (45) has given a precise but complicate empirical equation to correlate the properties of carbon monoxide. Figure 17 shows that the difference in fugacity of carbon monoxide given by Goodwin's correlation and the PR equation is negligible. Therefore, the PR equation was used to calculate the fugacity of pure carbon monoxide.

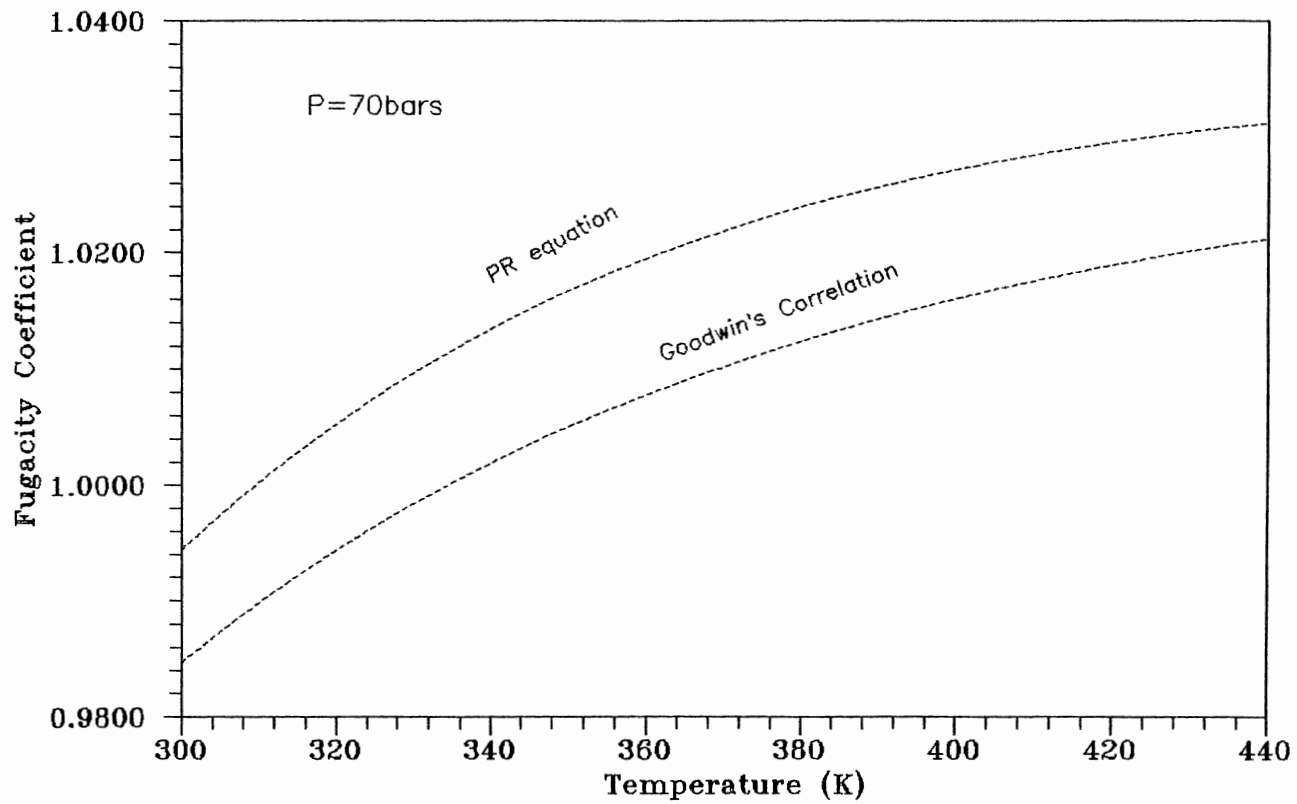


Figure 17. Comparison of Fugacity of Carbon Monoxide Predicted by the PR Equation and Goodwin's Correlation

The parameters regressed from the experimental data and the RMSE in solubilities from this correlation are presented in Table XVIII. The RMSE in solubility predictions is quite close to the experimental uncertainties and comparable to the prediction results from the equation of state representations (when two temperature dependent parameters are used), as Table XVIII shows.

TABLE XVIII
PARAMETERS IN KRICHEVSKY-KASARNOVSKY CORRELATION

solvent	T (K)	$H_{i,s}(T, P^s)$ (psia)	V_i cm^3/gmol	RMSE mole frac.
n-C ₂₀	348.2	7233 (72)*	76 (5)	0.0006
	373.2	6843 (60)	76 (6)	0.0004
	423.2	6252 (32)	94 (3)	0.0003
n-C ₂₈	373.2	5934 (120)	64 (14)	0.0010
	423.2	5503 (110)	81 (11)	0.0008
n-C ₃₆	373.2	4999 (18)	102 (2)	0.0004
	423.2	4513 (29)	121 (4)	0.0006

*: standard errors in the tabulated values are given in parentheses.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The solubilities of carbon monoxide in n-hexane, n-decane, benzene, n-octacosane, n-hexatriacontane have been measured at temperature from 50°C to 160°C and pressures up to 1500 psia. No experimental data have been found for the solubilities of carbon monoxide in n-hexane and n-decane in the literatures searched in this work.

2. The solubilities of carbon monoxide in benzene agree with those of Connolly within 0.0008 mole fraction.

3. The solubilities of carbon monoxide in n-octacosane, n-hexatriacontane from this work are in agreement with literature data within 0.004 mole fraction.

4. Good representations are achieved for all the binary systems investigated using the SRK or PR equation along with the classic quadratic mixing rule if two temperature-dependent binary interaction parameters are used; the differences between representations and experiment are with experimental uncertainties.

5. Good representations are achieved for all the binary systems investigated except carbon monoxide + n-hexatriacontane using the SRK or PR equation along with

the classic quadratic mixing rule if only one temperature dependent binary interaction parameters is used; the differences between representations and experiment are within experimental uncertainties.

6. The Henry's constants of carbon monoxide in n-eicosane, n-octacosane, n-hexatriacosane have been obtained by using the Krichevsky-Kasarnovsky equation.

Recommendations

1. The solvent injection pump should be replaced by one with larger capacity to facilitate studies of lower solubility systems such as carbon monoxide + naphthalene.

2. Further studies are recommended on carbon monoxide + cyclic hydrocarbons (naphthionic and aromatic) that are found in coal to better define the behavior of these systems.

BIBLIOGRAPHY

1. Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria," 2nd edition, Prentice Hall, Englewood Cliffs, NJ(1986).
2. Shibata, S. K.; Sandler, S. I., Ind. Eng. Chem. Res., 28:1893-1898(1989).
3. Knapp, H., Fluid Phase Equilibrium, 29:1-23(1986).
4. Solubility Data Series, Volume 43, Pergamon Press, Oxford(1989).
5. Wichterle, I.; Linek, J.; Hala, E., Vapor Liquid Equilibrium Data Bibliography, Elsevier, New York (1973, 1976, 1979, 1982, 1985).
6. Prausnitz, J. M., ACS Symposium Series, 60:231-282(1977).
7. Chao, K. C.; Greenkorn, R. A., "Thermodynamics of Fluids - An Introduction to Equilibrium Theory," Marcel Dekker Inc., New York (1975).
8. Van der Waals, J. D., Die Continuitaet des Gasfoermigen und Fluessigen Zustands. Leipzig, Barth (1899,1900).
9. Mayer, J. M.; Mayer, M. G., " Statistical Mechanics," Chapter 13, Wiley, New York (1940).
10. Kato, K.; Nagahuma, K.; Hirata, M., Fluid Phase Equilibria, 7:219-231(1981).
11. Valderrama, J. O.; Obaid-ur-Rehman, S.; Cisternas, L. A., Fluid Phase Equilibria, 40:217-233(1988)
12. Gasem, K. A. M., Ph. D. Dissertation, Oklahoma State University, Stillwater, Oklahoma (1986).
13. Panagiotopoulos, A. Z.; Reid, R. L., ACS Symposium Series, 300:571-582(1985).
14. Panagiotopoulos, A. Z.; Kumar, S., Fluid Phase Equilibria, 22:77-88(1985).

15. Panagiotopoulos, A. Z.; Reid, R. L., ACS Symposium Series, 329:115-129(1987).
16. Stryjek, R., Can. J. Chem. Eng., 64:334-340(1986).
17. Adachi, Y., Fluid Phase Equilibria, 3:255-271(1979).
18. Vidal, J., Chem. Eng. Sci., 33:787-791(1978).
19. Van Laar, J. J., Z. Physik Chem., 72:723(1910).
20. Huron, M. J.; Vidal, J., Fluid Phase Equilibria, 3:255-271(1979).
21. Mollerup, J., Fluid Phase Equilibria, 25:323-327(1986).
22. Michelsen, M. L., Fluid Phase Equilibria, 60:213-219(1990).
23. Larsen, B. L.; Rasmussen, P.; Fredenslund, A., Ind. Eng. Chem. Res., 26:2274-2281(1987).
24. Dahl, S.; Michelsen, M. L., AIChE Journal, 36:1829-1836(1990)
25. Dahl, S.; Fredenslund, A.; Rasmussen, P., Ind. Eng. Chem. Res., 30:1936-1945(1991).
26. Mollerup, J., Fluid Phase Equilibria, 25:323-327(1986).
27. Whiting, W. B.; Prausnitz, J. M., Fluid Phase Equilibria, 9:119-147(1982).
28. Panagiotopoulos, A. Z., Reid, R. L., Fluid Phase Equilibria, 29:525-534(1986).
29. Luedecke, D.; Prausnitz, J. M., Fluid Phase Equilibria, 22:1-19(1985).
30. Lee, K. H.; Sandler, S. I., Fluid Phase Equilibria, 34:113-147(1987).
31. Danner, R. P., Fluid Phase Equilibria, 29:415-430(1986).
32. Adachi, Y.; Sugie, H., Fluid Phase Equilibria, 24:353-362(1985).
33. De Leeuw, V. V.; et al., Paper Prepared for Presentation at the AIChE Annual Meeting 1990, Session on Advances in Phase Equilibria and Fluid Mixtures.
34. Bufkin, B., M. S. Thesis, Oklahoma State University, Stillwater, Oklahoma (1983).

35. Barrick, M. W., M. S. Thesis, Oklahoma State University, Stillwater, Oklahoma (1985).
36. Reamer, H. H.; Olds, R. H.; Sage, B. H.; Lacey, W. N., Ind, Eng. Chem., 34:1526-1531(1942).
37. Darwish, N. A., Ph. D. Dissertation, Oklahoma State University, Stillwater, Oklahoma (1991).
38. Clifford, A. A., "Multivariate Error Analysis," John Wiley & Sons, New York(1973).
39. Makranczy, J.; Megyery Balog, K.; Rusz, L.,; Patyi, L., Hung. J. Ind. Chem., 4:269-280(1976).
40. Connolly, J. F., Amer. Petr. Inst. Report, 45:62-67(1965).
41. Huang, S. H.; Lin, H. M., Tsai, F. N.; Chao, K. C., Ind. Eng. Chem. Res., 27:162-169(1988).
42. ESDU Engineering Series Data, Physical Data, Chemical Engineering Sub-Series, Volume 3(1987,1989,1990).
43. Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K., "The Properties of Gases and Liquids," 2nd edition, McGraw Hill, New york(1977).
44. Srivatsan, S., M. S. Thesis, Oklahoma State University, Stillwater, Oklahoma(1991).
45. Goodwin, R. D., J. Phys. Chem. Ref. Data, 14:849-(1985).

APPENDIX

SRK AND PR EQUATION OF STATE REPRESENTATION
OF CARBON MONOXIDE + HYDROCARBONS

TABLE A.1

SRK AND PR EQUATION OF STATE REPRESENTATIONS
OF SOLUBILITY OF CARBON MONOXIDE IN n-HEXANE

Temperature K (°F)	Soave Parameters (PR Parameters)		Error in Mole Fraction*	
	k_{ij}	L_{ij}	RMS	MAX
323.2 (122.0)	0.0608 (0.0716)	0.0006 (-0.0001)	0.0002	0.0003
	0.0624 (0.0857)		0.0002	0.0004
373.2 (212.0)	0.0297 (0.0518)	0.0115 (0.0044)	0.0002	0.0004
	0.0633 (0.0633)		0.0003	0.0006
373.2 (302.0)	0.0146 (0.0495)	0.0329 (0.0151)	0.0005	0.0008
	0.1072 (0.0870)		0.0003	0.0006
323.2	0.0850	-0.0065	0.0019	0.0046
373.2	(0.0860)	(-0.0059)		
423.2	0.0657 (0.0705)		0.0019	0.0049

* The RMS and maximum errors in CO mole fraction are essentially the same for the SRK and PR equations of state.

TABLE A.2

 SRK AND PR EQUATION OF STATE REPRESENTATIONS
 OF SOLUBILITY OF CARBON MONOXIDE IN BENZENE

Temperature K (°F)	Soave Parameters (PR Parameters)		Error in Mole Fraction*	
	k_{1j}	l_{ij}	RMS	MAX
323.2 (122.0)	-0.0122 (0.0046)	0.0326 (0.0375)	0.0000	0.0001
	0.0953 (0.1157)		0.0002	0.0003

373.2 (212.0)	-0.0321 (0.0060)	0.0306 (0.0280)	0.0001	0.0001
	0.0700 (0.0886)		0.0002	0.0003

423.2 (320.0)	-0.0316 (0.0125)	0.0332 (0.0251)	0.0000	0.0000
	0.0803 (0.0886)		0.0001	0.0002

323.2	0.1465	-0.0230	0.0008	0.0024
373.2	(-0.0998)	(-0.0699)		
423.2				
	0.0884 (0.1070)		0.0008	0.0023

* The RMS and maximum errors in CO mole fraction are essentially the same for the SRK and PR equations of state.

TABLE A.3

SRK AND PR EQUATION OF STATE REPRESENTATIONS
OF SOLUBILITY OF CARBON MONOXIDE IN n-DECANE

Temperature K (°F)	Soave Parameters (PR Parameters)		Error in Mole Fraction*	
	k_{ij}	l_{ij}	RMS	MAX
310.9 (100.0)	0.1356	-0.0031	0.0003	0.0005
	(0.1378)	(-0.0023)		
	0.1204		0.0003	0.0007
	(0.1280)			

344.3 (160.0)	0.1115	-0.0004	0.0002	0.0003
	(0.1220)	(-0.0019)		
	0.1094		0.0002	0.0003
	0.1137			

377.6 (220.0)	0.0800	0.0043	0.0002	0.0004
	(0.1025)	(0.0004)		
	0.1006		0.0003	0.0005
	(0.1008)			

310.9	0.1104	0.0007	0.0014	0.0032
344.3	(0.0676)	(0.0118)		
377.6	0.1136		0.0014	0.0032
	(0.1184)			

* The RMS and maximum errors in CO mole fraction are essentially the same for the SRK and PR equations of state.

TABLE A.4

SRK AND PR EQUATION OF STATE REPRESENTATIONS OF SOLUBILITY
OF CARBON MONOXIDE IN n-OCTACOSANE

Temperature K (°F)	Soave Parameters (PR Parameters)		Error in Mole Fraction*	
	k_{1j}	l_{1j}	RMS	MAX
373.2(212.0)	0.1498 (0.1701)	-0.0071 (-0.0084)	0.0002	0.0004
	0.0438 (0.0699)		0.0008	0.0018
423.2(302.0)	0.1413 (0.1711)	0.0100 (-0.0130)	0.0008	0.0011
	0.0031 (0.0239)		0.0012	0.0019
373.2	0.0427	-0.0013	0.0028	0.0050
423.2	(-0.0142)	(0.0051)		
	0.0246 (0.0448)		0.0030	0.0051

* The RMS and maximum errors in CO mole fraction are essentially the same for the SRK and PR equations of state.

TABLE A.5

SRK AND PR EQUATION OF STATE REPRESENTATIONS OF SOLUBILITY
OF CARBON MONOXIDE IN n-HEXATRIACONTANE

Temperature K (°F)	Soave Parameters (PR Parameters)		Error in Mole Fraction*	
	k_{ij}	l_{ij}	RMS	MAX
323.2 (212.0)	0.1937	-0.0122	0.0001	0.0003
	(0.2162)	(-0.0134)		
	-0.0045		0.0025	0.0029
	(0.0333)			

373.2 (302.0)	0.1218	-0.0151	0.0005	0.0008
	(0.1593)	(-0.0175)		
	-0.1299		0.0026	0.0035
	(-0.0788)			

323.2	0.3063	-0.0219	0.0069	0.0120
373.2	(0.2149)	(-0.0175)		
	-0.0542		0.0084	0.0150
	(-0.0128)			

* The RMS and maximum errors in CO mole fraction are essentially the same for the SRK and PR equations of state.

TABLE A.6
 SRK AND PR EQUATION OF STATE REPRESENTATIONS
 OF SOLUBILITY OF METHANE IN n-DECANE

Temperature K (°F)	Soave Parameters (PR Parameters)		Error in Mole Fraction*	
	K_{ij}	l_{ij}	RMS	!MAX!
344.3 (160.0)	0.0590	-0.0123	0.0005	0.0007
	(0.0575)	(-0.0115)		
	0.0285		0.0015	0.0025
	(0.0308)			

377.6 (220.0)	0.0529	-0.0103	0.0005	0.0007
	(0.0516)	(-0.0107)		
	0.0273		0.0011	0.0018
	(0.0268)			

344.3	0.0564	-0.0114	0.0005	0.0011
377.6	(0.0548)	(-0.0111)		
	0.0280		0.0016	0.0023
	(0.0291)			

* The RMS and maximum errors in CH₄ mole fraction are essentially the same for both the SRK and PR equations of state.

VITA

XIAOHUA YI

Candidate for the Degree of
Master of Science

Thesis: BINARY VAPOR-LIQUID PHASE EQUILIBRIUM FOR CARBON
MONOXIDE + HYDROCARBONS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Shimen, Hunan, China, February
14, 1964, the son of Ziwen Yi and Tintin Chen.
Married to Yanfang Liu on July 20, 1990.

Education: Graduated from the First High School, Shimen,
Hunan, China, in August 1980; received Bachelor of
Engineering Degree in Chemical Engineering from
Tinjing University, Tinjing, China, in August 1984.
Completed requirements for the Master of Science in
May, 1992.

Professional Experience: Research Assistant, School of
Chemical Engineering, Oklahoma State University,
January, 1991 to May 1992.