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MEASUREMENT AND PREDICTION OF VAPOR-LIQUID EQUILIBRIA IN SYSTEMS CONTAINING NITROGEN, CARBON DIOXIDE, AND ETHANE

by

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Golden, Colorado

Date 15 September 1982

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ABSTRACT

Vapor-liquid equilibria data were measured for the binary system carbon dioxide-ethane at eight temperatures from 207 to 270 K, the binary system nitrogen-carbon dioxide at 220 and 270 K, and the binary system nitrogen-ethane at 220, 260, and 270 K. The ternary system nitrogen-carbon dioxide-ethane was studied at 220 K and 0.803, 4.000, and 9.000 MPa and at 270 K and 3.450, 6.000, 8.400, 9.000, and 9.600 MPa.

The data were modeled with the Peng-Robinson, Soave-Redlich-Kwong, and Fuller equations of state. The binary data were used to fit a single interaction parameter for each equation of state, and these binary interaction parameters were used in each equation of state to predict the ternary vapor-liquid equilibria. The equations fit the data well at low pressures, but fail near the critical region of the binary and ternary systems.

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ACKNOWLEDGEMENTS

I wish to thank the Gas Research Institute, Basic Research Division (grant number 5082-260-0743) for the financial support of this project. I would also like to thank my advisors Dr. Kidnay and Dr. Sloan for their advice and guidance.

INTRODUCTION

The phase equilibria of carbon dioxide with the other components of natural gas is becoming increasingly important for two reasons. First, the increasing use of natural gas will require future processing of high carbon dioxide gases that were deemed unfit for production in the past. Second, the injection of carbon dioxide to stimulate oil well production generates gases with high concentrations of carbon dioxide.

Economical production of natural gases with appreciable amounts of carbon dioxide requires reliable models for the prediction of the phase equilibria of carbon dioxide with other components of natural gas. All of the models currently in use require binary vapor-liquid equilibria data to fit at least one adjustable parameter. It is the goal of this work to establish a base of accurate data which will be used to determine binary interaction parameters, to evaluate current equations of state and mixing rules, and, eventually, to propose better models.

EXPERIMENTAL APPARATUS

The majority of the data was measured on the same appratus as that used by Al-Sahhaf et al. (1983). A schematic diagram is shown in Figure 1. The system was of the vapor recirculation type. The stainless steel equilibrium cell was suspended in a 22 L glass dewar containing a 50 volume percent mixture of chloroform and carbon tetrachloride. The bath could be cooled by a two-stage refrigerator or by liquid nitrogen. The bath was mixed with a two-propeller, variable-speed stirrer.

The temperature was measured to an accuracy of ±0.02 K with a calibrated (IPTS-68) platinum resistance thermometer connected to a Mueller bridge and a Keithley null detector. The temperature of the bath was controlled by a Bailey proportional controller with a 1700-watt heater. The pressure was measured with a series of Heise gauges with pressure ranges of 0-100 psia, 0-500 psia, and 0-2500 psia. Each gauge had an accuracy of ±0.1% of the full-scale reading, and the gauges were calibrated with an air dead-weight tester to the maximum pressure of the dead-weight tester, 600 psia, or the maximum range of the gauge. The calibrations are given in Appendix A.

A diaphragm pump was used to circulate the vapor, and vapor samples were taken by isolating a portion of the

EXPERIMENTAL APPARATUS

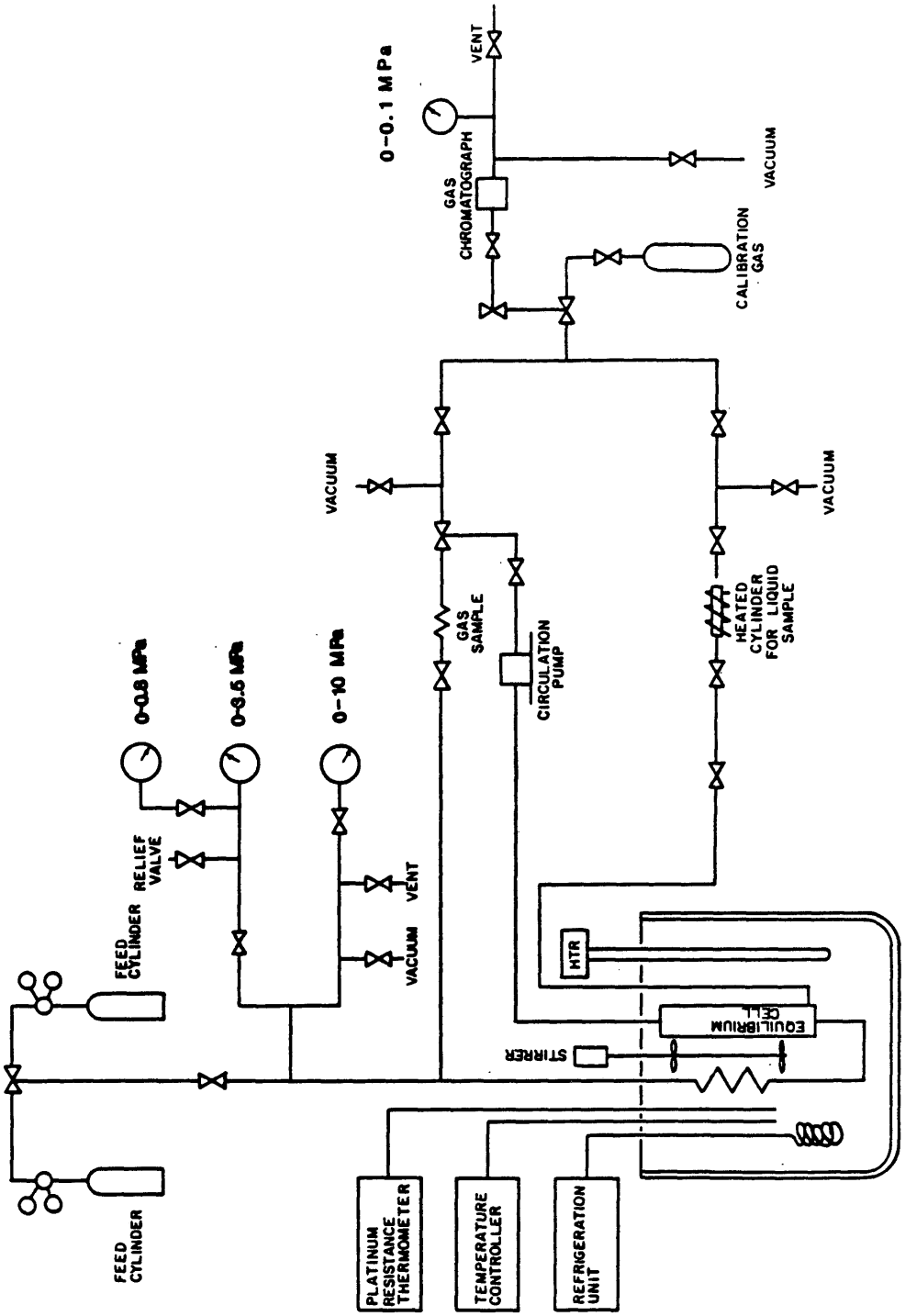

Figure 1

recirculation line. Liquid samples were taken directly from the cell with a capillary line. Both samples were analyzed in a Beckman model 72-5 gas chromatograph equipped with a thermal conductivity detector. Samples were introduced to the chromatograph with a 1 cc gas sample valve. Separation was accomplished with a 24 ft. 1/8 in. stainless steel column packed with chromosorb 106. Peak areas were obtained with a Hewlett-Packard electronic integrator, and were related to compositions through the use of calibration curves. The calibration curves were determined with the pure components and six sample mixtures that were prepared gravimetrically in this laboratory. The calibration data is presented in Table 1 and Figure 2. The three calibration curves were each fit to a linear equation with a zero intercept using least squares. The estimated error in calculated mole fractions using these calibration curves is ±0.002.

After most of the data had been taken, major modifications were made to the apparatus. The most important change was the replacement of the stainless steel equilibrium cell with a brass cell containing a sapphire window. A diagram of the cell is given in Figure 3. Two Teflon o-rings are used to seal the window. The smaller o-ring prevents leakage between the window and the tightening

Table 1

Gas Chromatograph Calibration Data

Sample	Component	Average Area	Partial Pressure
CO_2	CO_2	207367	616.8
C_2H_6	C_2H_6	219150	616.8
N_2	N_2	178900	616.8
1	N_2	37183	129.25
	CO_2	9347	28.00
	C_2H_6	162700	459.55
2	N_2	104633	360.98
	CO_2	85993	255.72
	C_2H_6	0	0.00
3	N_2	30623	105.54
	CO_2	106900	319.17
	C_2H_6	69347	191.99
4	N_2	88007	301.66
	CO_2	50833	150.41
	C_2H_6	58803	164.62
5	N_2	142533	485.78
	CO_2	0	0.00
	C_2H_6	47093	130.92
6	N_2	0	0.00
	CO_2	28580	81.32
	C_2H_6	192550	535.38

Component	Slope
N_2	0.0034350
CO_2	0.0029748
C_2H_6	0.0028040

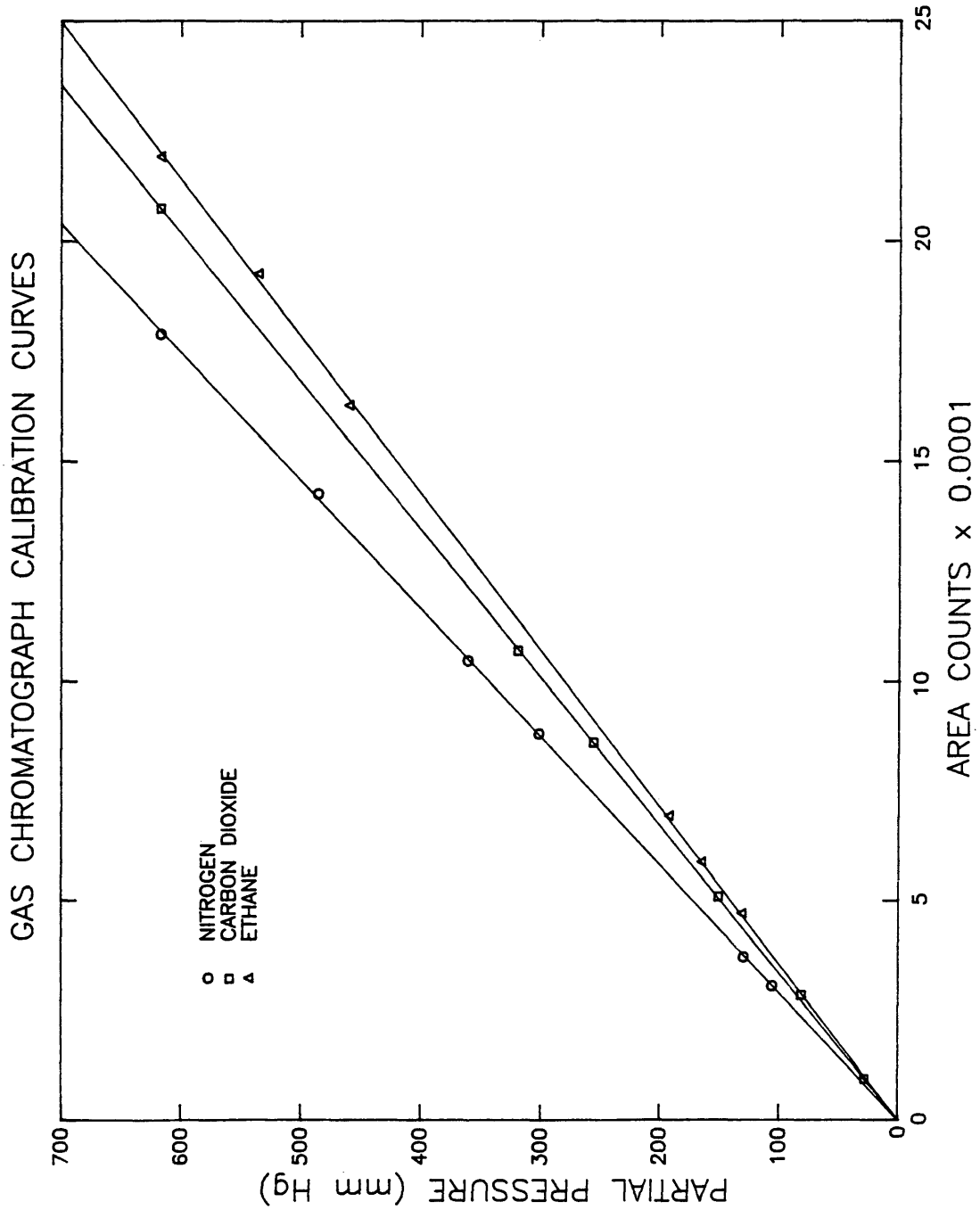
GAS CHROMATOGRAPH CALIBRATION CURVES
NITROGEN
CARBON DIOXIDE
ETHANE
PARTIAL PRESSURE (mm Hg)
AREA COUNTS x 0.0001
0
100
200
300
400
500
600
700
0
5
10
15
20
25

Figure 2

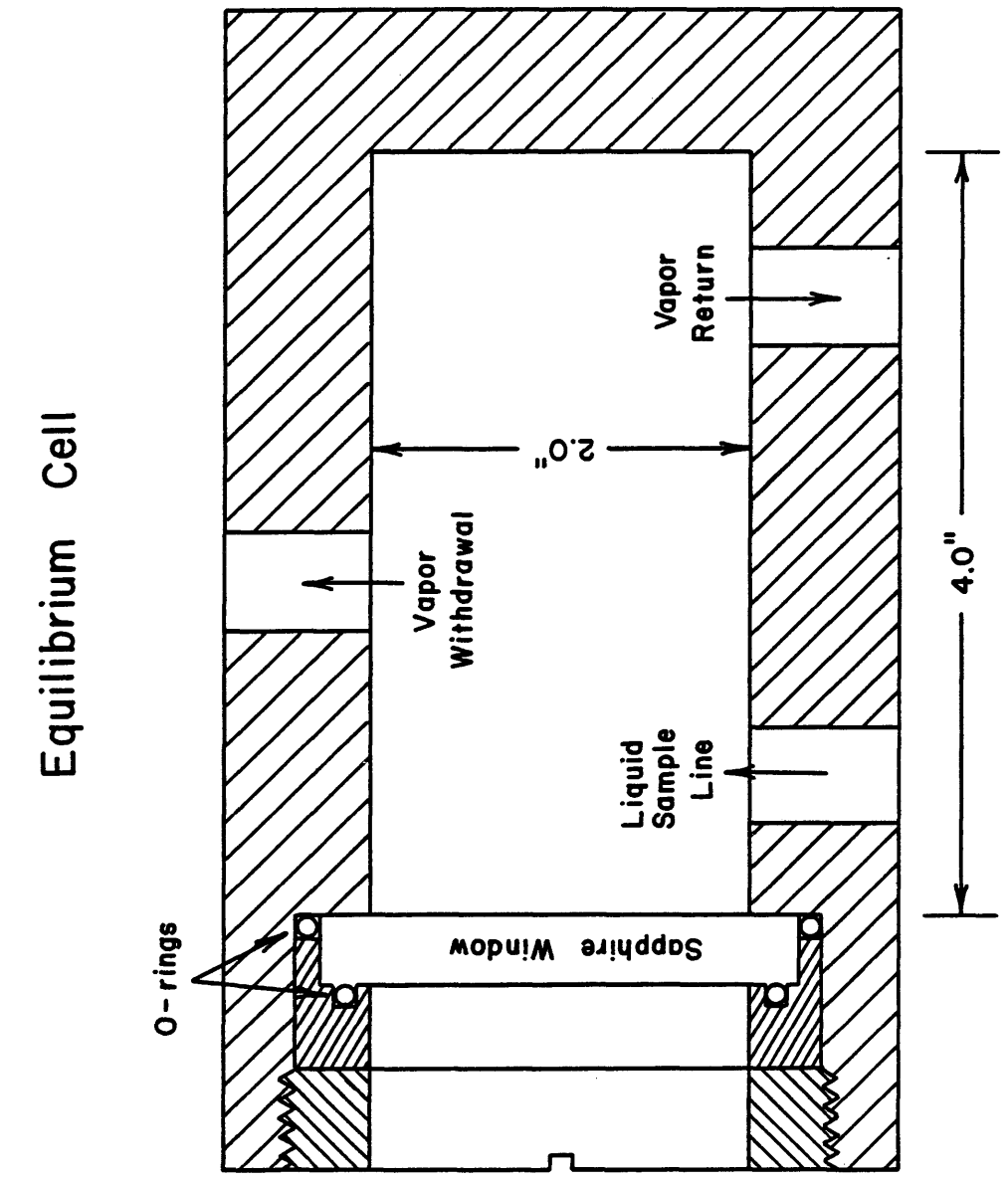
Equilibrium Cell
Vapor Return
2.0"
Vapor Withdrawal
Liquid Sample Line
4.0"
Sapphire Window
O-rings

Figure 3

screw, and the larger o-ring prevents leakage through the threads in the tightening screw. The smaller o-ring is on the outside of the cell, so this seal actually increases in effectiveness as the pressure in the cell increases. The cell and window were designed for a pressure of 20.7 MPa, have been tested successfully to 14 MPa, and have been used successfully up to 9.6 MPa.

The purpose of installing a visual cell was to allow the operator to observe phase transitions and the level of liquid in the cell. The two phase transitions that are important to be able to see are the appearance of a solid carbon dioxide phase and the change from a vapor-liquid region to a single-phase region at the critical point. The redesigned cell has worked extremely well for observing critical points and for making certain that there is enough liquid in the cell. To date, no solid-liquid-vapor equilibria work has been attempted to determine how well the operator will be able to see the appearance of a solid carbon dioxide phase.

In addition to the installation of the new cell, several other changes were made. A 100 atmosphere Hiese pressure gauge was added to increase the accuracy of the high pressure measurements. The 1700-watt control heater was replaced with two separate 500-watt heaters. This has

improved the temperature control to better than ±0.01 K. The electrical outlets were rewired so that each piece of equipment can now be turned off individually with a switch on the front panel. All of the tubing was replaced to decrease the amount of dead volume in the system, and the bath fluid was changed to Freon 11. Freon 11 freezes at 162 K, and the former bath fluid froze at approximately 200 K, so the operating range of the equipment has been extended approximately 30 degrees.

The carbon dioxide and ethane were supplied by Matheson Gas, and had minimum purities of 99.995 and 99.99 mole percent respectively. The nitrogen was supplied by General Air and had a minimum purity of 99.99 mole percent. All gases were used without further purification.

The temperature and pressure measurements were checked regularly by measuring the vapor pressures of carbon dioxide and ethane, and comparing with the vapor pressures given by Goodwin et al. (1976) for ethane and Angus, et al. (1976) for carbon dioxide. In every case, the difference between the literature vapor pressure and the measured value was less than the calibration error in the pressure measurement. A comparison of the measured vapor pressures with the literature values is given in Table 2.

Table 2

Vapor Pressure Measurements

Temperature (K)	Measured Vapor Pressure (MPa)	Literature Vapor Pressure (MPa)	Date
Carbon Dioxide:			
220.00	0.598	0.5996	6/14/85
270.00	3.200	3.2034	3/08/85
Ethane:			
207.00	0.2943	0.2950*	6/14/85
210.00	0.3334	0.3340	6/16/85
220.00	0.491	0.4922	6/13/85
223.15	0.550	0.5520*	5/13/85
230.00	0.699	0.7004	5/30/85
250.00	1.302	1.301	5/28/85
263.15	1.860	1.859*	3/05/85
270.00	2.212	2.210	3/06/85

*Interpolated value (Interlopation was done assuming a linear relationship between ln(P) and 1/T)

CO_2 reference - Angus, S., et al., 1976

C_2H_6 reference - Goodwin, et al., 1976

EXPERIMENTAL PROCEDURES

The following procedures were used to obtain vapor pressures, binary data, and ternary data.

Start-up

1) Turn on the stirrer, Mueller bridge temperature controller, liquid-sample heater, Mueller bridge, current supply for the Mueller bridge, and the null detector.

2) Fully open the valve on the liquid nitrogen tank, and the liquid-nitrogen flow-control valve on the front panel.

3) Set the desired operating temperature on the Mueller bridge by finding the resistance that corresponds to the desired temperature.

4) Turn on the temperature controller, and set the set point well below the desired temperature.

5) When the temperature of the bath reaches the desired temperature (as indicated by a zero deflection on the null meter), reduce the liquid nitrogen flow to a very low level. Adjust the set point of the controller so that it operates at approximately 40 percent of its maximum power output. This can be achieved by adjusting the controller set point and the liquid nitrogen flowrate. During operation of the equipment, the null meter should be on the 1 microvolt scale.

Vapor Pressure Measurements

The temperature of the bath should already be set and controlled to within ±0.01 K.

1) Turn on the vacuum pump and evacuate the system with the valves to the appropriate gauges open. Flush the system with the component whose vapor pressure you wish to measure. Repeat this step two or three times to ensure that no impurites will exist in the system.

2) Fill the system with the component whose vapor pressure you wish to measure to a pressure greater than atmospheric pressure. Open the vent valve, and vent the system to atmospheric pressure. Set the atmospheric pressure as measured from the barometer on each gauge which will be used.

3) Add the pure component to the system until the pressure does not increase upon further addition of the gas, then add a little more to raise the liquid level above the liquid sample line. With the visual cell, it is very easy to know how much material to add to obtain the proper level, but with the blind cell, experience was the only guide to getting the proper level.

4) Turn on the circulation pump, and circulate the vapor until the pressure has been constant for approximately one half hour. Turn off the circulation pump, and measure the

pressure. Sample both liquid and vapor phases, and analyze them in the GC to make sure that no impurities exist in the system.

Binary Measurements

The cell should already contain a pure component with enough liquid to cover the liquid-sample line.

1) Add the second component of the binary mixture in increments with vapor circulation between increments until the desired pressure is approximately reached.

2) Turn on the circulation pump and circulate the vapor until the pressure has remained constant for approximately one hour. Turn off the pump, read the pressure, and sample both phases.

Ternary Measurements

The cell should already contain a binary mixture with a sufficient amount of liquid.

1) Add enough of the third component to bring the total composition to approximately where you would like to make the measurement.

2) Circulate the vapor until equilibrium is reached - usually about one hour. Check the pressure. If the pressure is too high, vent some vapor. If the pressure is too low, add some of the lightest component. Repeat this

procedure until the correct pressure is obtained at equilibrium, and then sample both phases.

Sampling and Sample Analysis

The vapor phase should be sampled first and analyzed before the liquid phase so that the next equilibrium point can be started while the liquid phase is analyzed.

1) To sample the vapor phase, turn off the circulation pump and close the valves around the vapor sample loop.

2) To sample the liquid phase, evacuate the liquid-sample cylinder and close off the sample cylinder. Open the valve between the system and the cylinder to fill the cylinder. Evacuate the cylinder, and flush with the sample one more time. Then take the final sample.

3) The samples are analyzed by evacuating the sample loop in the GC and all of the tubing between the GC and the sample, flushing with helium several times, and then expanding the sample into the evacuated GC sample loop.

LITERATURE REVIEW

Carbon Dioxide-Ethane Binary System

Several studies of the carbon dioxide-ethane system have been made, and they are summarized in Table 3. Mollerup (1975) performed a consistency test on all of the data available in the literature at that time, and concluded that the data of Fredenslund and Mollerup (1974) are thermodynamically consistent, but the data of Hakuta, et al. (1969), Hamam and Lu (1974), and Kurata and Swift (1974) are "probably not consistent."

Khazanova, et al. (1966) report only interpolated values for the equilibrium compositions, and their pressure measurement is stated to be accurate to ±0.5 atmospheres. Gugnoni, et al. (1974) did not measure vapor-phase compositions. Nagahama, et al. (1974) used ethane with a purity of 99.0 percent, and did not report any vapor pressures. Ohgaki and Katayama used ethane with a purity of 99.7 percent, and their reported vapor pressures for ethane are 0.5 to 0.9 percent higher than those reported by Goodwin, et al. (1976).

The work of Kuenen (1897) and Kuenen and Robson (1902) is no doubt excellent for its time, but the measurements were made almost a century ago before modern methods of

Table 3

Summary of Previous Work

System	Reference	Temperature Range (K)
CO_2-C_2H_6	Davalos, et al., 1976	250
	Fredenslund and Mollerup, 1974	223-293
	Gugnoni, et al., 1974	241-283
	Hakuta, et al., 1969	273
	Hamam and Lu, 1974	222-288
	Khazanova, et al., 1966	283-293
	Kuenen and Robson, 1902	195-292
	Kuenen, 1897	281-297
	Nagahama, et al., 1974	252
	Ohgaki and Katayama, 1977	283-298
	Robinson and Kalra, 1974	288
	Kurata and Swift, 1971	222-266
N_2-CO_2	Zenner and Dana, 1963	218-273
	Somait and Kidnay, 1978	270
	Al-Sahhaf, et al., 1983	220-240
	Dorau, et al., 1983	223-273
	Masahiro, et al., 1985	273-298

Table 3 (cont.)

Summary of Previous Work

System	Reference	Temperature Range (K)
N_2-C_2H_6	Cosway and Katz, 1959	144-200
	Ellington et al., 1959	101-302
	Chang and Lu, 1967	122-171
	Cannon et al., 1968	144-228
	Stryjek et al., 1974	139-194
	Grauso et al., 1977	200-290
	Gupta et al., 1980	260-280
	Kremer and Knapp, 1983	120-133
	Wisotzki and Schneider, 1985	90-148

purification, temperature, pressure, and composition measurement had been developed.

Based on the gas purities, reported vapor pressures, and the consistency testing done by Mollerup, I feel that the data of Fredenslund and Mollerup are the most accurate available in the literature. Therefore, I have used their data for comparison and in the equation-of-state modeling.

Nitrogen-Carbon Dioxide Binary System

Several studies of this system have been made as indicated in Table 3. Comparisons were made with the data of Al-Sahhaf, et al. (1983) at 220 K and with the data of Somait and Kidnay (1978) at 270 K.

Nitrogen-Ethane Binary System

This system has been studied extensively as indicated in Table 3. No data were available at 220 K, but comparisons were made with the data Gupta, et al. (1980) at 260 and 270 K. The data of Grausø et al. (1977) and Zeck and Knapp (1985) were also used for comparison at 260 K.

Nitrogen-Carbon Dioxide-Ethane Ternary System

No data have been published for the nitrogen-carbon dioxide-ethane ternary system.

EXPERIMENTAL RESULTS

In order to obtain an internally consistent set of experimental vapor-liquid equilibria data for a three-component system it is necessary to measure the ternary system and the three constituent binaries at the same temperatures. The temperatures chosen for this work were 220 and 270 K. It was desirable to obtain complete isotherms for modeling, so the lower temperature was set by the triple point of carbon dioxide (216.58 K). Below this temperature, the phase envelope for carbon dioxide-ethane does not extend completely to the pure carbon dioxide point. The upper temperature of 270 K was chosen because the operating temperature of the equipment must be several degrees below room temperature. All of the experimental data are presented in Appendix B. All of the figures showing the experimental data also contain predicted curves which will be discussed later.

Carbon Dioxide-Ethane Binary System

The results of the carbon dioxide-ethane measurements are shown in Figures 4-11. In several instances, only partial isotherms were measured since the objective was to compare with existing data. Considerably more data were gathered on this system than originally planned because at 270 K, the results of this work differed from the results of

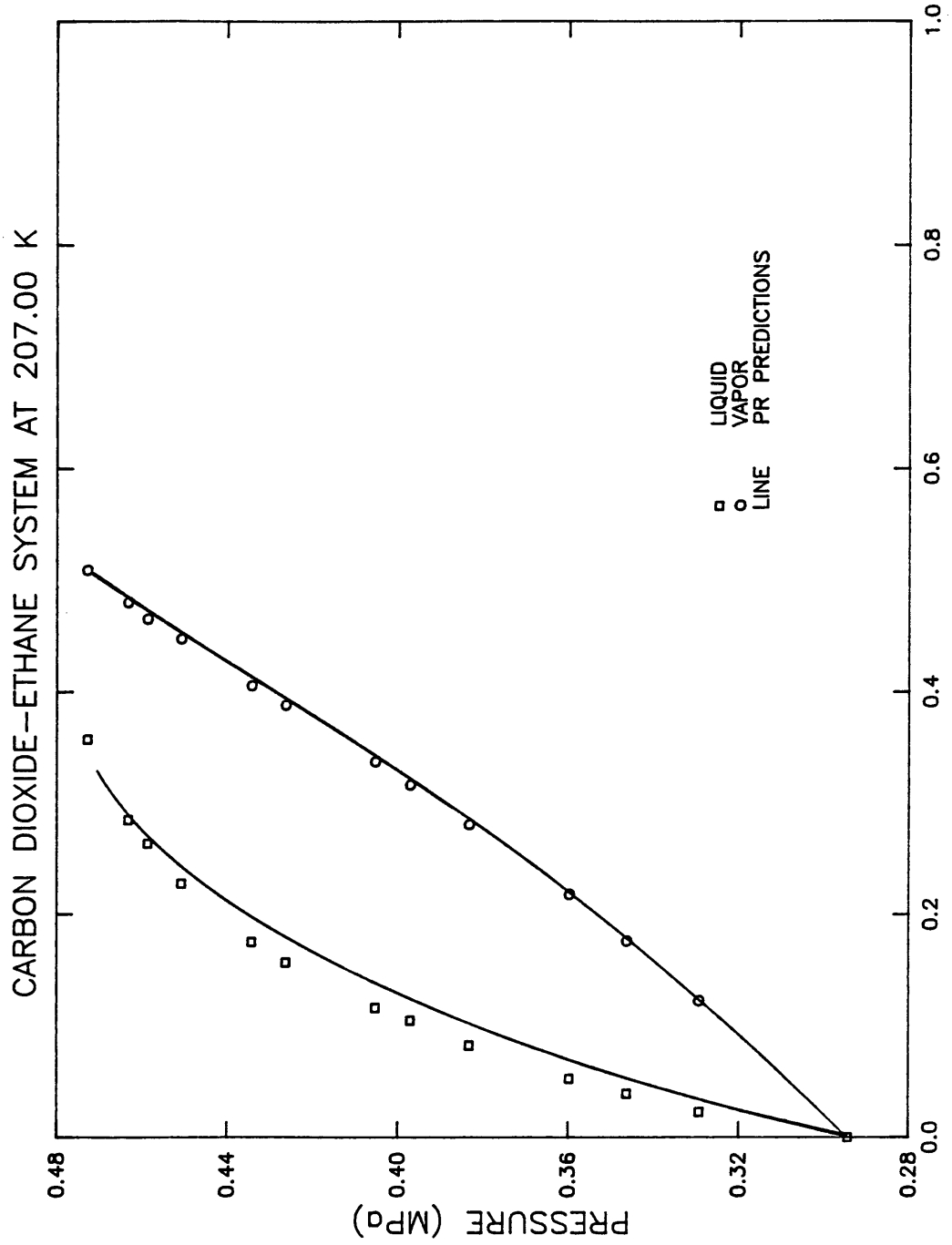
CARBON DIOXIDE–ETHANE SYSTEM AT 207.00 K
PRESSURE (MPa)
MOLE FRACTION CARBON DIOXIDE
LIQUID
VAPOR
PR PREDICTIONS
LINE
0.48
0.44
0.40
0.36
0.32
0.28
0.0
0.2
0.4
0.6
0.8
1.0

Figure 4

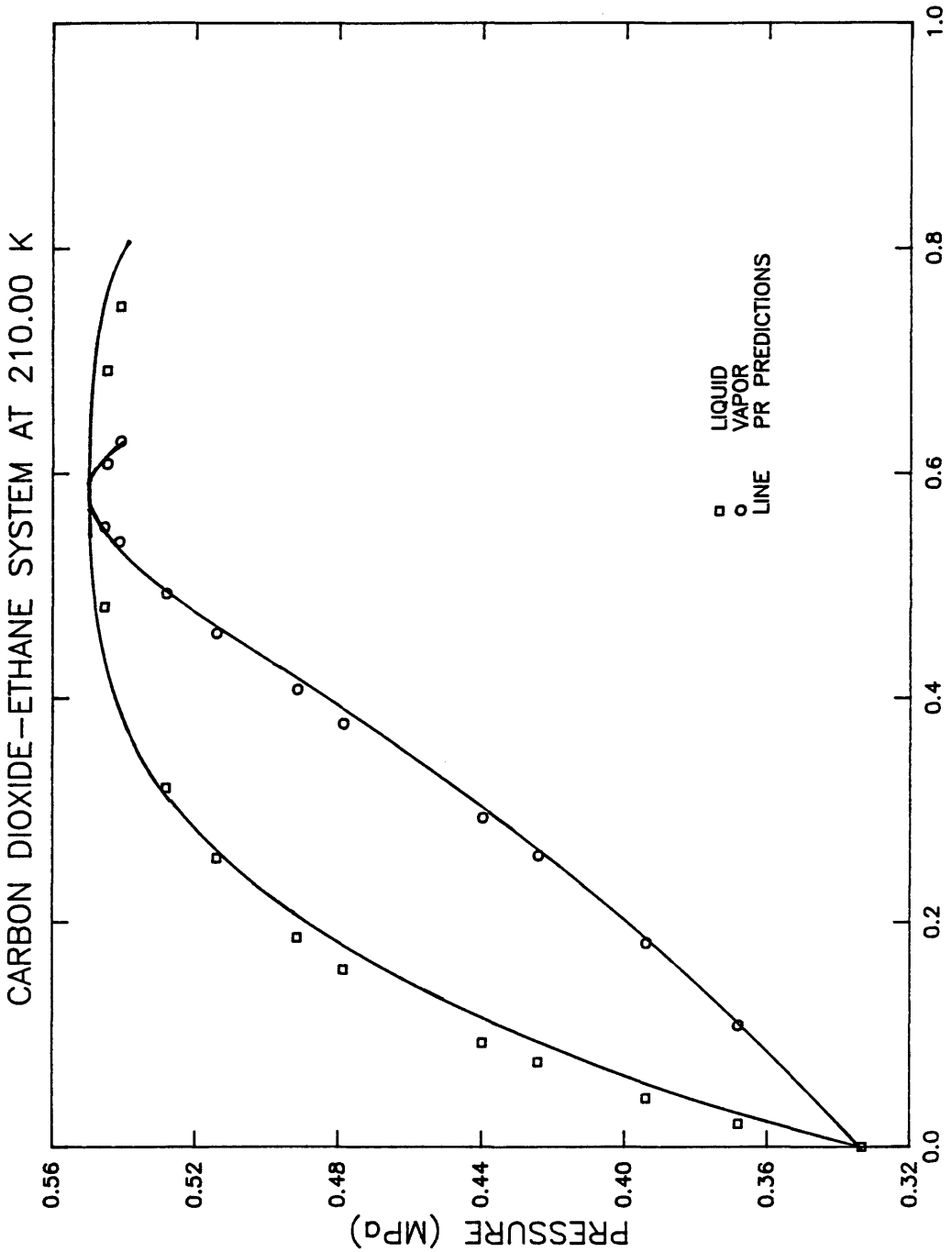
CARBON DIOXIDE–ETHANE SYSTEM AT 210.00 K
PRESSURE (MPa)
MOLE FRACTION CARBON DIOXIDE
LIQUID
VAPOR
LINE PR PREDICTIONS
0.56
0.52
0.48
0.44
0.40
0.36
0.32
0.0
0.2
0.4
0.6
0.8
1.0

Figure 5

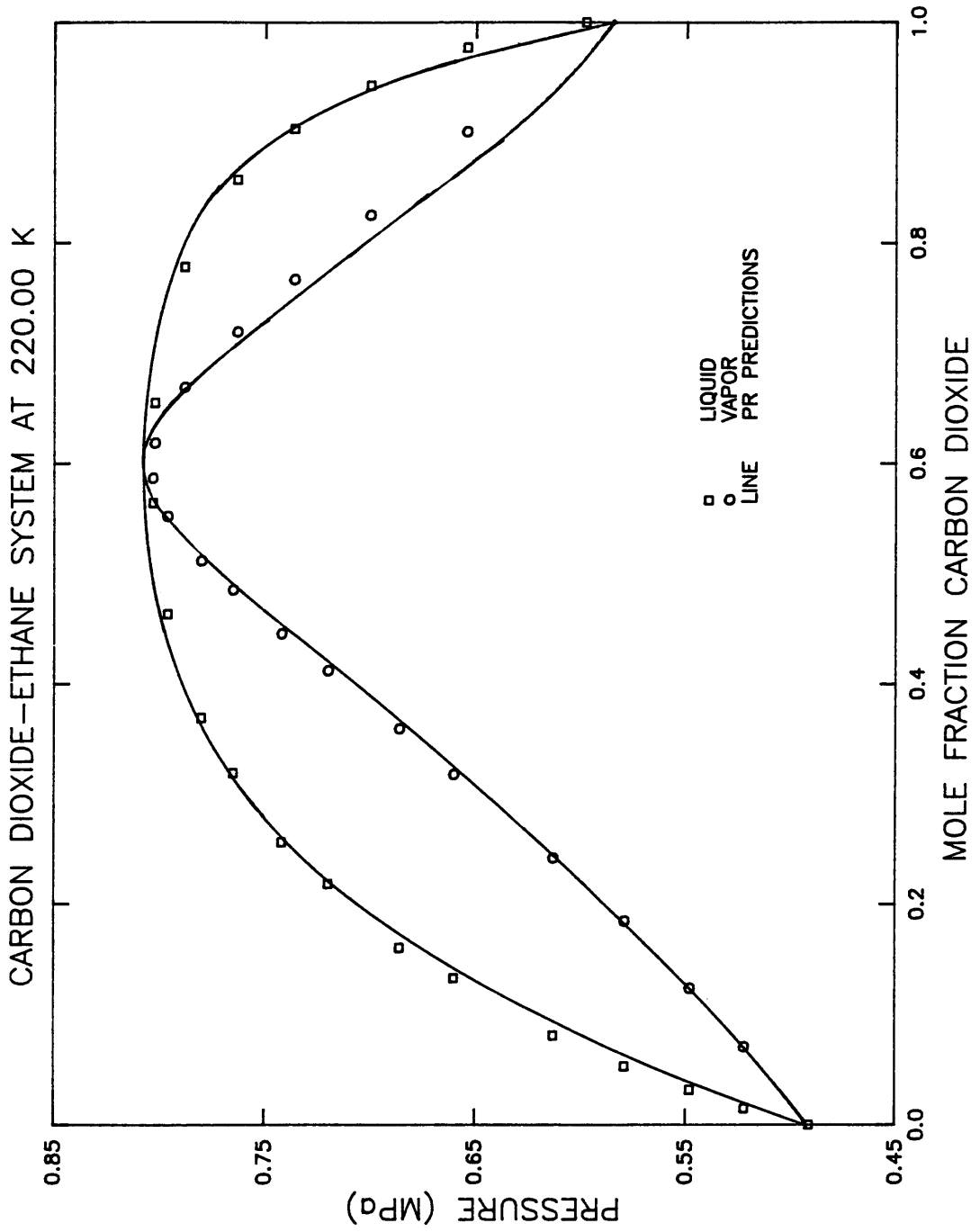
CARBON DIOXIDE–ETHANE SYSTEM AT 220.00 K
PRESSURE (MPa)
MOLE FRACTION CARBON DIOXIDE
0.85
0.75
0.65
0.55
0.45
0.0
0.2
0.4
0.6
0.8
1.0
LIQUID
VAPOR
LINE PR PREDICTIONS

Figure 6

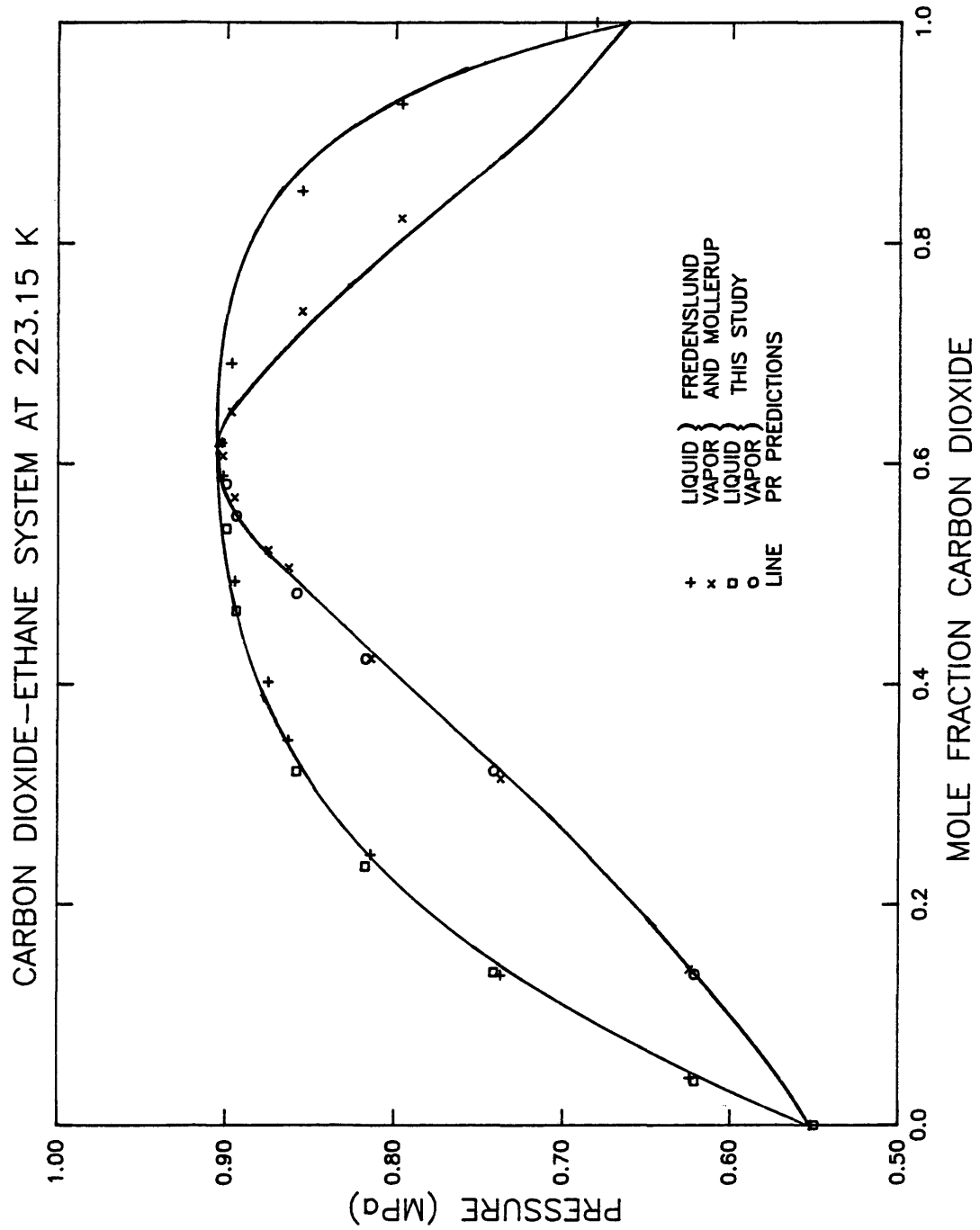
CARBON DIOXIDE–ETHANE SYSTEM AT 223.15 K
PRESSURE (MPa)
MOLE FRACTION CARBON DIOXIDE
1.00
0.90
0.80
0.70
0.60
0.50
0.0
0.2
0.4
0.6
0.8
1.0
LIQUID } FREDENSLUND
VAPOR } AND MOLLERUP
LIQUID } THIS STUDY
VAPOR }
LINE PR PREDICTIONS

Figure 7

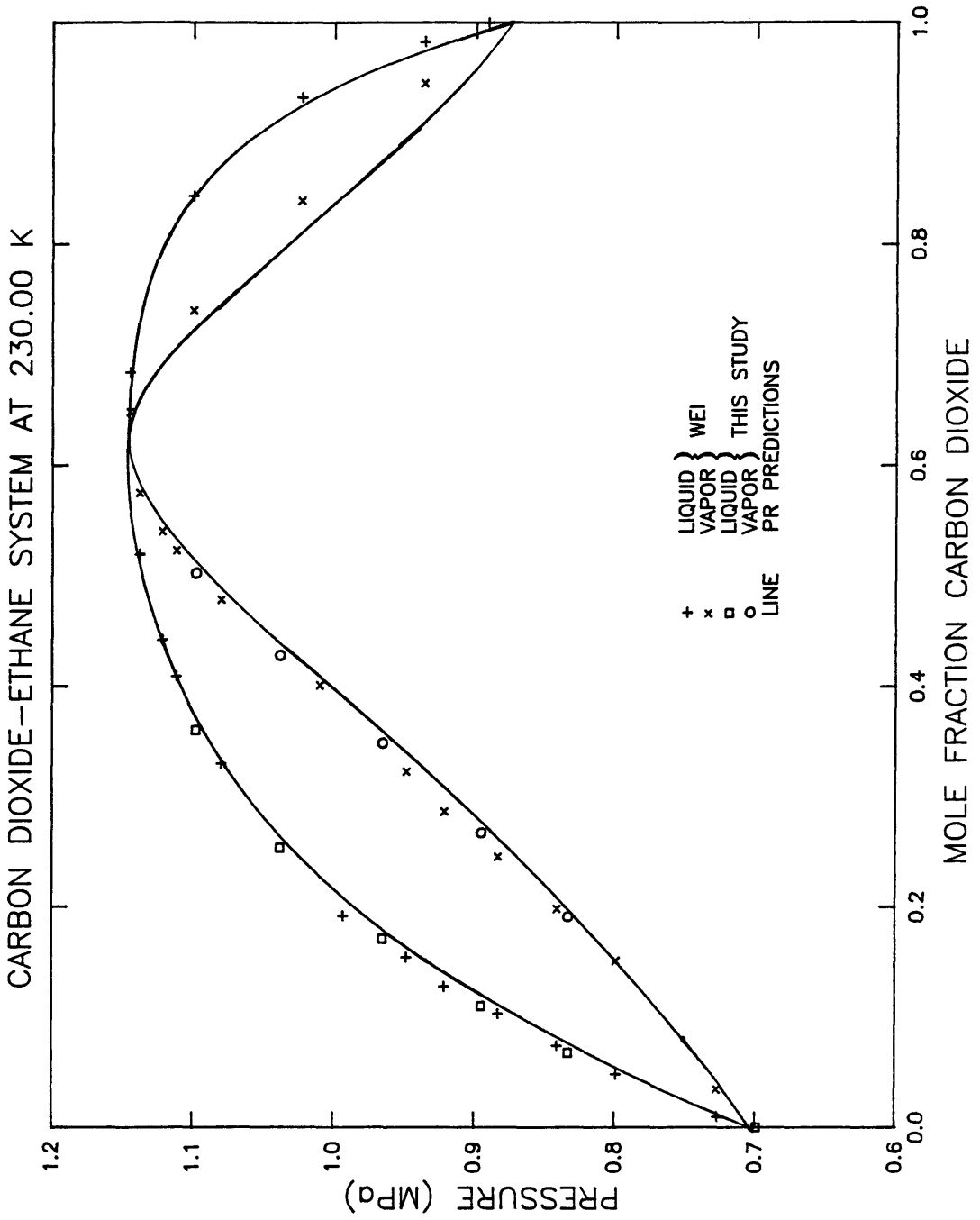
CARBON DIOXIDE–ETHANE SYSTEM AT 230.00 K
PRESSURE (MPa)
MOLE FRACTION CARBON DIOXIDE
LIQUID } WEI
VAPOR }
LIQUID } THIS STUDY
VAPOR }
LINE PR PREDICTIONS
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.0
0.2
0.4
0.6
0.8
1.0

Figure 8

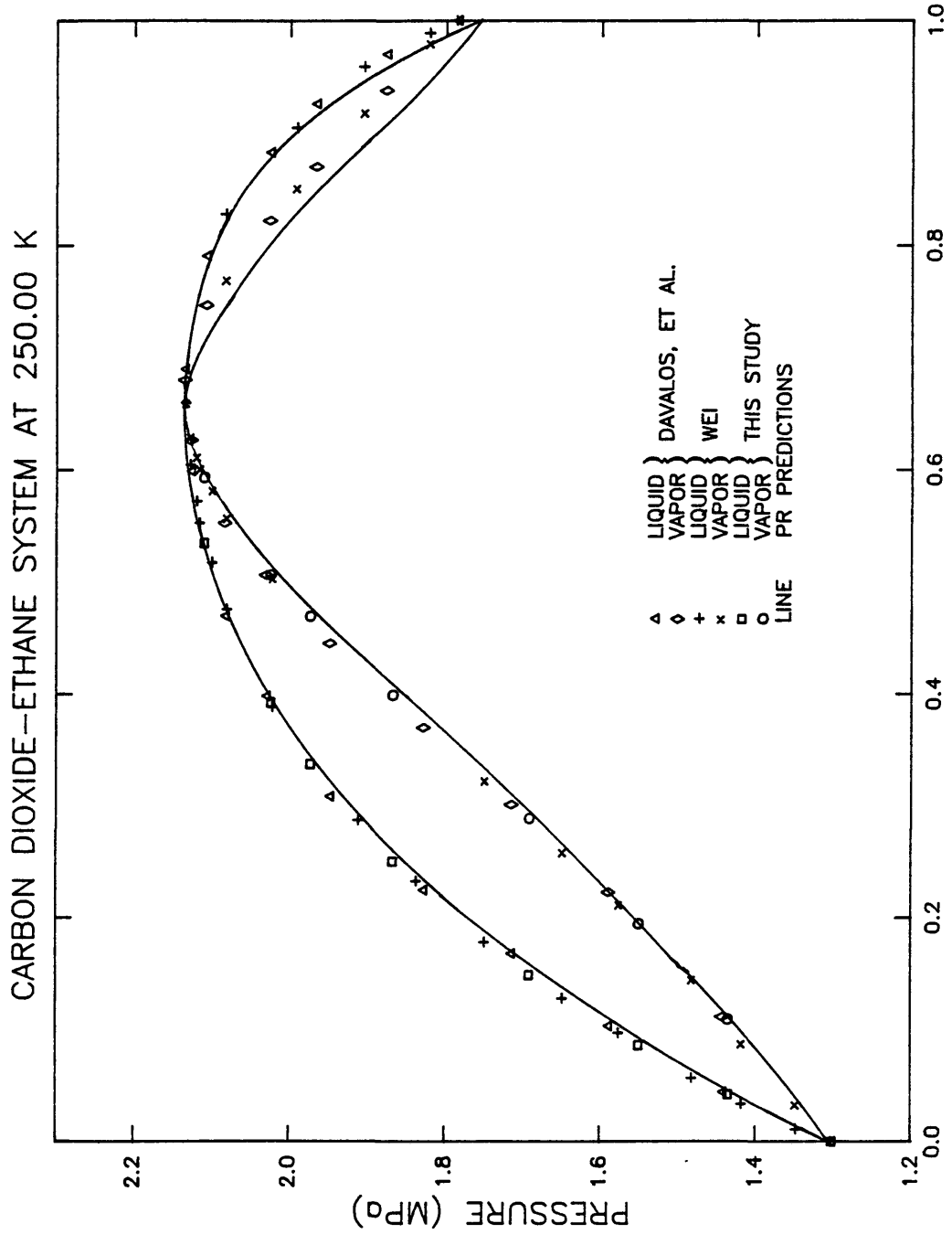
CARBON DIOXIDE–ETHANE SYSTEM AT 250.00 K
PRESSURE (MPa)
MOLE FRACTION CARBON DIOXIDE
2.2
2.0
1.8
1.6
1.4
1.2
0.0
0.2
0.4
0.6
0.8
1.0
LIQUID } DAVALOS, ET AL.
VAPOR }
LIQUID } WEI
VAPOR }
LIQUID } THIS STUDY
VAPOR }
LINE PR PREDICTIONS

Figure 9

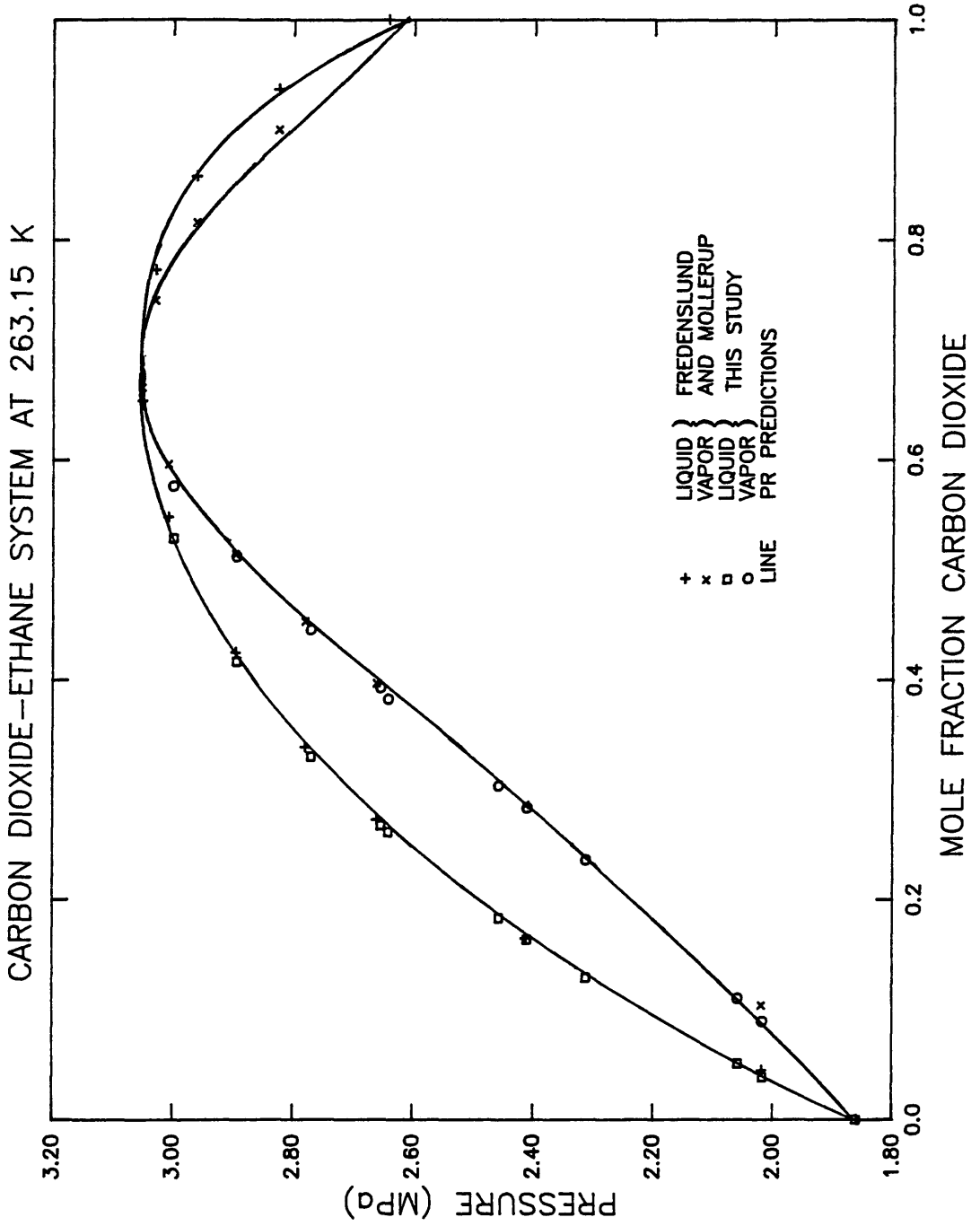
CARBON DIOXIDE–ETHANE SYSTEM AT 263.15 K
PRESSURE (MPa)
MOLE FRACTION CARBON DIOXIDE
3.20
3.00
2.80
2.60
2.40
2.20
2.00
1.80
0.0
0.2
0.4
0.6
0.8
1.0
+ LIQUID } FREDENSLUND
× VAPOR } AND MOLLERUP
□ LIQUID } THIS STUDY
○ VAPOR }
LINE PR PREDICTIONS

Figure 10

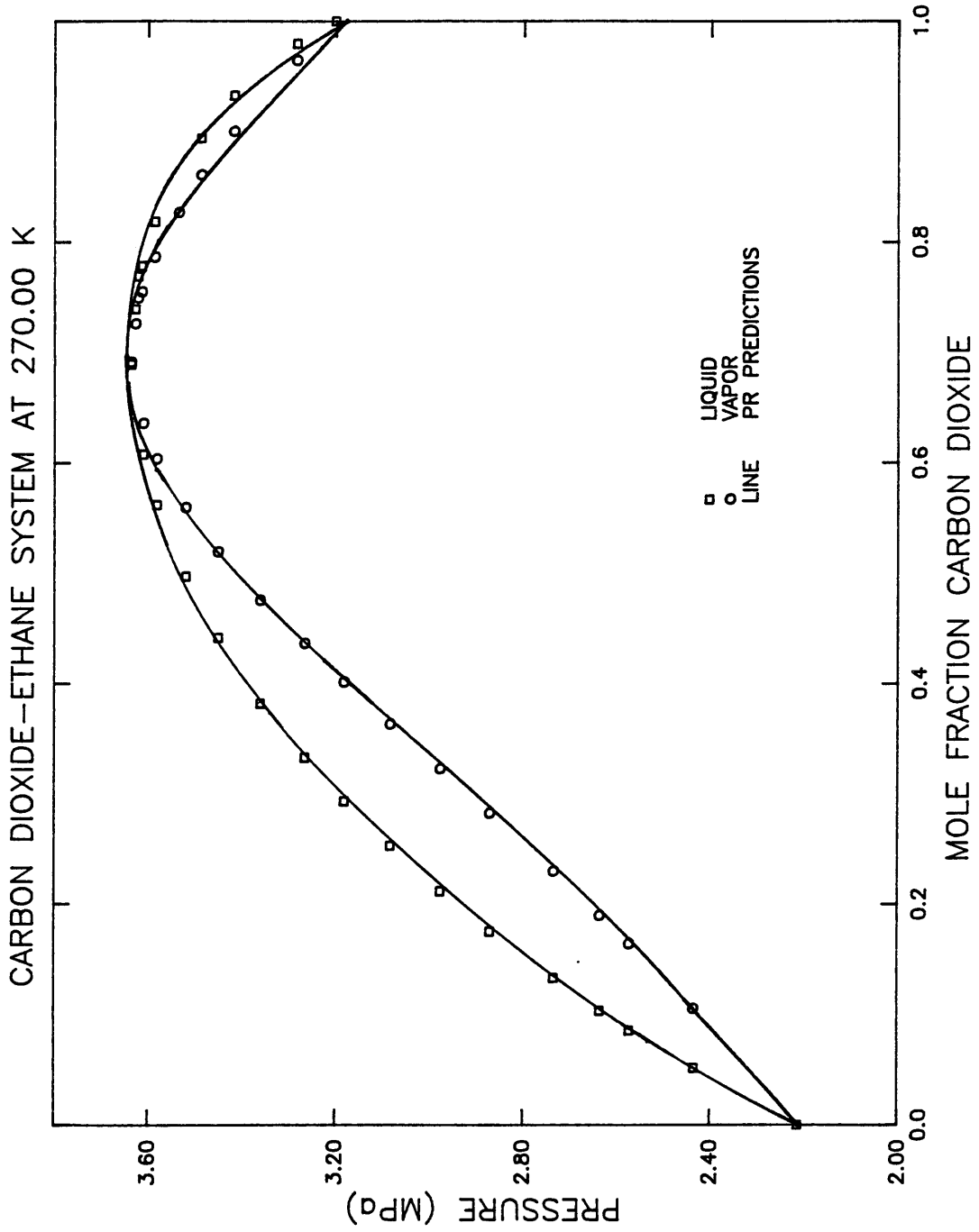
CARBON DIOXIDE–ETHANE SYSTEM AT 270.00 K
PRESSURE (MPa)
3.60
3.20
2.80
2.40
2.00
0.0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION CARBON DIOXIDE
LIQUID
VAPOR
PR PREDICTIONS
LINE

Figure 11

Wei (1983) that were also obtained in this laboratory, and more data were needed to determine which measurements were in error.

Data were first measured at 223.15 and 263.15 K to compare with Fredenslund and Mollerup. The agreement between the two data sets is excellent at both temperatures. Partial isotherms were also measured at 230 and 250 K, and the results compare well with the data of Davalos (1976) and Wei(1983). The 207 and 210 K isotherms were extended to near the point at which carbon dioxide begins to freeze; however, the last equilibrium points of these two isotherms do not represent solid-liquid-vapor equilibria. All of the data show very little scatter.

For many azeotropic systems, including the carbon dioxide-ethane system, the pressure at the azeotrope is an exponential function of reciprocal absolute temperature. This relationship is illustrated in Figure 12 where a plot of ln P(azeotrope) versus 1/T is a straight line over the entire temperature range at which an azeotrope exists. The composition of the azeotrope as a function of temperature is shown in Figure 13. The flatness of the equilibrium curves makes estimation of the azeotropic pressure very accurate but estimation of the azeotropic composition relatively

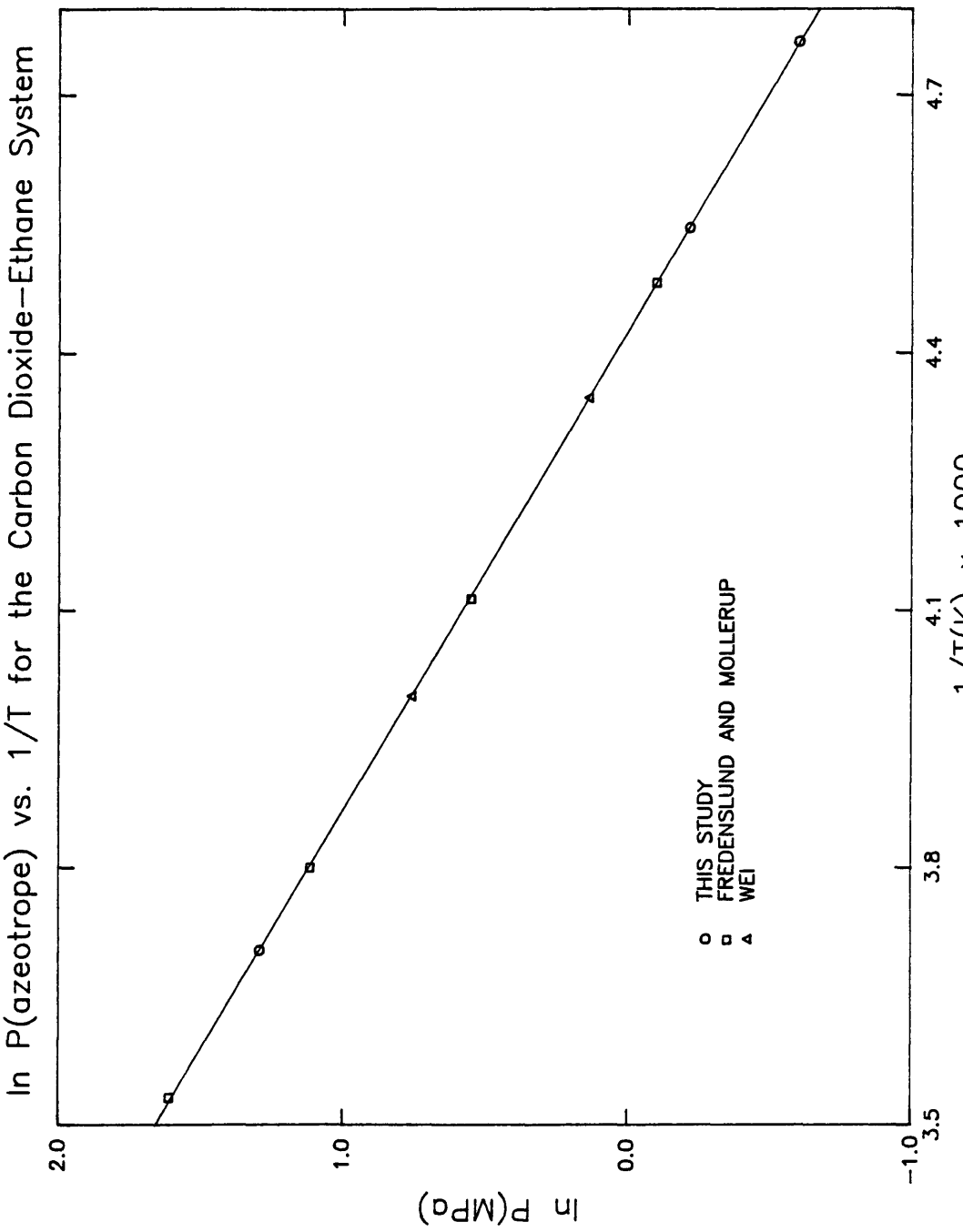

Figure 12

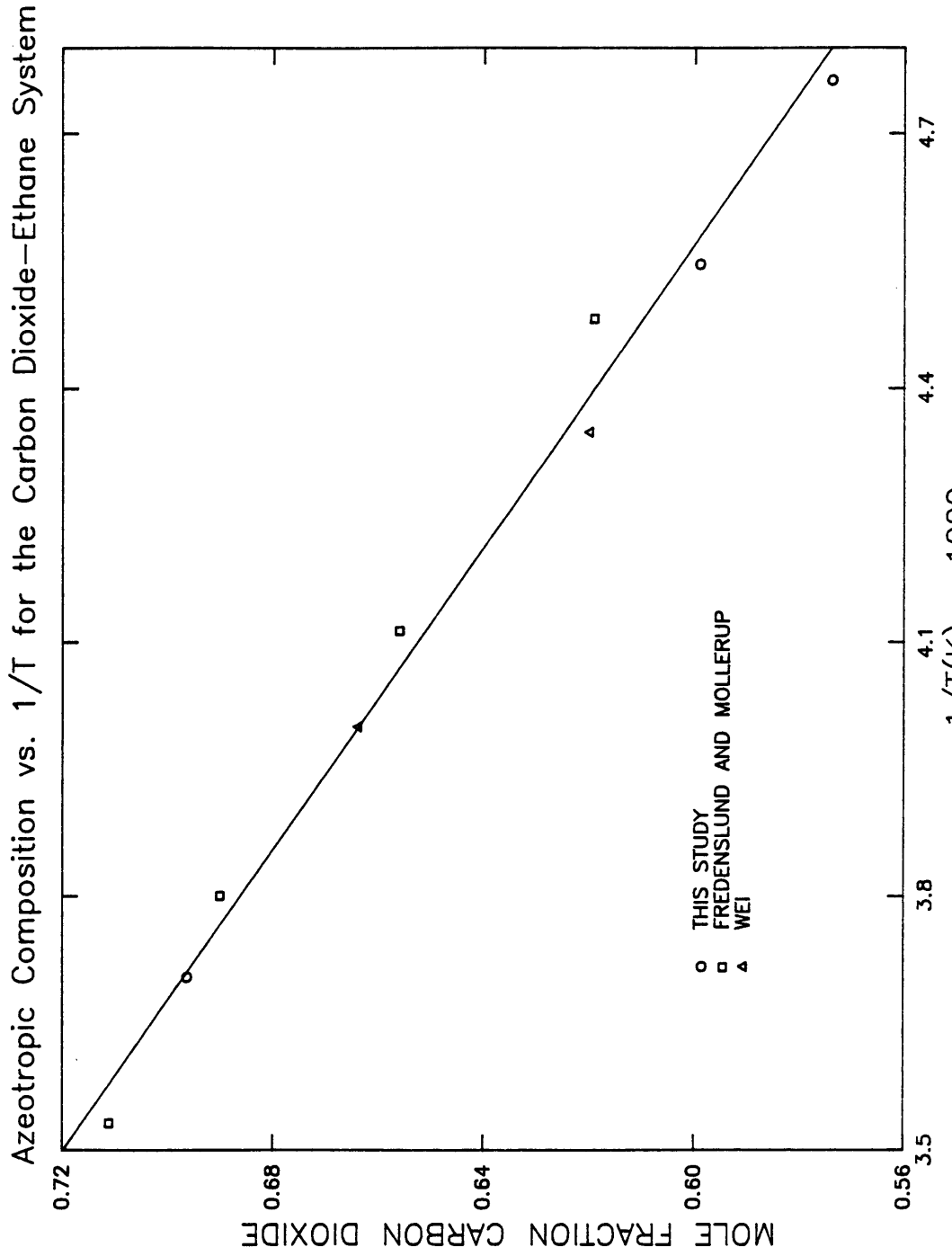
Azeotropic Composition vs. 1/T for the Carbon Dioxide–Ethane System
MOLE FRACTION CARBON DIOXIDE
0.72
0.68
0.64
0.60
0.56
3.5
3.8
4.1
4.4
4.7
1/T(K) x 1000
THIS STUDY
FREDENSLUND AND MOLLERUP
WEI

Figure 13

inaccurate. This results in the scatter observed in the azeotropic composition.

Nitrogen-Carbon Dioxide Binary System

The nitrogen-carbon dioxide system was studied at temperatures of 220 and 270 K, and the results are shown in Figures 14 and 15. Good agreement was obtained with the data of Al-Sahhaf, et al. (1983) at 220 K and with Somait and Kidnay (1978) at 270 K.

This is an interesting system because although 220 K is well above the critical temperature of nitrogen, the binary phase envelope does not close to form a critical point. However, at 270 K the isotherm does form a closed loop. Using an equation of state that accurately predicts compressibility factors, Kreglewski and Hall (1983), predicted that at temperatures where the isotherms close, there is a region of gas-gas equilibria above the vapor-liquid critical pressure.

Considerable difficulty was encountered with regard to liquid sampling for this binary at 220 K. While attempting to correct the sampling problem, a number of data points were taken where the liquid-phase compositions were unreliable. This is the reason for the separate table in Appendix B containing only vapor phase compositions.

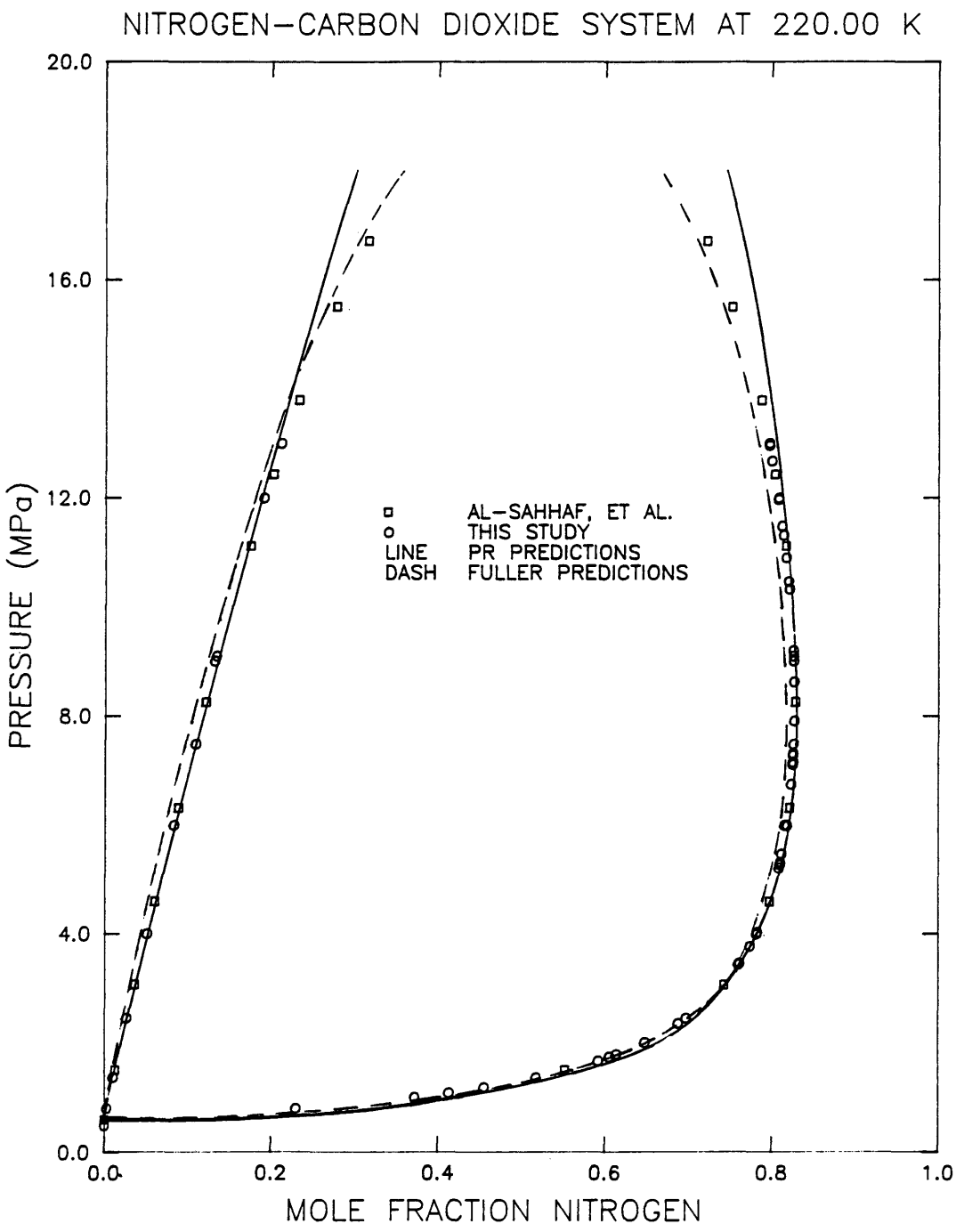
NITROGEN–CARBON DIOXIDE SYSTEM AT 220.00 K
PRESSURE (MPa)
MOLE FRACTION NITROGEN
20.0
16.0
12.0
8.0
4.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
AL–SAHHAF, ET AL.
THIS STUDY
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS

Figure 14

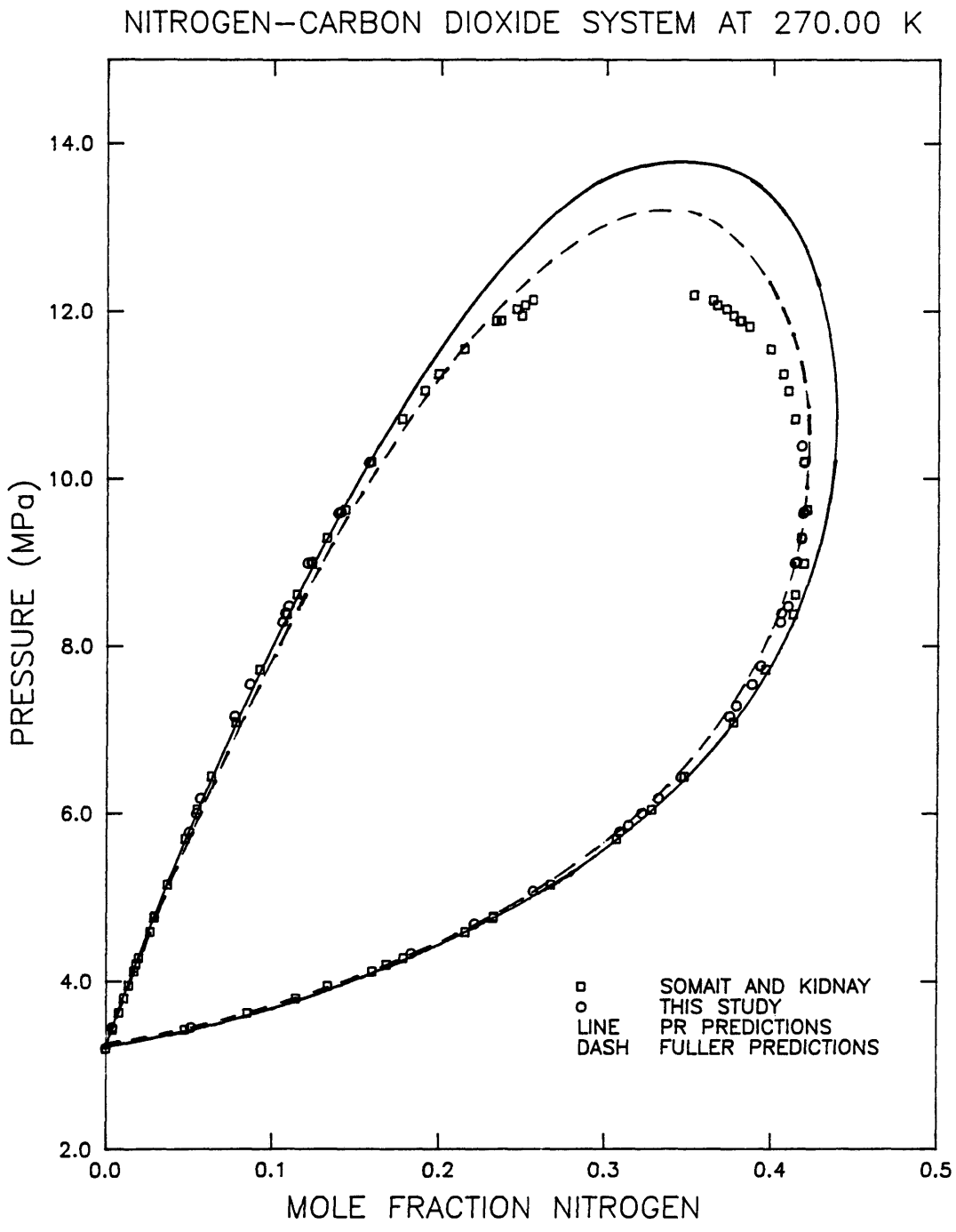
NITROGEN–CARBON DIOXIDE SYSTEM AT 270.00 K
PRESSURE (MPa)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.1
0.2
0.3
0.4
0.5
MOLE FRACTION NITROGEN
SOMAIT AND KIDNAY
THIS STUDY
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS

Figure 15

Nitrogen-Ethane Binary System

Measurements were made on the nitrogen-ethane system at 220, 260, and 270 K, and are shown in Figures 16-18. At 270 K, good agreement was obtained with Gupta et al. (1980) except near the critical point. The data for this work at 270 K and above 8 MPa were measured with the rebuilt equipment including the visual cell. The rebuilt apparatus had been tested previously with good results on the nitrogen-carbon dioxide binary at 270 K. Gupta et al. only reported compositions for either the liquid or the vapor phase, and never both at pressures near the critical. For this reason, it is very possible that their measurements above the phase envelope measured in this work could actually be in the single-phase region. They did not have the benefit of a visual cell, and thus it was not possible to see if there were two phases present.

Since disagreement was found at 270 K, data were also taken at 260 K for the nitrogen-ethane binary to compare with the data of Grausø (1977), Zeck and Knapp (1986), and the data of Gupta et al. (1980). No data were available near the critical point, however, good agreement was obtained over the entire pressure range measured.

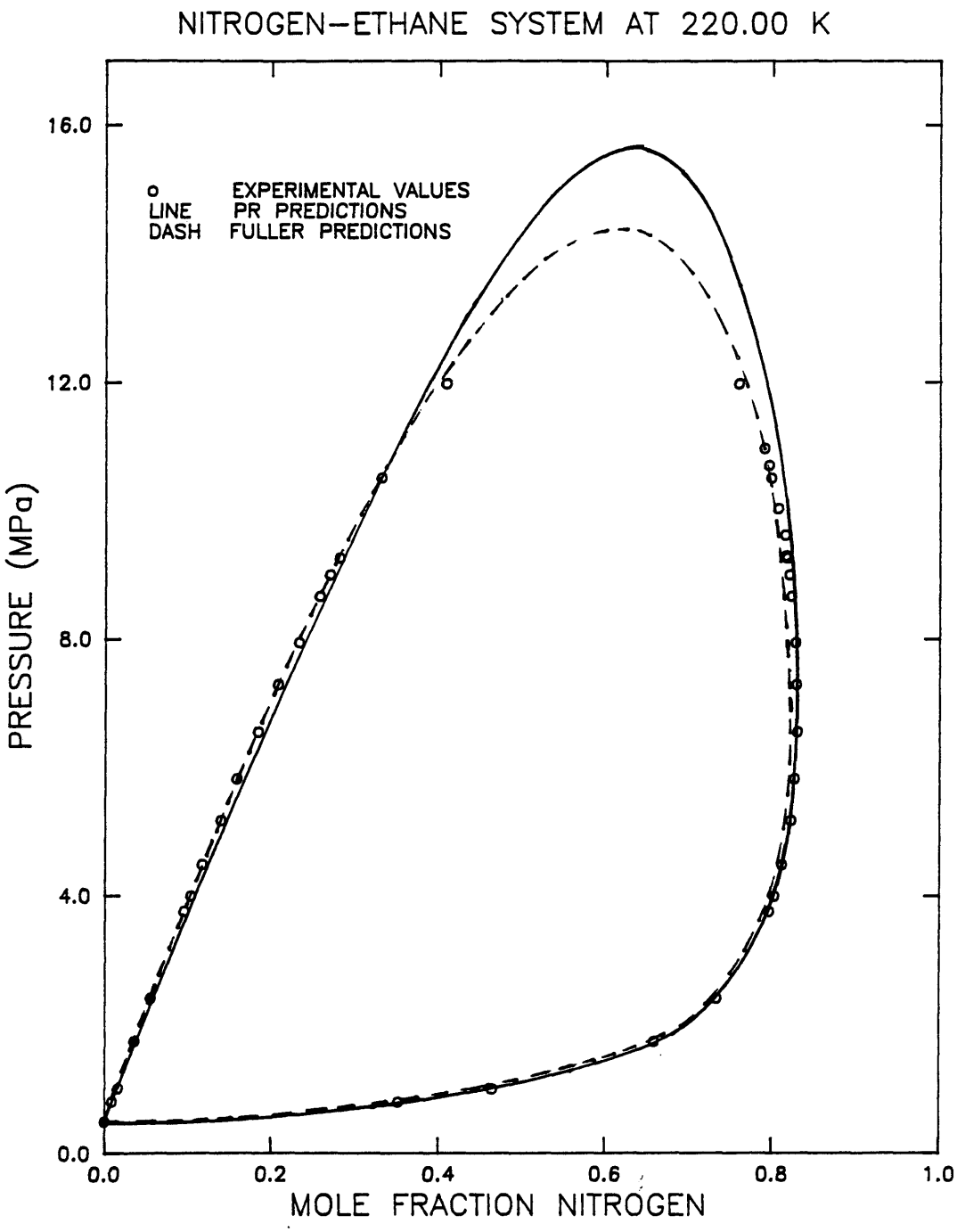
NITROGEN–ETHANE SYSTEM AT 220.00 K
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
PRESSURE (MPa)
16.0
12.0
8.0
4.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
MOLE FRACTION NITROGEN

Figure 16

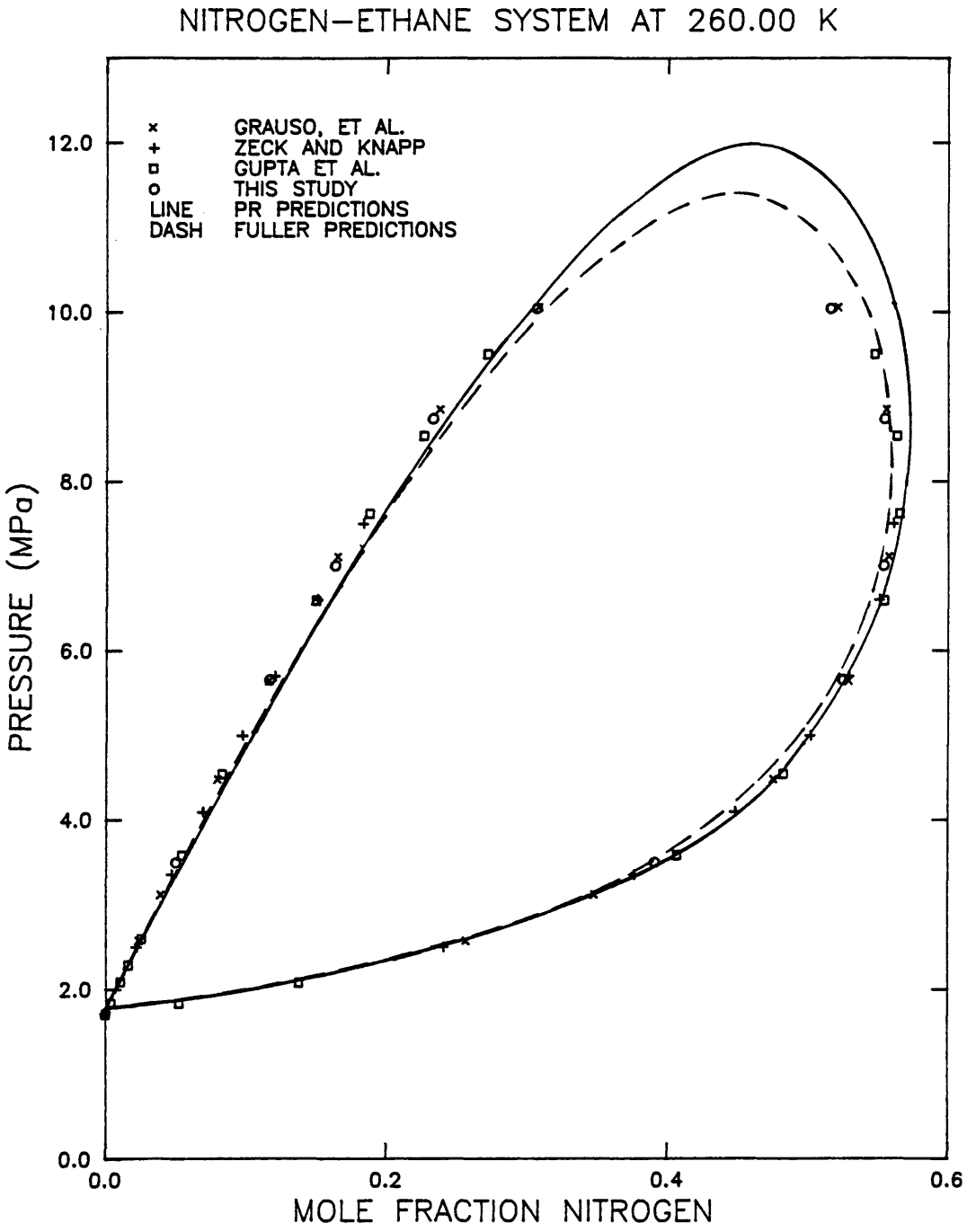
NITROGEN–ETHANE SYSTEM AT 260.00 K
GRAUSO, ET AL.
ZECK AND KNAPP
GUPTA ET AL.
THIS STUDY
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
PRESSURE (MPa)
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
0.2
0.4
0.6
MOLE FRACTION NITROGEN

Figure 17

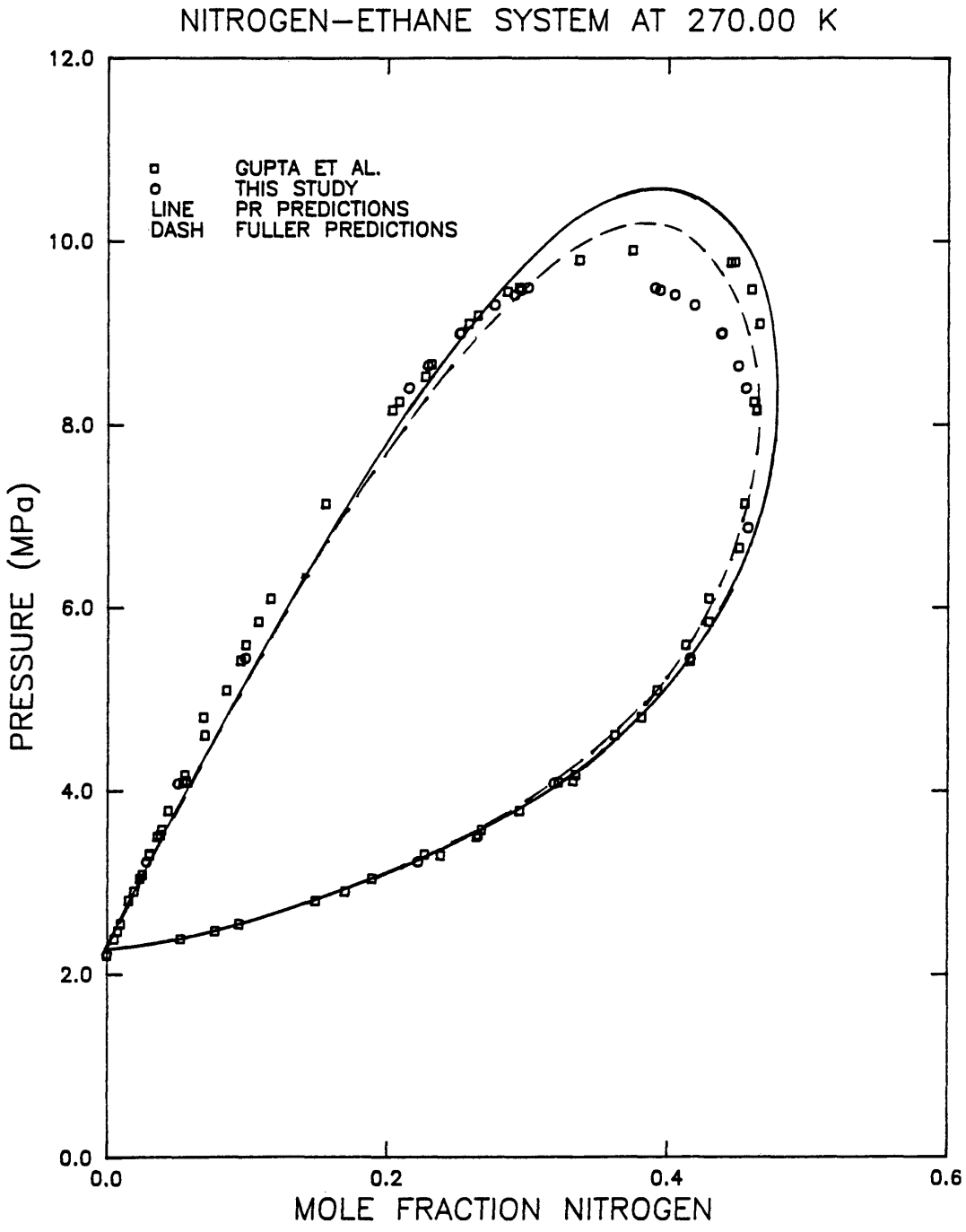
NITROGEN–ETHANE SYSTEM AT 270.00 K
GUPTA ET AL.
THIS STUDY
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
PRESSURE (MPa)
MOLE FRACTION NITROGEN
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0
0.2
0.4
0.6

Figure 18

Nitrogen-Carbon Dioxide-Ethane Ternary System

The results of the ternary measurements are presented in Figures 19-26. One isobar, 270 K and 2.45 MPa, was measured below the pressure of the carbon dioxide-ethane azeotrope, one isobar, 220 K and 0.803 MPa, was measured at the pressure of the azeotrope, and the remaining isobars were measured above the pressure of the azeotrope.

This ternary system exhibits some unusual behavior. At low pressures, the liquid curve is concave downward. As the pressure is increased at constant temperature, the liquid curve becomes almost flat, and then begins curving upward. At 270 K and 8.4 MPa, the liquid and vapor curves have come together to form two separate phase envelopes, each with a critical point. Apparently, at 270 K and a pressure between 6 and 8.4 MPa there will be a ternary azeotrope.

The final diagram at 270 K and 9.6 MPa is above the critical pressure of the nitrogen-ethane binary, and thus the left side of the diagram has disappeared.

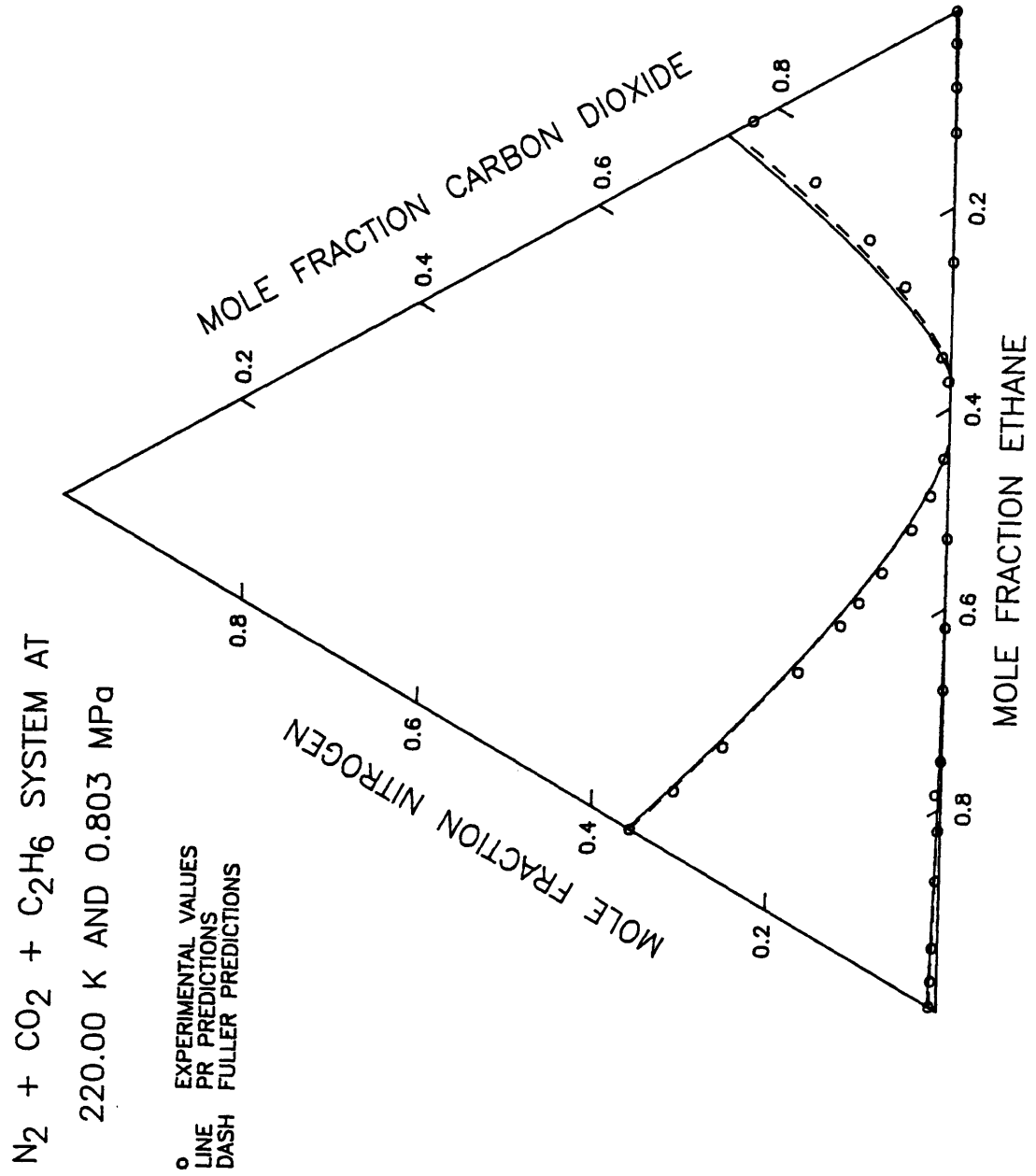
N_2 + CO_2 + C_2H_6 SYSTEM AT
220.00 K AND 0.803 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION NITROGEN
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 19

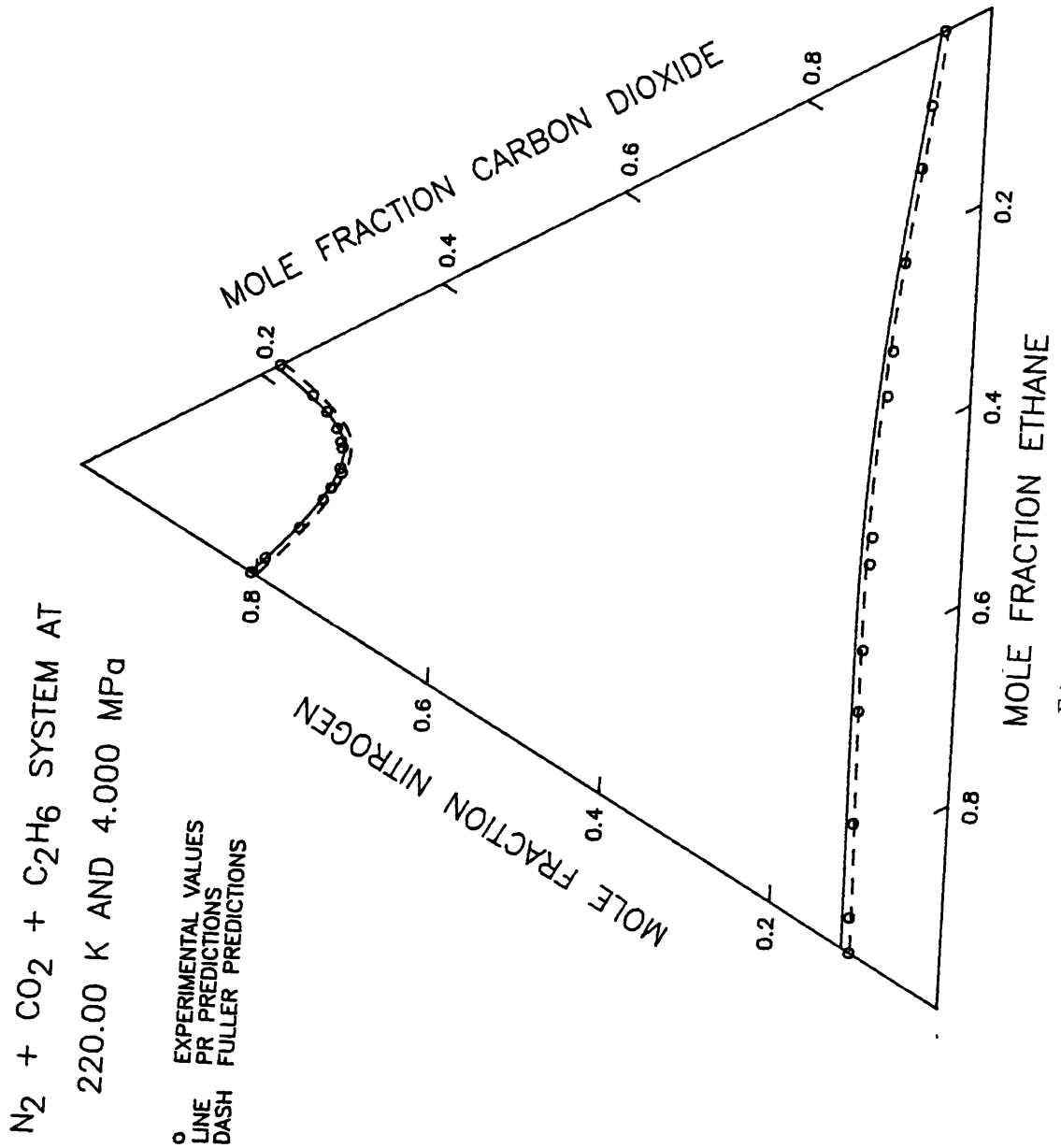
N_2 + CO_2 + C_2H_6 SYSTEM AT
220.00 K AND 4.000 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION NITROGEN
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 20

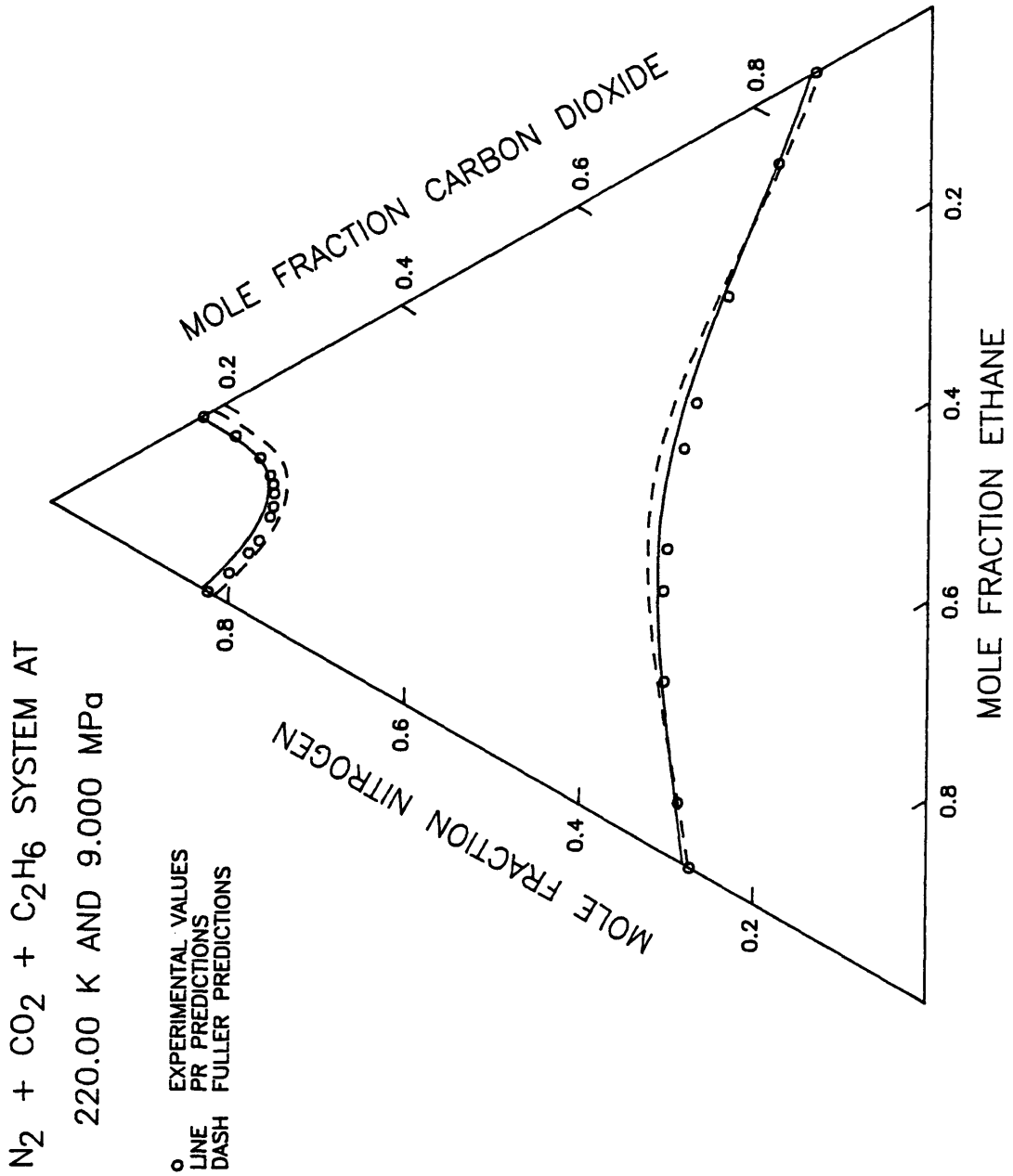
N_2 + CO_2 + C_2H_6 SYSTEM AT
220.00 K AND 9.000 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION NITROGEN
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 21

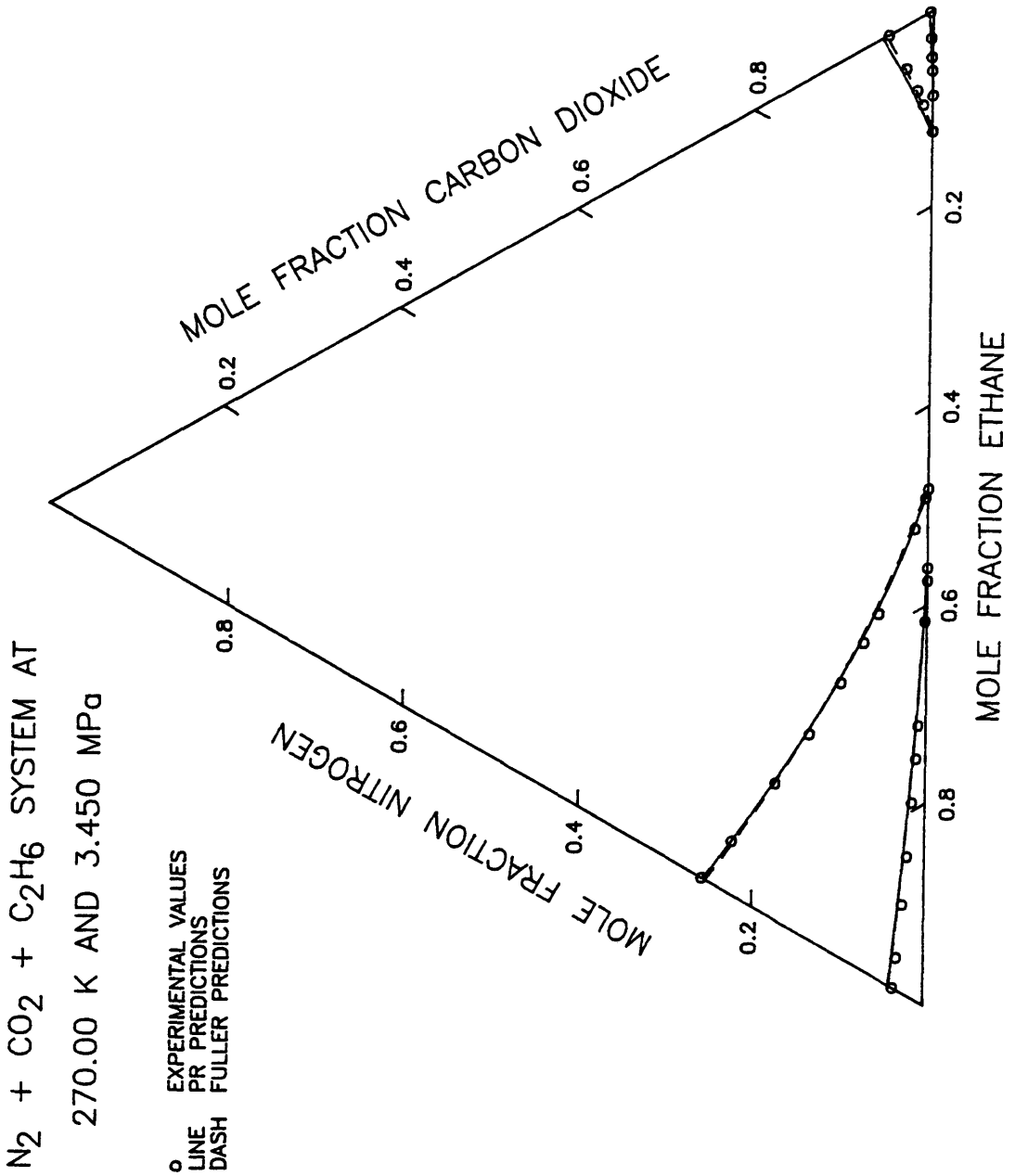
N_2 + CO_2 + C_2H_6 SYSTEM AT
270.00 K AND 3.450 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION NITROGEN
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 22

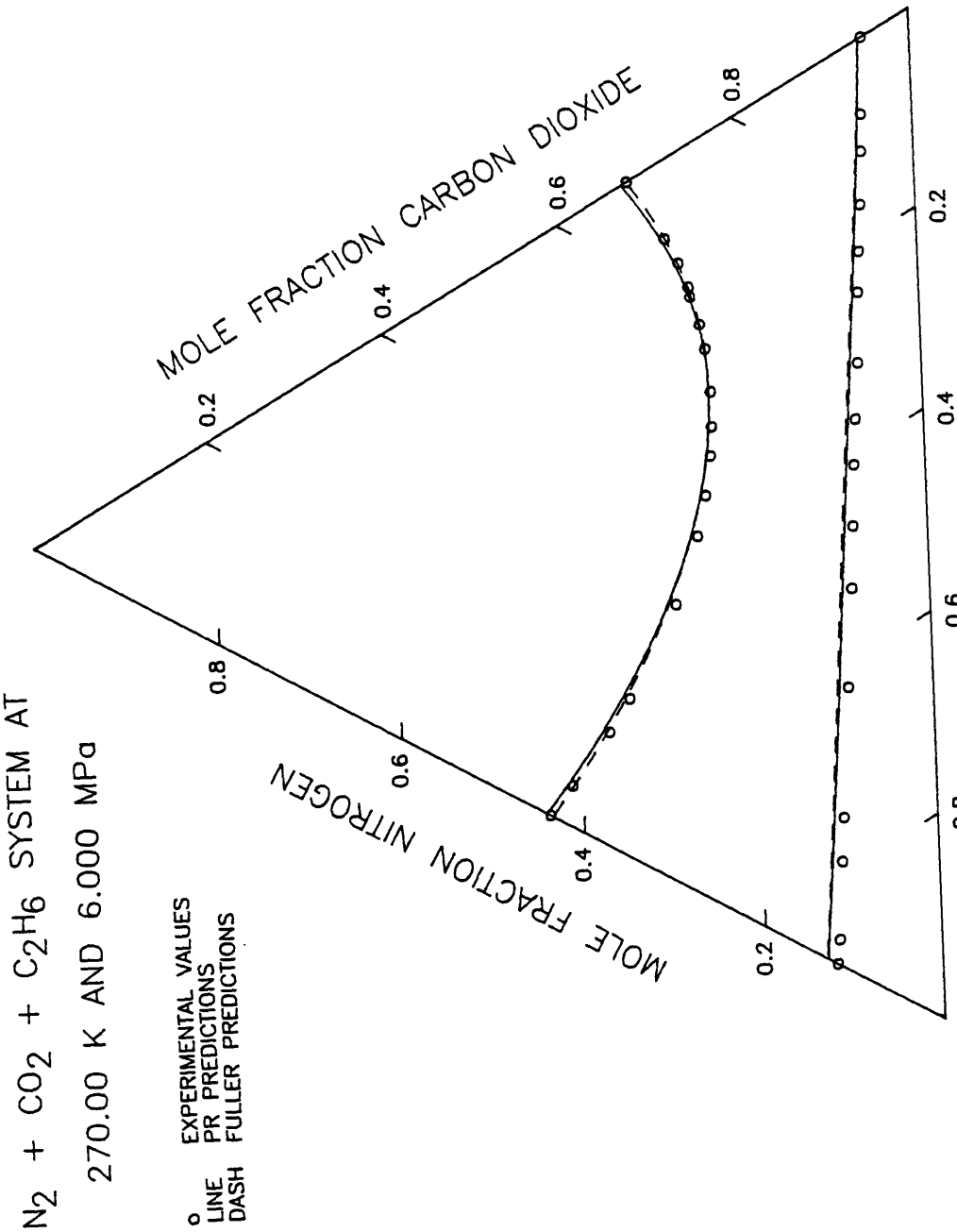
N_2 + CO_2 + C_2H_6 SYSTEM AT
270.00 K AND 6.000 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION NITROGEN
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 23

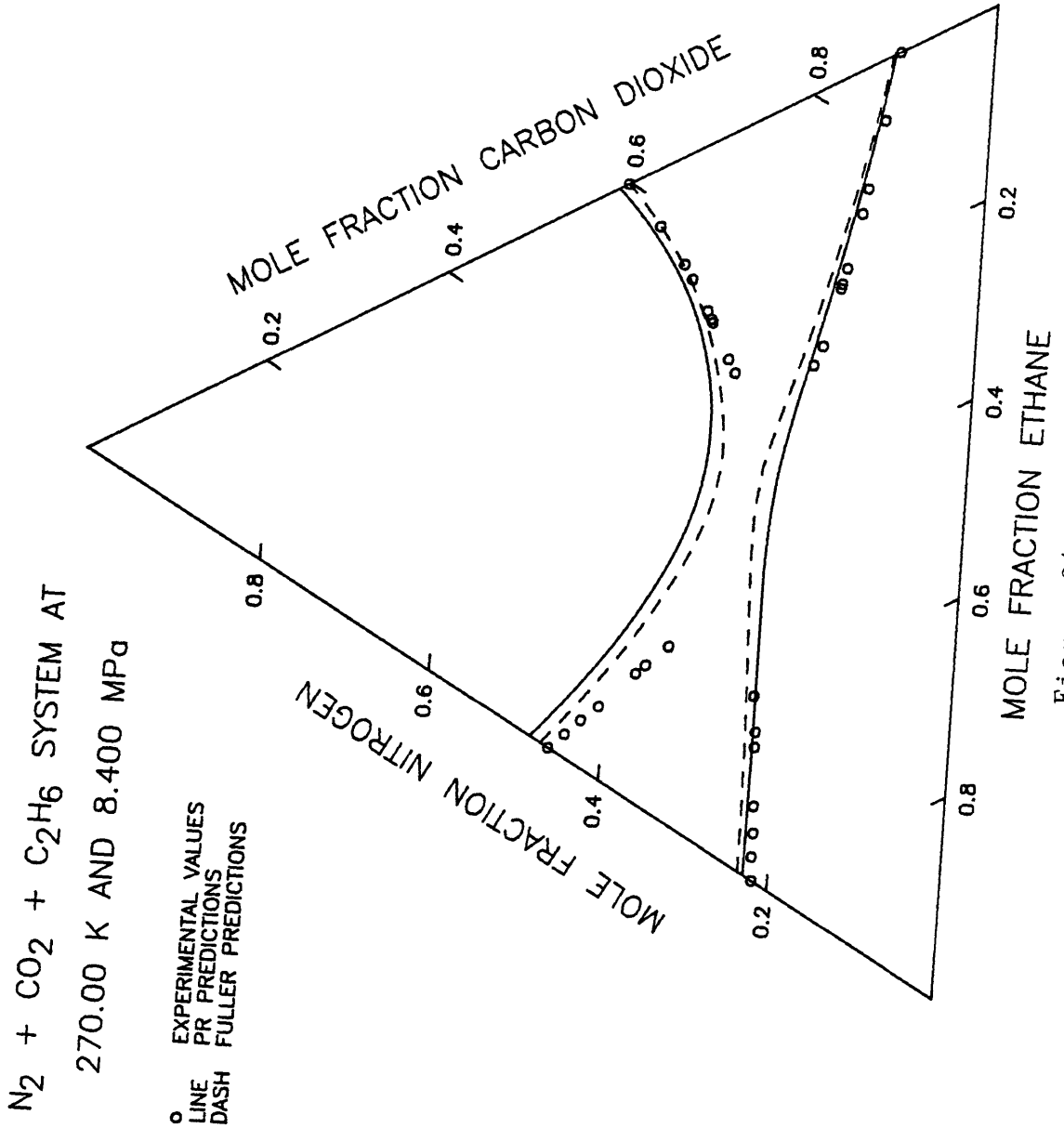
N_2 + CO_2 + C_2H_6 SYSTEM AT
270.00 K AND 8.400 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION NITROGEN
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 24

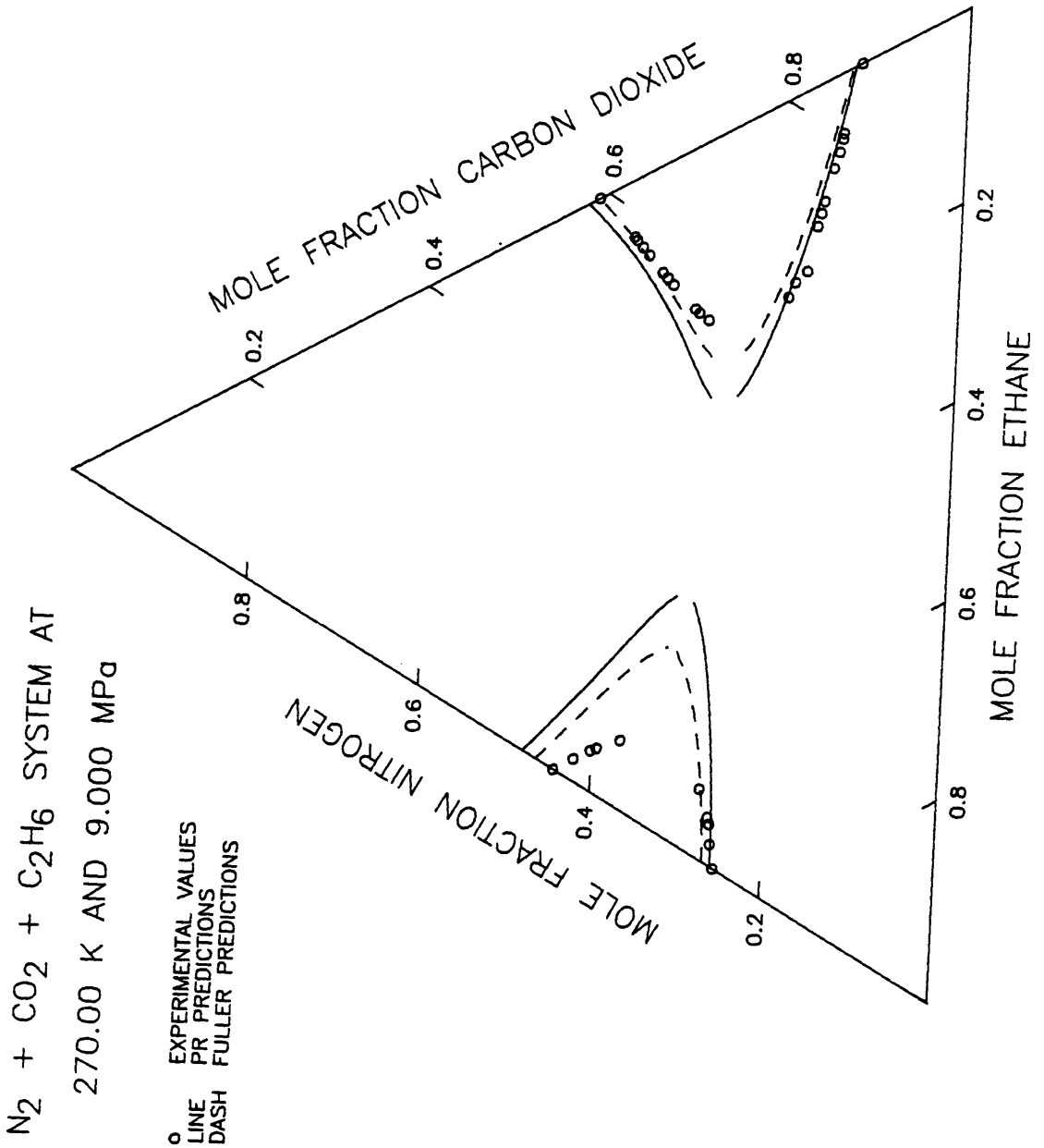
N_2 + CO_2 + C_2H_6 SYSTEM AT
270.00 K AND 9.000 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION NITROGEN
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 25

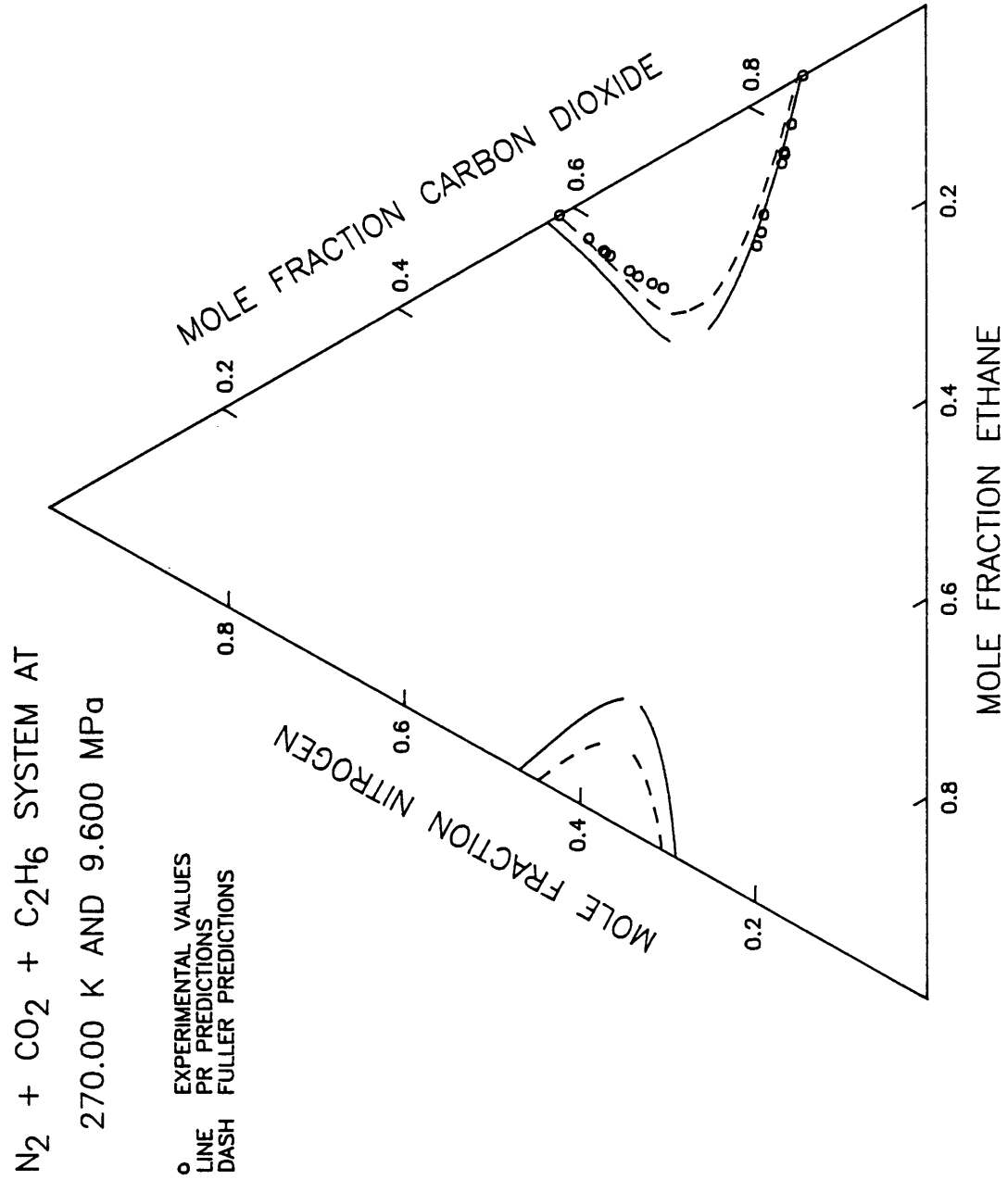
N_2 + CO_2 + C_2H_6 SYSTEM AT
270.00 K AND 9.600 MPa
o EXPERIMENTAL VALUES
LINE PR PREDICTIONS
DASH FULLER PREDICTIONS
MOLE FRACTION NITROGEN
MOLE FRACTION CARBON DIOXIDE
MOLE FRACTION ETHANE
0.2
0.4
0.6
0.8

Figure 26

MODELING OF VLE DATA

In vapor-liquid equilibria, the criteria for equilibrium are that the temperature, pressure, and fugacity of any component must be the same in each phase. If an equation of state is used to model both phases, then each fugacity can be expressed with fugacity coefficients. That is,

$$y_i \phi_i^v = x_i \phi_i^l \qquad \text{or} \qquad y_i = K_i x_i \tag{1}$$

The Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Fuller equations of state have been chosen to calculate the fugacity coefficients in this study.

Soave-Redlich-Kwong Equation of State

The SRK equation, proposed by Soave (1972), is

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b)} \tag{2}$$

For a pure component i,

$$b_i = 0.08664 RT_c/P_c \tag{3}$$

$$a_i(T_c) = 0.42747(RT_c)^2/P_c \tag{4}$$

$$a_i(T) = \alpha a_i(T_c) \tag{5}$$

$$\alpha = \{1 + m[1 - (T_r)^{0.5}]\}^2 \tag{6}$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \tag{7}$$

R = gas constant

T_c = critical temperature

P_c = critical pressure

ω = accentric factor

The standard linear mixing rule for b and quadratic mixing rule for a with one binary interaction parameter were used.

$$b = \sum_i x_i b_i \tag{8}$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{9}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{10}$$

An equation for the fugacity coefficients can be derived using the following rigorous thermodynamic equation.

$$RT\ln(\phi_i) = \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - RT\ln(Z) \tag{11}$$

Combining this equation with the equation of state and the mixing rules yields

$$\ln(\phi_i) = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{B}\ln(1 + B/Z)* \left[(2 \sum_j x_j a_{ij})/a - b_i/b\right] \tag{12}$$

$$A = aP/(RT)^2 \tag{13}$$

$$B = bP/(RT) \tag{14}$$

$$Z = Pv/(RT) \tag{15}$$

ϕ_i = fugacity coefficient (16)

Peng-Robinson Equation of State

The PR equation, proposed by Peng and Robinson (1974), is given by

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{17}$$

For a pure component i,

$$b_i = 0.07780RT_c/P_c \tag{18}$$

$$a_i(T_c) = 0.45724(RT_c)^2/P_c \tag{19}$$

$$a_i(T) = \alpha a_i(T_c) \tag{20}$$

$$\alpha = \{1 + m[1 - (T_r)^{1/2}]\}^2 \tag{21}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{22}$$

Application of equation 11 to the PR equation with the standard mixing rules for a and b given above results in the following equation for the fugacity coefficient.

$$\ln(\phi_i) = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{2B\sqrt{2}}* \left[\left(2 \sum_j x_j a_{ij}\right)/a - \frac{b_i}{b}\right] \ln\left[\frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B}\right] \tag{23}$$

Fuller Equation of State

Fuller (1976) proposed a modified SRK equation of state containing three parameters as given below.

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + bc)} \tag{24}$$

The three parameters a, b, and c are parametrized in terms of a single temperature dependent variable which is defined at the critical point as

$$\beta_c = b/v_c \tag{25}$$

Equations for the parameters can be derived by requiring that the first and second derivatives of pressure with respect to volume be zero at the critical point and that the equation of state give the correct critical compressibility factor. The resulting equations are

$$c(\beta) = [(1/\beta - 0.75)^{1/2} - 1.5] \tag{26}$$

$$b(\beta) = \Omega_b(\beta)RT_c/P_c \tag{27}$$

$$\Omega_b(\beta) = \frac{(1 - \beta)(2 + c\beta) - (1 + c\beta)}{(2 + c\beta)(1 - \beta)^2} \tag{28}$$

$$a_i(T) = \Omega_a(\beta)R^2T_c\alpha/P_c \tag{29}$$

$$\Omega_a(\beta) = \frac{(1 + c\beta)^2\Omega_b(\beta)}{(1 - \beta)^2(2 + c\beta)} \tag{30}$$

$$\alpha = \{1 + q(\beta)[1 - (T_r)^{1/2}]\}^2 \tag{31}$$

$$q(\beta) = m(\beta/0.26)^{\frac{1}{4}} \tag{32}$$

$$m = 0.480 + 1.5740\omega - 0.176\omega^2 \tag{33}$$

$$Z_c = \frac{(1 - \beta_c)(2 + c_c\beta_c) - (1 + c_c\beta_c)}{(2 + c_c\beta_c)(1 - \beta_c)^2} \tag{34}$$

β was correlated against the critical compressibility factor and the parachor to minimize differences between calculated and experimental saturated-liquid volumes. The

resulting generalized correlations are

$$\beta = \beta_c + (\beta_o - \beta_c)\left\{\frac{2}{1 + \exp[\theta(T_r - 1)]} - 1\right\} \tag{35}$$

$$\beta_o/\beta_c = 7.7880 - 36.8316Z_c + 50.7061Z_c^2 \tag{36}$$

$$\theta = 10.9356 + 0.0285\overline{P} \tag{37}$$

v_c = critical volume

Z_c = critical compressibility factor

$\overline{P}$ = parachor

Quayle (1953) has tabulated the parachors of several hundred organic compounds and outlined a group contribution method to calculate the parachor of any compound.

The third parameter, c, only occurs in conjunction with b. Hence, the following mixing rule was used for c.

$$bc = \sum_i x_i b_i c_i \tag{38}$$

Equations 8-10 were used as the mixing rules for a and b. With these mixing rules, the equation of state, and equation 11, the fugacity coefficient equation is

$$\ln(\phi_i) = \ln\left(\frac{v}{v - b}\right) + \frac{b_i}{v - b} - \frac{ab_ic_i}{RTbc(v + bc)} - \ln(Z) + [(2\sum_j x_j a_{ij})/(RTbc) - ab_ic_i/(bc)^2]* \ln\left(\frac{v}{v + bc}\right) \tag{39}$$

The addition of a third parameter to the equation of state plus the additional temperature dependence introduced greatly improves the calculation of saturated liquid volumes while maintaining good vapor pressure predictions compared to the SRK equation. Since the equation of state is forced to fit at the critical point, it should be more accurate in the critical region for vapor-liquid equilibria calculations than either the SRK or PR equations.

Parameter Estimation

The phase equilibria models in use today require one or more interaction parameters that are fit to binary data. Therefore, determining the parameters that best fit the data is very important. Unfortunately, the best fit is not an absolute concept, and several different criteria have been used. The binary interaction parameters reported in this work were determined using the maximum likelihood method for implicit constraints as described by Neisen (1986). This method allows all of the measured variables, temperature, pressure, and liquid and vapor compositions, to vary. The objective of the method is to minimize the function

$$S = \sum \left[\left(\frac{T_{act} - T_{cal}}{\sigma_T} \right)^2 + \left(\frac{P_{act} - P_{cal}}{\sigma_P} \right)^2 + \left(\frac{x_{act} - x_{cal}}{\sigma_x} \right)^2 + \left(\frac{y_{act} - y_{cal}}{\sigma_y} \right)^2 \right] \quad (40)$$

with respect to the independent variables temperature and liquid mole fraction and the interaction parameters subject to the equilibrium constraints

$$F = y_1 - K_1 x_1 = 0 \tag{41}$$

$$G = y_2 - K_2 x_2 = 0 \tag{42}$$

In equation 40, σ_T, σ_P, σ_x, and σ_y are the estimated variances of the experimental data, and the sum is over all experimental points. The variables with the "act" subscripts are estimates of the actual values. A variance, s^2, for each model was calculated from

$$s^2 = S/(N - L) \tag{43}$$

N = number of data points

L = number of fitting parameters in the model

A computer program that implements the maximum likelihood method is given in Appendix C. The program will converge to the same value for the interaction parameter with any reasonable first guess. If no information about the interaction parameter is known, a guess of zero will work well. However, the method overpredicts the corrections to be made to the parameter if the initial guess is too far off. Therefore, the program takes reduced steps initially, and increases the steps with each iteration.

At each iteration, derivatives of the two constraints must be calculated with respect to temperature, pressure,

each parameter, and liquid and vapor mole fractions. These derivatives are all calculated numerically with a five point formula given below.

$$(\partial F/\partial x) = [2F(x+2\Delta x) - 16F(x+\Delta x) + 16F(x-\Delta x) - 2F(x-2\Delta x)]/(24\Delta x) \quad (44)$$

MODELING RESULTS

The binary data were used to fit binary interaction parameters, and these parameters were used with an isothermal flash program to generate the predictions. The critical properties used in the modeling are presented in Table 4. To avoid biasing the fit toward one section of an isotherm and to keep computation time at a reasonable level, approximately ten evenly spaced data points from each isotherm were used to fit the interaction parameters. The interaction parameters for each of the binary systems and the corresponding calculated deviations for the three equations of state are presented in Tables 5-7.

It is clear from the calculated deviations in Tables 5-7 that the SRK equation gives the poorest fit to the binary data for the nitrogen-carbon dioxide and nitrogen-ethane systems and a roughly equivalent fit to the PR and the Fuller equations for the carbon dioxide-ethane system. For this reason, only predictions for the PR and Fuller equations are shown. The direct comparison of these equations is useful in determining whether the slightly greater complexity of the Fuller equation results in significantly better predictions.

Table 4

Properties of Nitrogen, Carbon Dioxide, and Ethane

Property	Nitrogen	Carbon Dioxide	Ethane
T_c (K)	126.2	304.1	305.42
P_c (MPa)	3.394	7.375	4.88
Z_c	0.290	0.274	0.285
ω	0.040	0.239	0.099
Parachor	75.6	100.0	110.5

Critical properties reference - Ambrose, D., 1980

Parachor reference - Quayle, O. R., 1953

TABLE 5

Interaction Parameters for the Soave-Redlich-Kwong Equation

System	Temperature (K)	Model	# of points	Interaction Parameter	s^2
CO_2-C_2H_6	207.00	k_{12}	5	0.1533	44.46
	210.00	k_{12}	7	0.1462	65.78
	220.00	k_{12}	9	0.1415	19.54
	223.15	k_{12}	8	0.1386	38.88
	230.00	k_{12}	9	0.1416	16.84
	243.15	k_{12}	9	0.1342	12.94
	250.00	k_{12}	9	0.1378	10.97
	263.15	k_{12}	9	0.1349	11.44
	270.00	k_{12}	9	0.1347	4.16
	283.15	k_{12}	9	0.1343	2.94
	293.15	k_{12}	6	0.1353	5.78
	207.00-270.00	k_{12}	74	0.1412	40.16
	207.00-270.00	A+B/T	74	A = 0.08217 B = 13.58	23.96
N_2-CO_2	220.00	k_{12}	10	-0.0306	33.15
	270.00	k_{12}	11	-0.0209	44.42
	220.00-270.00	k_{12}	21	-0.0290	37.84
N_2-C_2H_6	220.00	k_{12}	17	0.0200	73.86
	260.00	k_{12}	5	0.0110	302.80
	270.00	k_{12}	6	-0.0051	544.43
	220.00-270.00	k_{12}	28	0.0169	194.25

TABLE 6

Interaction Parameters for the Peng-Robinson Equation

System	Temperature (K)	Model	# of points	Interaction Parameter	s^2
CO_2-C_2H_6	207.00	k_{12}	5	0.1464	41.90
	210.00	k_{12}	7	0.1402	62.06
	220.00	k_{12}	9	0.1365	24.33
	223.15	k_{12}	8	0.1338	47.30
	230.00	k_{12}	9	0.1375	26.27
	243.15	k_{12}	9	0.1314	20.57
	250.00	k_{12}	9	0.1351	25.84
	263.15	k_{12}	9	0.1319	10.08
	270.00	k_{12}	9	0.1314	3.12
	283.15	k_{12}	9	0.1278	1.55
	293.15	k_{12}	6	0.1273	4.50
	207.00-270.00	k_{12}	74	0.1366	37.01
	207.00-270.00	A+B/T	74	A = 0.09347 B = 9.938	27.56
N_2-CO_2	220.00	k_{12}	10	-0.0152	27.14
	270.00	k_{12}	11	-0.0100	26.76
	220.00-270.00	k_{12}	21	-0.0143	25.85
N_2-C_2H_6	220.00	k_{12}	17	0.0286	48.61
	260.00	k_{12}	5	0.0208	168.79
	270.00	k_{12}	6	0.0029	470.23
	220.00-270.00	k_{12}	28	0.0254	146.99

TABLE 7

Interaction Parameters for the Fuller Equation

System	Temperature (K)	Model	# of points	Interaction Parameter	s^2
CO_2-C_2H_6	207.00	k_{12}	5	0.1527	45.61
	210.00	k_{12}	7	0.1456	67.46
	220.00	k_{12}	9	0.1410	19.48
	223.15	k_{12}	8	0.1381	38.64
	230.00	k_{12}	9	0.1412	17.55
	243.15	k_{12}	9	0.1342	13.77
	250.00	k_{12}	9	0.1379	13.38
	263.15	k_{12}	9	0.1354	9.66
	270.00	k_{12}	9	0.1356	2.87
	283.15	k_{12}	9	0.1343	2.94
	293.15	k_{12}	6	0.1334	4.28
	207.00-270.00	k_{12}	74	0.1409	38.22
	207.00-270.00	A+B/T	74	A = 0.08717 B = 12.38	24.51
N_2-CO_2	220.00	k_{12}	10	-0.0610	32.16
	270.00	k_{12}	11	-0.0398	3.06
	220.00-270.00	k_{12}	21	-0.0582	20.57
N_2-C_2H_6	220.00	k_{12}	17	0.0075	10.26
	260.00	k_{12}	5	0.0160	74.17
	270.00	k_{12}	6	-0.0022	428.38
	220.00-270.00	k_{12}	28	0.0075	98.38

Carbon Dioxide-Ethane Binary System

Because of the excellent agreement between the data of Fredenslund and Mollerup and this study, the two data sets were used together to fit interaction parameters. Three different approaches were used to fit the interaction parameters. First, each isotherm was fit separately. Second, all of the isotherms between 207 and 270 K were fit with a constant interaction parameter. Third, the isotherms between 207 and 270 K were fit to a temperature dependent interaction parameter given by

$$k_{ij} = A + B/T \qquad T \text{ in } K \tag{45}$$

Typical differences between calculated and experimental variables were:

pressure	± 0.3%
temperature	± 0.02 K
liquid mole fraction	± 0.005
vapor mole fraction	± 0.005

With these values, the calculated deviation, s^2, would be approximately 22.

Figure 27 shows the interaction parameters as a function of temperature for the PR equation, and also shows the interaction parameters determined by Holste, et al. (1982). Since Holste, et al. obtained their values from measurements of interaction second virial coefficients, it is not to be expected that that their values would be numerically the same as those obtained with the Peng-

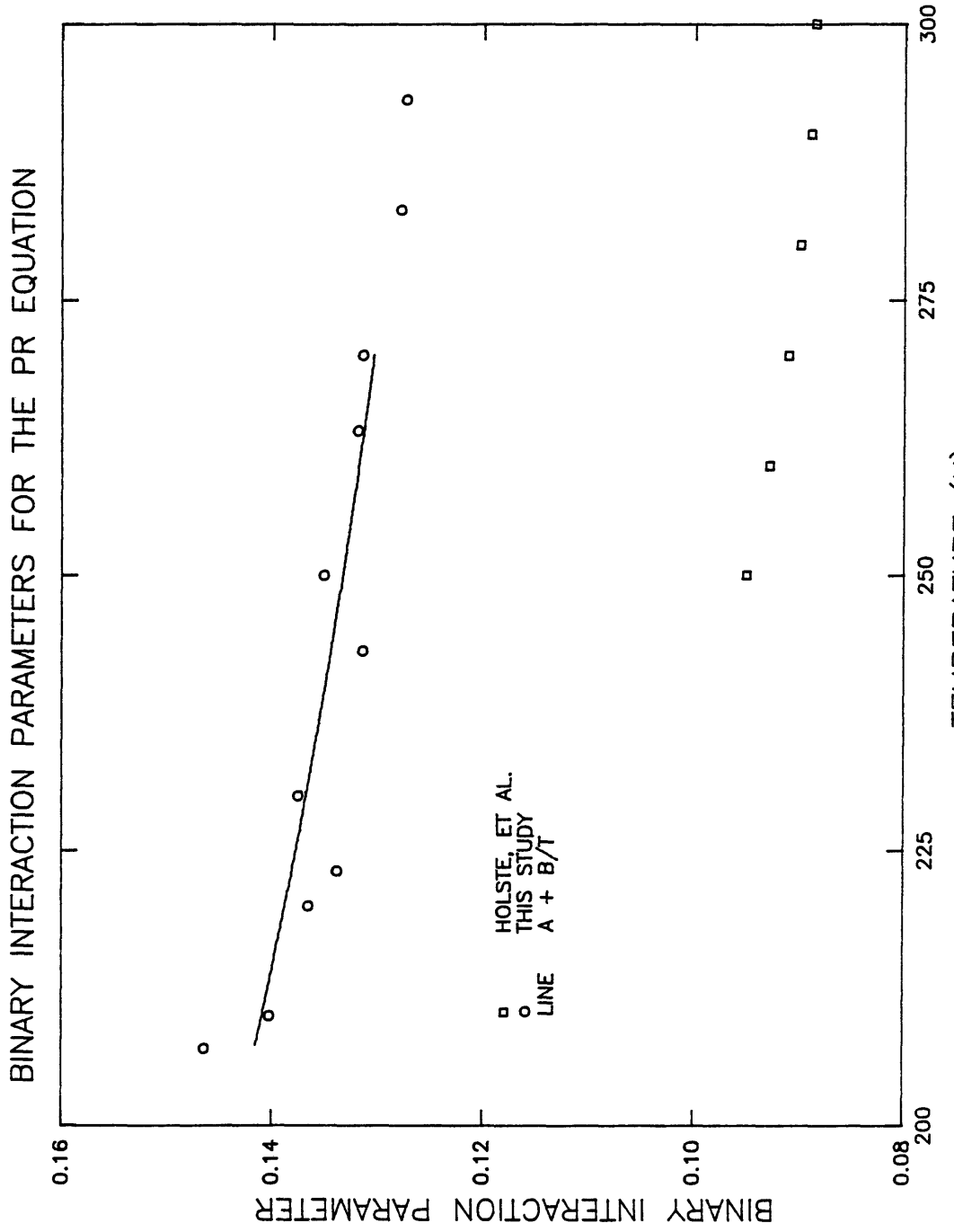
BINARY INTERACTION PARAMETERS FOR THE PR EQUATION
BINARY INTERACTION PARAMETER
TEMPERATURE (K)
0.16
0.14
0.12
0.10
0.08
200
225
250
275
300
HOLSTE, ET AL.
THIS STUDY
LINE A + B/T

Figure 27

Robinson equation. What is interesting, however, is that all of the data indicate a marked temperature dependence for k_{ij}. This is quite significant, since as pointed out by Holste, et al. "A knowledge of the correct temperature dependence for k_{ij} can have a profound effect on the results of many useful correlations, and thus on the design of units based upon such correlations."

The average interaction parameter does a reasonably good job of fitting the data, but based on an F-test using s as the variance of the models, the temperature-dependent interaction parameter is better at a confidence level of approximately 90% for all three equations. Therefore, the temperature-dependent model was used to calculate the phase equilibria in both the binary and ternary systems.

The binary calculations were made with an isothermal flash program, and the results for the carbon dioxide-ethane system are presented in Figures 4-11. All three equations gave basically the same predictions, so only the PR results are shown. The fit of the equations to the data is excellent at high temperatures, but gets progressively worse as the temperature decreases. At 207 and 210 K, below the triple point of carbon dioxide, the fit is relatively poor. This may be because only a partial isotherm exists at these conditions or because the interactions between the molecules

become greater and more difficult to predict at low temperatures.

Nitrogen-Carbon Dioxide System

The two isotherms for the nitrogen-carbon dioxide system were fit individually and simultaneously. The average k_{ij} was used in the binary and ternary predictions. The binary results are presented in Figures 14 and 15. At 220 K where no critical point exists, the fit is good even up to very high pressures, but at 270 K, the equations cannot fit the critical region.

Nitrogen-Ethane System

Again, the three isotherms for the nitrogen-ethane system were fit individually and simultaneously, and the average value was used in all of the predictions. The large deviations at 270 K result from the use of data very close to the critical point to fit the k_{ij}. As can be seen in Figures 16-18, the equations overpredict the critical region. It is possible to force a better fit in the critical region by adjusting the k_{ij}, but this can only be done by sacrificing accuracy in the low pressure region.

Nitrogen-Carbon Dioxide-Ethane System

The ternary phase equilibria were calculated with an isothermal, ternary flash program. This program is capable

of generating large numbers of data points to generate the predicted curves of Figures 19-26.

The PR equation does well in almost every case. It predicts the correct curvature for both the liquid and vapor phases, but it cannot accurately predict the critical region. At 270 K and 8.4 MPa, the PR equation predicts one continuous region of vapor-liquid equilibria, but the data show two separate phase envelopes with a single-phase region between them. At 270 K and 9.0 MPa, the predictions are qualitatively correct, but the predicted critical region is too large on both sides of the diagram. At 270 K and 9.6 MPa, the equation predicts a two phase region on the nitrogen-ethane side of the diagram where none exists.

In most cases, the predictions for the Fuller and PR equations are of equal accuracy. However, there are two notable differences. First, the Fuller equation cannot predict the critcal region well, but it does better than the PR equation. Second, at 220 K and 9.0 MPa, the Fuller equation accurately predicts the binary points for the liquid phase, but the ternary predictions are too high in nitrogen concentration.

CONCLUSIONS

Based upon vapor pressure measurements, comparisons with the data of other investigators, and the degree of scatter in the data, it can be concluded that an accurate, consistent set of binary and ternary vapor-liquid equilibria data for the system nitrogen-carbon dioxide-ethane has been obtained.

The SRK, PR, and Fuller equations gave comparable results for the carbon dioxide-ethane system for both the constant and temperature-dependent interaction parameter. For the nitrogen-carbon dioxide and nitrogen-ethane systems, the Fuller equation was best, and the SRK equation was poorest.

The Peng-Robinson equation of state with one binary interaction parameter adequately models the data except in the critical region. However, it is recommended that a temperature-dependent interaction parameter be used for the carbon dioxide system. Also, the mixing rules with just the binary interaction parameters modeled the ternary data very well, and only failed to provide accurate predictions in regions where the fit to the binary data was poor.

The Fuller equation does better than the PR equation in predicting the critical region of both the binary and ternary systems. However, in one instance (220 K and 9.0

MPa), the Fuller equation accurately predicted the liquid phase of the binaries, but inaccurately predicted the ternary data. It may be necessary to use a density-dependent mixing rule to model the high-pressure phase behavior even if the conditions are well removed from the critical point.

Overall, the Fuller equation represents an improvement over the SRK and PR equations. The cost of this improvement is the need for critical compressibilities and parachors as input to the equation. For the components found in natural gas, this is not a serious problem because accurate data for these two properties are readily available. In general, however, critical compressibilities are not known accurately. Therefore, the improved results obtained with the Fuller equation justify its use for natural gas systems, but it may not be practical for more complex systems.

RECOMMENDATIONS

With the visual cell, it should be possible to make better solid-liquid-vapor measurements. Future work should take advantage of this fact to study the solid-liquid-vapor equilibria of systems containing carbon dioxide and the light hydrocarbons. Particular attention should be given to the carbon dioxide-ethane system to complete measurements over the entire temperature range for which vapor-liquid equilibria exists for this system.

The modeling results indicate that current predictive methods such as the Peng-Robinson equation are adequate in most temperature and pressure ranges. However, further work needs to be done in the development of equations of state and mixing rules that can better model the critical region.

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APPENDIX A

Pressure Gauge Calibrations

Table 8

Calibration of 100 psia Hiese Pressure Gauge

Date of Calibration: March 26, 1986

Claimed Accuracy of Gauge: 0.1 psia

Standard: Ruska Air Dead Weight Tester

Measured Pressure (psia)	Standard Pressure (psia)	Error (Measured-Standard)
14.03	14.04	-0.01
20.00	20.03	-0.03
29.98	30.02	-0.04
39.95	49.90	-0.06
49.90	50.00	-0.10
59.90	59.99	-0.09
69.90	69.98	-0.08
79.85	79.97	-0.12
89.95	89.96	-0.11

Table 9

Calibration of 500 psia Hiese Pressure Gauge

Date of Calibration: March 26, 1986

Claimed Accuracy of Gauge: 0.5 psia

Standard: Ruska Air Dead Weight Tester

Measured Pressure (psia)	Standard Pressure (psia)	Error (Measured-Standard)
13.9	13.99	-0.09
63.8	63.94	-0.14
113.8	113.89	-0.09
164.0	163.84	+0.16
214.0	213.79	+0.21
263.5	263.73	-0.23
313.5	313.68	-0.18
363.5	363.63	-0.13
413.8	413.58	+0.22
493.7	493.50	+0.20

Table 10

Calibration of 100 atm Hiese Pressure Gauge

Date of Calibration: March 27, 1986

Claimed Accuracy of Gauge: 0.1 atm

Standard: Ruska Air Dead Weight Tester

Measured Pressure (atm)	Standard Pressure (atm)	Error (Measured-Standard)
0.94	0.95	-0.01
4.34	4.35	-0.01
7.74	7.75	-0.01
11.14	11.15	-0.01
14.54	14.55	-0.01
17.98	17.95	+0.03
21.36	21.35	+0.01
24.78	24.74	+0.04
28.16	28.14	+0.02
31.56	31.54	+0.02
34.98	34.94	+0.04
38.36	38.34	+0.02
40.42	40.38	+0.04

Table 11

Calibration of 2500 psia Hiese Pressure Gauge

Date of Calibration: March 27, 1986

Claimed Accuracy of Gauge: 2.5 psia

Standard: Ruska Air Dead Weight Tester

Measured Pressure (psia)	Standard Pressure (psia)	Error (Measured-Standard)
13.8	14.00	-0.2
63.6	63.95	-0.4
113.4	113.90	-0.5
163.4	163.85	-0.5
213.6	213.80	-0.2
263.4	263.75	-0.4
312.8	313.70	-0.9
362.8	363.65	-0.9
413.2	413.60	-0.4
463.2	463.55	-0.4
512.4	513.50	-1.1
562.0	563.45	-1.4
592.6	593.42	-0.8

APPENDIX B

Experimental Data

Table 13

CO_2-C_2H_6 System at 207.00 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
0.2943	0.0000	1.0000	0.0000	1.0000
0.3292	0.0229	0.9771	0.1226	0.8774
0.3462	0.0392	0.9608	0.1760	0.8240
0.3597	0.0529	0.9471	0.2178	0.7822
0.3832	0.0828	0.9172	0.2806	0.7194
0.3970	0.1053	0.8947	0.3162	0.6838
0.4052	0.1166	0.8834	0.3372	0.6628
0.4262	0.1572	0.8428	0.3881	0.6119
0.4342	0.1755	0.8245	0.4055	0.5945
0.4507	0.2276	0.7724	0.4474	0.5526
0.4586	0.2635	0.7365	0.4650	0.5350
0.4632	0.2848	0.7152	0.4799	0.5201
0.4728	0.3572	0.6428	0.5088	0.4912

Table 14

CO_2-C_2H_6 System at 210.00 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
0.3334	0.0000	1.0000	0.0000	1.0000
0.3680	0.0207	0.9793	0.1084	0.8916
0.3939	0.0438	0.9562	0.1816	0.8184
0.4242	0.0760	0.9240	0.2594	0.7406
0.4397	0.0932	0.9068	0.2931	0.7069
0.4786	0.1584	0.8416	0.3772	0.6228
0.4915	0.1867	0.8133	0.4076	0.5924
0.5140	0.2572	0.7428	0.4576	0.5424
0.5282	0.3198	0.6802	0.4928	0.5072
0.5414	----	----	0.5388	0.4612
0.5455	0.4810	0.5190	0.5520	0.4480
0.5447	0.6918	0.3082	0.6085	0.3915
0.5410	0.7485	0.2515	0.6287	0.3713

Table 15

CO_2-C_2H_6 System at 220.00 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
0.491	0.0000	1.0000	0.0000	1.0000
0.522	0.0150	0.9850	0.0706	0.9294
0.548	0.0317	0.9683	0.1239	0.8761
0.579	0.0532	0.9468	0.1846	0.8154
0.613	0.0812	0.9188	0.2418	0.7582
0.660	0.1332	0.8668	0.3178	0.6822
0.686	0.1608	0.8392	0.3592	0.6408
0.720	0.2186	0.7814	0.4120	0.5880
0.742	0.2564	0.7436	0.4454	0.5546
0.765	0.3190	0.6810	0.4850	0.5150
0.780	0.3693	0.6307	0.5114	0.4886
0.796	0.4631	0.5369	0.5518	0.4482
0.803	0.5641	0.4359	0.5866	0.4134
0.802	0.6552	0.3448	0.6186	0.3814
0.788	0.7782	0.2218	0.6692	0.3308
0.763	0.8572	0.1428	0.7195	0.2805
0.736	0.9035	0.0965	0.7668	0.2332
0.700	0.9428	0.0572	0.8247	0.1753
0.654	0.9772	0.0228	0.9006	0.0994
0.598	1.0000	0.0000	1.0000	0.0000

Table 16

CO_2-C_2H_6 System at 223.15 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
0.550	0.0000	1.0000	0.0000	1.0000
0.621	0.0401	0.9599	0.1368	0.8632
0.741	0.1386	0.8614	0.3210	0.6790
0.817	0.2346	0.7654	0.4229	0.5771
0.858	0.3209	0.6791	0.4820	0.5180
0.894	0.4662	0.5338	0.5522	0.4478
0.900	0.5406	0.4594	0.5812	0.4188

Table 17

CO_2-C_2H_6 System at 230.00 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
0.699	0.0000	1.0000	0.0000	1.0000
0.833	0.0681	0.9319	0.1910	0.8090
0.895	0.1106	0.8894	0.2670	0.7330
0.965	0.1712	0.8288	0.3482	0.6518
1.038	0.2538	0.7462	0.4280	0.5720
1.098	0.3605	0.6395	0.5022	0.4978

Table 18

CO_2-C_2H_6 System at 250.00 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
1.302	0.0000	1.0000	0.0000	1.0000
1.435	0.0424	0.9576	0.1092	0.8908
1.550	0.0865	0.9135	0.1944	0.8056
1.692	0.1489	0.8511	0.2885	0.7115
1.867	0.2501	0.7499	0.3988	0.6012
1.973	0.3373	0.6627	0.4688	0.5312
2.024	0.3922	0.6078	0.5058	0.4942
2.110	0.5344	0.4656	0.5930	0.4070

Table 19

CO_2-C_2H_6 System at 263.15 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
1.860	0.0000	1.0000	0.0000	1.0000
2.017	0.0388	0.9612	0.0895	0.9105
2.058	0.0512	0.9488	0.1105	0.8895
2.312	0.1293	0.8707	0.2360	0.7640
2.410	0.1638	0.8362	0.2834	0.7166
2.457	0.1832	0.8168	0.3035	0.6965
2.641	0.2613	0.7387	0.3824	0.6176
2.654	0.2675	0.7325	0.3928	0.6072
2.770	0.3302	0.6698	0.4456	0.5544
2.894	0.4167	0.5833	0.5118	0.4882
2.999	0.5283	0.4717	0.5760	0.4240

Table 20

CO_2-C_2H_6 System at 270.00 K

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
2.212	0.0000	1.0000	0.0000	1.0000
2.434	0.0517	0.9483	0.1056	0.8944
2.572	0.0858	0.9142	0.1641	0.8359
2.635	0.1036	0.8964	0.1898	0.8102
2.734	0.1332	0.8668	0.2297	0.7703
2.870	0.1751	0.8249	0.2824	0.7176
2.976	0.2116	0.7884	0.3227	0.6773
3.083	0.2527	0.7473	0.3632	0.6368
3.181	0.2931	0.7069	0.4014	0.5986
3.265	0.3328	0.6672	0.4362	0.5638
3.360	0.3819	0.6181	0.4751	0.5249
3.450	0.4412	0.5588	0.5190	0.4810
3.519	0.4967	0.5033	0.5594	0.4406
3.581	0.5616	0.4384	0.6036	0.3964
3.610	0.6076	0.3924	0.6360	0.3640
3.636	0.6893	0.3107	0.6914	0.3086
3.627	0.7392	0.2608	0.7261	0.2739
3.621	0.7690	0.2310	0.7494	0.2506
3.613	0.7783	0.2217	0.7550	0.2450
3.585	0.8182	0.1818	0.7864	0.2136

Table 20 (cont.)

PRESSURE (MPa)	X_{CO_2}	$X_{C_2H_6}$	Y_{CO_2}	$Y_{C_2H_6}$
3.534	----	----	0.8268	0.1732
3.486	0.8940	0.1060	0.8608	0.1392
3.416	0.9328	0.0672	0.9002	0.0998
3.282	0.9797	0.0203	0.9645	0.0355
3.200	1.0000	0.0000	1.0000	0.0000

Table 21

N_2-CO_2 System at 220.00 K

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	Y_{N_2}	Y_{CO_2}
0.492	0.0000	1.0000	0.0000	1.0000
0.803	0.0028	0.9972	0.2296	0.7704
1.373	0.0108	0.9892	0.5174	0.4826
2.457	0.0269	0.9731	0.6971	0.3029
3.774	----	----	0.7737	0.2263
4.000	0.0510	0.9490	0.7815	0.2185
5.993	0.0830	0.9170	0.8150	0.1850
7.485	0.1092	0.8908	0.8262	0.1738
9.004	0.1317	0.8683	0.8265	0.1735
9.098	0.1338	0.8662	0.8264	0.1736
11.995	0.1903	0.8097	0.8080	0.1920

Table 22

N_2-CO_2 Vapor Compositions at 220.00 K

PRESSURE (MPa)	Y_{N_2}	Y_{CO_2}
1.012	0.3715	0.6285
1.094	0.4126	0.5874
1.195	0.4548	0.5452
1.675	0.5920	0.4080
1.751	0.6054	0.3946
1.795	0.6136	0.3864
2.016	0.6479	0.3521
2.363	0.6876	0.3124
3.444	0.7598	0.2402
3.465	0.7610	0.2390
4.029	0.7821	0.2179
5.207	0.8081	0.1919
5.270	0.8094	0.1906
5.313	0.8096	0.1904
5.466	0.8114	0.1886
5.985	0.8182	0.1818
6.746	0.8232	0.1768
7.111	0.8253	0.1747
7.143	0.8250	0.1750
7.151	0.8256	0.1744

Table 22 (cont.)

N_2-CO_2 Vapor Compositions at 220.00 K

Pressure (MPa)	Y_{N_2}	Y_{CO_2}
7.281	0.8255	0.1745
7.310	0.8258	0.1742
7.910	0.8268	0.1732
8.625	0.8266	0.1734
9.198	0.8258	0.1742
10.320	0.8208	0.1792
10.460	0.8199	0.1801
10.894	0.8170	0.1830
11.311	0.8136	0.1864
11.478	0.8118	0.1882
11.968	0.8076	0.1924
12.677	0.7991	0.2009
12.962	0.7964	0.2036

Table 23

N_2-CO_2 System at 270.00 K

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	Y_{N_2}	Y_{CO_2}
3.202	0.0000	1.0000	0.0000	1.0000
3.451	0.0038	0.9962	0.0509	0.9491
4.334	----	----	0.1830	0.8170
4.686	----	----	0.2212	0.7788
5.074	----	----	0.2565	0.7435
5.779	0.0498	0.9502	0.3087	0.6913
5.860	----	----	0.3139	0.6861
6.004	0.0542	0.9458	0.3222	0.6778
6.182	0.0566	0.9434	0.3322	0.6678
6.436	----	----	0.3456	0.6544
7.165	0.0770	0.9230	0.3747	0.6253
7.289	----	----	0.3785	0.6215
7.546	0.0861	0.9139	0.3879	0.6121
7.766	----	----	0.3930	0.6070
8.289	0.1055	0.8945	0.4049	0.5951
8.392	0.1070	0.8930	0.4055	0.5945
8.476	0.1090	0.8910	0.4095	0.5905
8.991	0.1206	0.8794	0.4137	0.5863
9.001	0.1230	0.8770	0.4148	0.5852
9.283	----	----	0.4176	0.5824

Table 23 (cont.)

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	Y_{N_2}	Y_{CO_2}
9.586	0.1388	0.8612	0.4186	0.5814
9.600	0.1404	0.8596	0.4188	0.5812
9.618	----	----	0.4204	0.5796
10.193	0.1572	0.8428	0.4192	0.5808
10.393	----	----	0.4174	0.5826

Table 24

N_2-C_2H_6 System at 220.00 K

PRESSURE (MPa)	X_{N_2}	$X_{C_2H_6}$	Y_{N_2}	$Y_{C_2H_6}$
0.492	0.0000	1.0000	0.0000	1.0000
0.804	0.0090	0.9910	0.3517	0.6483
1.007	0.0160	0.9840	0.4638	0.5362
1.745	0.0356	0.9644	0.6584	0.3416
2.416	0.0552	0.9448	0.7332	0.2668
3.762	0.0952	0.9048	0.7961	0.2039
4.000	0.1035	0.8965	0.8024	0.1976
4.487	0.1168	0.8832	0.8116	0.1884
5.179	0.1394	0.8606	0.8221	0.1779
5.829	0.1582	0.8418	0.8264	0.1736
6.562	0.1838	0.8162	0.8298	0.1702
7.296	0.2077	0.7923	0.8286	0.1714
7.945	0.2326	0.7674	0.8276	0.1724
8.664	0.2572	0.7428	0.8225	0.1775
8.998	0.2692	0.7308	0.8200	0.1800
9.261	0.2810	0.7190	0.8173	0.1827
9.293	----	----	0.8159	0.1841
9.618	----	----	0.8146	0.1854
10.034	----	----	0.8061	0.1939
10.510	0.3310	0.6690	0.7982	0.2018

Table 24 (cont.)

N_2-C_2H_6 System at 220.00 K

PRESSURE (MPa)	X_{N_2}	$X_{C_2H_6}$	Y_{N_2}	$Y_{C_2H_6}$
10.704	----	----	0.7952	0.2048
10.969	----	----	0.7898	0.2102
11.980	0.4080	0.5920	0.7592	0.2408

Table 25

N_2-C_2H_6 System at 260.00 K

PRESSURE (MPa)	X_{N_2}	$X_{C_2H_6}$	Y_{N_2}	$Y_{C_2H_6}$
3.497	0.0500	0.9500	0.3905	0.6095
5.657	0.1165	0.8835	0.5248	0.4752
7.000	0.1630	0.8370	0.5539	0.4461
8.740	0.2325	0.7675	0.5546	0.4454
10.041	0.3063	0.6937	0.5155	0.4845

Table 26

N_2-C_2H_6 System at 270.00 K

PRESSURE (MPa)	X_{N_2}	$X_{C_2H_6}$	Y_{N_2}	$Y_{C_2H_6}$
2.212	0.0000	1.0000	0.0000	1.0000
3.222	0.0282	0.9718	0.2216	0.7784
4.080	0.0508	0.9492	0.3184	0.6816
5.447	0.0985	0.9015	0.4159	0.5841
6.870	----	----	0.4570	0.5430
8.397	0.2148	0.7852	0.4554	0.5446
8.640	0.2282	0.7718	0.4499	0.5501
8.994	0.2510	0.7490	0.4378	0.5622
8.998	0.2515	0.7485	0.4384	0.5616
9.304	0.2758	0.7242	0.4186	0.5814
9.415	0.2900	0.7100	0.4044	0.5956
9.465	0.2944	0.7056	0.3939	0.6061
9.490	0.2995	0.7005	0.3902	0.6098
13.000	0.2108	0.7892	0.7963	0.2037

Table 27

N_2-CO_2-C_2H_6 System at 220.00 K and 0.803 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
0.803	0.0028	0.9972	0.0000	0.2296	0.7704	0.0000
0.803	0.0020	0.9658	0.0322	0.1581	0.7466	0.0953
0.803	0.0011	0.9223	0.0766	0.0953	0.7218	0.1829
0.803	0.0002	0.8773	0.1225	0.0542	0.6963	0.2495
0.804	0.0000	0.7488	0.2512	0.0106	0.6485	0.3409
0.803	----	----	----	0.0024	0.6283	0.3693
0.804	0.0000	0.4723	0.5277	0.0060	0.5494	0.4446
0.803	0.0000	0.3835	0.6165	0.0203	0.5047	0.4750
0.803	0.0009	0.3209	0.6782	0.0405	0.4605	0.4990
0.804	0.0018	0.2486	0.7496	0.0730	0.4005	0.5265
0.804	0.0068	0.2126	0.7806	0.0985	0.3574	0.5441
0.804	0.0033	0.1782	0.8185	0.1188	0.3242	0.5570
0.804	0.0046	0.1277	0.8677	0.1654	0.2534	0.5812
0.804	0.0067	0.0597	0.9336	0.2482	0.1356	0.6162
0.804	0.0080	0.0260	0.9660	0.3028	0.0634	0.6338
0.804	0.0090	0.0000	0.9910	0.3517	0.0000	0.6483

Table 28

N_2-CO_2-C_2H_6 System at 220.00 K and 4.000 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
4.000	0.0510	0.9490	0.0000	0.7815	0.2185	0.0000
4.002	0.0614	0.8688	0.0698	0.7428	0.2093	0.0479
4.000	0.0692	0.8020	0.1288	0.7262	0.2019	0.0719
4.000	0.0820	0.7012	0.2168	0.7138	0.1918	0.0944
4.002	0.0904	0.6081	0.3015	0.7084	0.1816	0.1100
3.999	0.0940	0.5613	0.3447	0.7063	0.1764	0.1173
4.000	0.1026	0.4154	0.4820	0.7079	0.1552	0.1369
4.003	0.1040	0.3878	0.5082	0.7058	0.1516	0.1426
3.998	0.1065	0.3008	0.5927	0.7165	0.1310	0.1525
4.000	----	----	----	0.7170	0.1306	0.1524
4.000	0.1077	0.2388	0.6535	0.7254	0.1142	0.1604
4.002	0.1066	0.1272	0.7662	0.7504	0.0726	0.1770
3.998	0.1050	0.0343	0.8607	0.7870	0.0228	0.1902
4.000	0.1035	0.0000	0.8965	0.8024	0.0000	0.1976

Table 29

N_2-CO_2-C_2H_6 System at 220.00 K and 9.000 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
9.004	0.1317	0.8683	0.0000	0.8265	0.1725	0.0010
9.002	0.1730	0.7556	0.0714	0.7892	0.1719	0.0389
8.998	0.2293	0.5943	0.1764	0.7612	0.1642	0.0746
9.004	0.2646	0.4698	0.2656	0.7495	0.1521	0.0984
9.000	0.2784	0.4166	0.3050	0.7459	0.1451	0.1090
9.004	----	----	----	0.7450	0.1364	0.1186
9.004	0.2972	0.3062	0.3966	0.7461	0.1225	0.1314
9.000	0.3013	0.2622	0.4365	0.7494	0.1107	0.1399
9.000	0.2997	0.1721	0.5282	0.7621	0.0804	0.1575
9.003	----	----	----	0.7738	0.0622	0.1640
9.004	0.2831	0.0583	0.6586	0.7959	0.0308	0.1733
8.998	0.2696	0.0000	0.7304	0.8200	0.0000	0.1800

Table 30

N_2-CO_2-C_2H_6 System at 270.00 K and 3.450 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
3.451	0.0038	0.9962	0.0000	0.0509	0.9491	0.0000
3.447	0.0026	0.9707	0.0267	0.0304	0.9258	0.0438
3.449	0.0015	0.9521	0.0464	0.0180	0.9100	0.0720
3.447	0.0008	0.9387	0.0605	0.0108	0.8992	0.0900
3.449	0.0000	0.9142	0.0858	0.0000	0.8778	0.1222
3.451	0.0000	0.4394	0.5606	0.0000	0.5190	0.4810
3.453	0.0000	0.4267	0.5733	0.0034	0.5081	0.4885
3.451	0.0025	0.3848	0.6127	0.0150	0.4711	0.5139
3.447	0.0090	0.2768	0.7142	0.0551	0.3654	0.5795
3.449	0.0116	0.2419	0.7465	0.0721	0.3283	0.5996
3.449	0.0155	0.1957	0.7888	0.0973	0.2753	0.6274
3.447	0.0204	0.1389	0.8407	0.1327	0.2056	0.6617
3.451	0.0254	0.0883	0.8863	0.1713	0.1366	0.6921
3.449	0.0317	0.0320	0.9363	0.2202	0.0537	0.7261
3.451	0.0354	0.0000	0.9646	0.2538	0.0000	0.7462

Table 31

N_2-CO_2-C_2H_6 System at 270.00 K and 6.000 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
6.004	0.0542	0.9458	0.0000	0.3222	0.6778	0.0000
6.008	0.0572	0.8679	0.0749	0.2818	0.6404	0.0778
6.002	0.0588	0.8304	0.1108	0.2673	0.6233	0.1094
6.001	----	----	----	0.2570	0.6046	0.1384
5.997	0.0617	0.7765	0.1618	0.2554	0.5957	0.1489
5.993	0.0655	0.7287	0.2058	0.2459	0.5726	0.1815
6.001	0.0683	0.6873	0.2444	0.2410	0.5506	0.2084
5.998	0.0712	0.6156	0.3132	0.2366	0.5102	0.2532
6.001	0.0764	0.5575	0.3661	0.2370	0.4753	0.2877
6.001	0.0798	0.5105	0.4097	0.2397	0.4453	0.3150
5.998	0.0835	0.4479	0.4686	0.2462	0.4027	0.3511
5.997	0.0872	0.3848	0.5280	0.2573	0.3573	0.3854
5.994	0.0951	0.2839	0.6210	0.2843	0.2774	0.4383
5.998	0.1052	0.1502	0.7446	0.3400	0.1588	0.5012
6.001	0.1085	0.1052	0.7863	0.3640	0.1146	0.5214
6.004	0.1144	0.0254	0.8602	0.4078	0.0412	0.5510
6.002	0.1176	0.0000	0.8824	0.4339	0.0000	0.5661

Table 32

N_2-CO_2-C_2H_6 System at 270.00 K and 8.400 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
8.392	0.1070	0.8930	0.0000	0.4055	0.5945	0.0000
8.400	0.1195	0.8172	0.0633	0.3663	0.5740	0.0597
8.406	0.1335	0.7410	0.1255	0.3364	0.5527	0.1109
8.394	0.1385	0.7130	0.1485	0.3266	0.5432	0.1302
8.395	0.1516	0.6512	0.1972	0.3072	0.5225	0.1703
8.400	0.1564	0.6331	0.2105	0.3021	0.5170	0.1809
8.409	0.1570	0.6280	0.2150	0.3004	0.5145	0.1851
8.399	0.1735	0.5613	0.2652	0.2799	0.4892	0.2309
8.397	0.1827	0.5369	0.2804	0.2714	0.4801	0.2485
8.391	0.2256	0.1800	0.5944	0.3265	0.1741	0.4994
8.400	0.2213	0.1458	0.6329	0.3511	0.1416	0.5073
8.404	0.2212	0.1305	0.6483	0.3616	0.1273	0.5111
8.398	0.2176	0.0734	0.7090	0.4014	0.0718	0.5268
8.393	0.2161	0.0470	0.7369	0.4205	0.0470	0.5325
8.410	0.2163	0.0232	0.7605	0.4376	0.0235	0.5389
8.397	0.2148	0.0000	0.7852	0.4554	0.0000	0.5446

Table 33

N_2-CO_2-C_2H_6 System at 270.00 K and 9.000 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
8.991	0.1206	0.8794	0.0000	0.4137	0.5863	0.0000
8.998	0.1384	0.7994	0.0622	0.3722	0.5702	0.0576
8.995	0.1387	0.7936	0.0677	0.3690	0.5685	0.0625
9.000	0.1420	0.7785	0.0795	0.3619	0.5654	0.0727
9.009	0.1480	0.7590	0.0930	0.3541	0.5616	0.0843
9.005	0.1570	0.7210	0.1220	0.3380	0.5530	0.1090
8.993	0.1601	0.7074	0.1325	0.3322	0.5507	0.1171
8.992	0.1639	0.6923	0.1438	0.3251	0.5476	0.1273
9.005	0.1736	0.6423	0.1841	0.2992	0.5371	0.1637
9.005	0.1865	0.6242	0.1893	0.2943	0.5357	0.1700
8.997	0.1936	0.6055	0.2009	0.2833	0.5342	0.1825
8.995	0.2705	0.0701	0.6594	0.3637	0.0692	0.5671
8.995	0.2601	0.0471	0.6928	0.3903	0.0467	0.5630
8.988	0.2577	0.0414	0.7009	0.3974	0.0407	0.5619
9.001	0.2559	0.0222	0.7219	0.4161	0.0224	0.5615
8.995	0.2430	0.0000	0.7570	0.4376	0.0000	0.5624

Table 34

N_2-CO_2-C_2H_6 System at 270.00 K and 9.600 MPa

PRESSURE (MPa)	X_{N_2}	X_{CO_2}	$X_{C_2H_6}$	Y_{N_2}	Y_{CO_2}	$Y_{C_2H_6}$
9.600	0.1404	0.8596	0.0000	0.4188	0.5812	0.0000
9.613	0.1536	0.8040	0.0424	0.3855	0.5746	0.0399
9.606	0.1623	0.7720	0.0657	0.3685	0.5706	0.0609
9.600	0.1616	0.7699	0.0685	0.3662	0.5698	0.0640
9.613	0.1648	0.7592	0.0760	0.3610	0.5693	0.0697
9.589	----	----	----	0.3386	0.5654	0.0960
9.589	0.1856	0.6973	0.1171	0.3290	0.5646	0.1064
9.613	0.1887	0.6783	0.1330	0.3129	0.5655	0.1216
9.602	0.1938	0.6624	0.1438	0.3000	0.5674	0.1326

APPENDIX C

Computer Programs

```
C       This program implements the maximum likelihood
C       method for two constraints.  The program is general,
C       and can be used to fit parameters for any type of
C       model by writing the appropriate subroutines to
C       calculate the two constraint functions and their
C       derivatives.  In this program, the subroutine
C       FUNCTIONS is used to calculate the two constraint
C       functions and their derivatives.

C       N is the maximum number of data points.  K is the
C       number of constraints, and must be kept at 2.  L is
C       the number of parameters.

        PARAMETER N = 75,K = 2,L = 1
        PARAMETER NK = N*K
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 XM(NK),YM(N),ZM(N),XR(NK),YR(N),ZR(N),
     #         LAMBDA(NK,NK),DELTA(N,N),GAMMA(N,N),PARAM(L),
     #         TC(2),PC(2),W(2),FR(N),GR(N),DFDX(N,NK),
     #         DGDX(N,NK),DFDY(N,N),DFDZ(N,N),DGDY(N,N),
     #         DGDZ(N,N),DFDPAR(N,L),DGDPAR(N,L),
     #         DFDZINV(N,N),DFDYINV(N,N),DUMNN1(N,N),
     #         DUMNN2(N,N),DUMNNK1(N,NK),GZFZINV(N,N),
     #         GYFYINV(N,N),GYGZFZFY(N,N),GZGYFYFZ(N,N),
     #         GRGZFZFR(N),GXGZFZFX(N,NK),DUMN1(N),
     #         DUMNL1(N,L),GPGZFZFP(N,L),GRGYFYFR(N),
     #         GXGYFYFX(N,NK),GPGYFYFP(N,L),FSUPR(N),
     #         FSUBX(N,NK),FSUBP(N,L),GSUPR(N),GSUBX(N,NK),
     #         GSUBP(N,L),FSUBXT(NK,N),FSUBPT(L,N),
     #         GSUBXT(NK,N),GSUBPT(L,N),FXTGAMMA(NK,N),
     #         DUMNKNK1(NK,NK),D(NK,NK),DUMNKNK2(NK,NK),
     #         DUMNKL1(NK,L),DUMNKL2(NK,L),R(NK,L),
     #         FPTGAMMA(L,N),GPTDELTA(L,N),DUMLL1(L,L),
     #         T(L,L),RT(L,NK),DUMLNK1(L,NK),DELXM(NK),
     #         DELYM(N),DELZM(N),DUML1(L),DUML2(L),U(L),
     #         Q(NK),DUMNK1(NK),DUMNK2(NK),DELPAR(L),
     #         DELX(NK),DUMN2(N),DELZ(N),DELY(N),NCOMP(2),
     #         TCD(3),PCD(3),WD(3),GXTDELTA(NK,N),
     #         DUMLL2(L,L),PARA(2),ZC(2),PARAD(3),ZCD(3)
        CHARACTER FILNAM1*12

        WRITE (6,*) 'ENTER YOUR COMPONENT NUMBERS WITH
     # COMPONENT 1 FIRST.'
        WRITE (6,*)
        WRITE (6,*) '1-NITROGEN'
        WRITE (6,*) '2-CARBON DIOXIDE'
        WRITE (6,*) '3-ETHANE'
        WRITE (6,*)
```

```
      READ (5,*) NCOMP(1),NCOMP(2)

C     The following are critical temperatures (K),
C     critical pressures (MPa), accentric factors,
C     parachors, and critical compressibility factors.

      TCD(1) = 126.2
      TCD(2) = 304.1
      TCD(3) = 305.42
      PCD(1) = 492.3*0.0068947
      PCD(2) = 1069.7*0.0068947
      PCD(3) = 707.8*0.0068947
      WD(1) = 0.040
      WD(2) = 0.239
      WD(3) = 0.099
      PARAD(1) = 75.6
      PARAD(2) = 100.0
      PARAD(3) =110.5
      ZCD(1) = 0.290
      ZCD(2) = 0.274
      ZCD(3) = 0.285

      DO I = 1,2
         TC(I) = TCD(NCOMP(I))
         PC(I) = PCD(NCOMP(I))
         W(I) = WD(NCOMP(I))
         PARA(I) = PARAD(NCOMP(I))
         ZC(I) = ZCD(NCOMP(I))
      ENDDO
      WRITE (6,*)

C     The Mansoori mixing rule is a three parameter mixing
C     rule, the standard mixing rule has one parameter,
C     and the temperature dependent mixing rule has two
C     parameters.

      WRITE (6,*) 'WHAT TYPE OF MIXING RULE DO YOU WANT?'
      WRITE (6,*) '1-MANSOORI          2-STANDARD'
      WRITE (6,*) '3-TEMPERATURE DEPENDENT'
      READ (5,*) NMIX
      WRITE (6,*)

C     The equations of state available are:  Peng-
C     Robinson, Soave-Redlich-Kwong, and Fuller
C     modification of the Soave-Redlich-Kwong.

      IF (NMIX .NE. 1) THEN
         WRITE (6,*) 'WHAT EQUATION OF STATE DO YOU WANT.'
```

```
            WRITE (6,*) '1-PR          2-SRK          3-FULLER'
            READ (6,*) NEQ
         ENDIF

C        The data may be contained in any number of data
C        files, but each file must have the form:
C               Temperature
C               Pressure (MPa),x,y
C               Pressure (MPa),x,y
C               etc.

         WRITE (6,*) 'HOW MANY EXPERIMENTAL DATA FILES DO
     # YOU HAVE?'
         READ (5,*) NF
         NEXP = 0
         DO I = 1,NF
            WRITE (6,*) 'INPUT FILE NAME #',I
            READ (5,5) FILNAM1
5           FORMAT (A12)
            OPEN (UNIT = 10,FILE = FILNAM1, STATUS = 'OLD')
            READ (10,*) TEMP
10          NEXP = NEXP + 1
            XM(2*NEXP-1) = TEMP
            READ (10,*,END = 20) ZM(NEXP),XM(2*NEXP),YM(NEXP)
            GO TO 10
20          NEXP = NEXP - 1
            CLOSE (10)
         ENDDO
         NEXPK = NEXP*K

C        XR is a vector of the independent variables.  YR and
C        ZR are vectors of the dependent variables.

         DO I = NEXPK,2,-2
            XR(I) = XM(I)
            XR(I-1) = XM(I-1)
            YR(I/2) = YM(I/2)
            ZR(I/2) = ZM(I/2)
         ENDDO

C        GAMMA, DELTA, AND LAMBDA are diagonal matrices with
C        each diagonal element equal to the reciprocal of the
C        square of the estimated variances for the variables.

         DO I = 1,NEXP
            DO J = 1,NEXP
               GAMMA(I,J) = 0.0
               DELTA(I,J) = 0.0
```

```
            ENDDO
         ENDDO
         DO I = 1,NEXPK
            DO J = 1,NEXPK
               LAMBDA(I,J) = 0.0
            ENDDO
         ENDDO
         DO I = 1,NEXP
            LAMBDA(2*I,2*I) = 1.0/0.002**2
            LAMBDA(2*I-1,2*I-1) = 1.0/0.02**2
            GAMMA(I,I) = 1.0/0.002**2
            IF (ZM(I) .LT. 0.62) THEN
               DELTA(I,I) = 1.0/0.00068947**2
            ELSEIF (ZM(I) .GT. 3.103) THEN
               DELTA(I,I) = 1.0/0.017237**2
            ELSE
               DELTA(I,I) = 1.0/0.0034474**2
            ENDIF
         ENDDO
         SUMSQ = 0.0
         ITER = 0
         ITERMAX = 100
         FRACT = 0.5
         DO I = 1,L
            PARAM(I) = 0.0
         ENDDO

C        In order for the program to have converged, the
C        difference between the sum of squares of the latest
C        two iterations must be less than 100*EPS percent.

         WRITE (6,*) 'INPUT CONVERGENCE CRITERIA.'
         READ (5,*) EPS

C        For the standard mixing rule, a guess for the
C        interaction parameter is requested.  An accurate
C        guess will make convergence very rapid.  If no
C        information is available, a guess of zero will be
C        sufficient.

         IF (NMIX .EQ. 2) THEN
            WRITE (6,*) 'GUESS A VALUE FOR K12.'
            READ (5,*) PARAM(1)
         ENDIF
```

```
C  ***********************************************************
C       Begin calculational loop.
30    ************************************************************
        Begin calculational loop.
C       Subroutine FUNCTIONS calculates the two constraints
C       and their derivatives.  GR and FR are the two
C       constraint functions.  The nomenclature is such that
C       the derivative of FR with respect to the independent
C       variable X is DFDX.

        CALL FUNCTIONS(XR,YR,ZR,NMIX,NEQ,N,K,L,NK,NEXP,PARAM
     #                 ,TC,PC,W,PARA,ZC,FR,DFDX,DFDY,DFDZ,
     #                 DFDPAR,GR,DGDX,DGDY,DGDZ,DGDPAR)

C       Calculate Gy - Gz*Fz*Fy.

        CALL MATDIAGINV(DFDY,NEXP,N,DFDYINV)
        CALL MATDIAGINV(DFDZ,NEXP,N,DFDZINV)
        CALL MATMULT(DGDZ,NEXP,NEXP,N,N,DFDZINV,NEXP,N,
     #               GZFZINV)
        CALL MATMULT(DGDY,NEXP,NEXP,N,N,DFDYINV,NEXP,N,
     #               GYFYINV)
        CALL MATMULT(GZFZINV,NEXP,NEXP,N,N,DFDY,NEXP,N,
     #               DUMNN1)
        CALL MATADD(DGDY,DUMNN1,NEXP,NEXP,N,N,-1,DUMNN2)
        CALL MATDIAGINV(DUMNN2,NEXP,N,GYGZFZFY)

C       Calculate Gz - Gy*Fy*Fz.

        CALL MATMULT(GYFYINV,NEXP,NEXP,N,N,DFDZ,NEXP,N,
     #               DUMNN1)
        CALL MATADD(DGDZ,DUMNN1,NEXP,NEXP,N,N,-1,DUMNN2)
        CALL MATDIAGINV(DUMNN2,NEXP,N,GZGYFYFZ)

C       Calculate Gr - Gz*Fz*Fr.

        CALL MATMULT(GZFZINV,NEXP,NEXP,N,N,FR,1,1,DUMN1)
        CALL MATADD(GR,DUMN1,NEXP,1,N,1,-1,GRGZFZFR)

C       Calcualte Gx - Gz*Fz*Fx.

        CALL MATMULT(GZFZINV,NEXP,NEXP,N,N,DFDX,NEXPK,NK,
     #               DUMNNK1)
        CALL MATADD(DGDX,DUMNNK1,NEXP,NEXPK,N,NK,-1,
     #              GXGZFZFX)
```

```
C       Calculate Gp - Gz*Fz*Fp.

        CALL MATMULT(GZFZINV,NEXP,NEXP,N,N,DFDPAR,L,L,
     #               DUMNL1)
        CALL MATADD(DGDPAR,DUMNL1,NEXP,L,N,L,-1,GPGZFZFP)

C       Calculate Gr - Gy*Fy*Fr.

        CALL MATMULT(GYFYINV,NEXP,NEXP,N,N,FR,1,1,DUMN1)
        CALL MATADD(GR,DUMN1,NEXP,1,N,1,-1,GRGYFYFR)

C       Calculate Gx - Gy*Fy*Fx.

        CALL MATMULT(GYFYINV,NEXP,NEXP,N,N,DFDX,NEXPK,NK,
     #               DUMNNK1)
        CALL MATADD(DGDX,DUMNNK1,NEXP,NEXPK,N,NK,-1,
     #              GXGYFYFX)

C       Calculate Gp - Gy*Fy*Fp.

        CALL MATMULT(GYFYINV,NEXP,NEXP,N,N,DFDPAR,L,L,
     #               DUMNL1)
        CALL MATADD(DGDPAR,DUMNL1,NEXP,L,N,L,-1,GPGYFYFP)

C       Calculate fR.

        CALL MATMULT(GYGZFZFY,NEXP,NEXP,N,N,GRGZFZFR,1,1,
     #               DUMN1)
        CALL MATADD(YR,DUMN1,NEXP,1,N,1,-1,FSUPR)

C       Calculate fx.

        CALL MATMULT(GYGZFZFY,NEXP,NEXP,N,N,GXGZFZFX,NEXPK,
     #               NK,FSUBX)
        CALL MATNEG(FSUBX,NEXP,NEXPK,N,NK)

C       Calculate fp.

        CALL MATMULT(GYGZFZFY,NEXP,NEXP,N,N,GPGZFZFP,L,L,
     #               FSUBP)
        CALL MATNEG(FSUBP,NEXP,L,N,L)

C       Calculate gR.

        CALL MATMULT(GZGYFYFZ,NEXP,NEXP,N,N,GRGYFYFR,1,1,
     #               DUMN1)
        CALL MATADD(ZR,DUMN1,NEXP,1,N,1,-1,GSUPR)
```

```
C       Calculate gx.

        CALL MATMULT(GZGYFYFZ,NEXP,NEXP,N,N,GXGYFYFX,NEXPK,
     #               NK,GSUBX)
        CALL MATNEG(GSUBX,NEXP,NEXPK,N,NK)

C       Calculate gp.

        CALL MATMULT(GZGYFYFZ,NEXP,NEXP,N,N,GPGYFYFP,L,L,
     #               GSUBP)
        CALL MATNEG(GSUBP,NEXP,L,N,L)

C       Calculate the transposes of fx,fp,gx, and gp.

        CALL MATTRANS(FSUBX,NEXP,NEXPK,N,NK,FSUBXT)
        CALL MATTRANS(FSUBP,NEXP,L,N,L,FSUBPT)
        CALL MATTRANS(GSUBX,NEXP,NEXPK,N,NK,GSUBXT)
        CALL MATTRANS(GSUBP,NEXP,L,N,L,GSUBPT)

C       Calculate matrix D.

        CALL MATMULT(FSUBXT,NEXPK,NEXP,NK,N,GAMMA,NEXP,N,
     #               FXTGAMMA)
        CALL MATMULT(FXTGAMMA,NEXPK,NEXP,NK,N,FSUBX,NEXPK,
     #               NK,D)
        CALL MATADD(LAMBDA,D,NEXPK,NEXPK,NK,NK,1,DUMNKNK1)
        CALL MATMULT(GSUBXT,NEXPK,NEXP,NK,N,DELTA,NEXP,N,
     #               GXTDELTA)
        CALL MATMULT(GXTDELTA,NEXPK,NEXP,NK,N,GSUBX,NEXPK,
     #               NK,DUMNKNK2)
        CALL MATADD(DUMNKNK1,DUMNKNK2,NEXPK,NEXPK,NK,NK,1,D)

C       Calculate matrix R.

        CALL MATMULT(FXTGAMMA,NEXPK,NEXP,NK,N,FSUBP,L,L,
     #               DUMNKL1)
        CALL MATMULT(GXTDELTA,NEXPK,NEXP,NK,N,GSUBP,L,L,
     #               DUMNKL2)
        CALL MATADD(DUMNKL1,DUMNKL2,NEXPK,L,NK,L,1,R)

C       Calculate matrix T.

        CALL MATMULT(FSUBPT,L,NEXP,L,N,GAMMA,NEXP,N,
     #               FPTGAMMA)
        CALL MATMULT(GSUBPT,L,NEXP,L,N,DELTA,NEXP,N,
     #               GPTDELTA)
        CALL MATMULT(FPTGAMMA,L,NEXP,L,N,FSUBP,L,L,DUMLL1)
        CALL MATMULT(GPTDELTA,L,NEXP,L,N,GSUBP,L,L,DUMLL2)
```

```
      CALL MATADD(DUMLL1,DUMLL2,L,L,L,L,1,T)

C     Calculate the part of delta parameter.

      CALL MATTRANS(R,NEXPK,L,NK,L,RT)
      CALL MATSYMINV(D,NEXPK,NK,IRR)
      IF (IRR .EQ. 1) THEN
         WRITE (6,*) 'A SINGULAR MATRIX WAS FOUND.'
         GO TO 999
      ENDIF
      CALL MATMULT(RT,L,NEXPK,L,NK,D,NEXPK,NK,DUMLNK1)
      CALL MATMULT(DUMLNK1,L,NEXPK,L,NK,R,L,L,DUMLL1)
      CALL MATADD(T,DUMLL1,L,L,L,L,-1,DUMLL2)
      CALL MATSYMINV(DUMLL2,L,L,IRR)
      IF (IRR .EQ. 1) THEN
         WRITE (6,*) 'A SINGULAR MATRIX WAS FOUND.'
         GO TO 999
      ENDIF

C     Calculate the difference between calculated and
C     experimental values.

      DO I = 1,NEXP
         DELXM(2*I) = XR(2*I) - XM(2*I)
         DELXM(2*I-1) = XR(2*I-1) - XM(2*I-1)
         DELYM(I) = YR(I) - YM(I)
         DELZM(I) = ZR(I) - ZM(I)
      ENDDO

C     Calculate matrix U.

      CALL MATMULT(FPTGAMMA,L,NEXP,L,N,DELYM,1,1,DUML1)
      CALL MATMULT(GPTDELTA,L,NEXP,L,N,DELZM,1,1,DUML2)
      CALL MATADD(DUML1,DUML2,L,1,L,1,1,U)

C     Calculate matrix Q.

      CALL MATMULT(LAMBDA,NEXPK,NEXPK,NK,NK,DELXM,1,1,Q)
      CALL MATMULT(FXTGAMMA,NEXPK,NEXP,NK,N,DELYM,1,1,
     #             DUMNK1)
      CALL MATADD(Q,DUMNK1,NEXPK,1,NK,1,1,DUMNK2)
      CALL MATMULT(GXTDELTA,NEXPK,NEXP,NK,N,DELZM,1,1,
     #             DUMNK1)
      CALL MATADD(DUMNK2,DUMNK1,NEXPK,1,NK,1,1,Q)

C     Complete calculation of delta parameter.

      CALL MATMULT(DUMLNK1,L,NEXPK,L,NK,Q,1,1,DUML1)
```

```
      CALL MATADD(U,DUML1,L,1,L,1,-1,DUML2)
      CALL MATMULT(DUMLL2,L,L,L,L,DUML2,1,1,DELPAR)
      WRITE (6,*)'DELPAR ',(DELPAR(I),I=1,L)

C     Calculate delta X.

      CALL MATNEG(DELPAR,L,1,L,1)
      CALL MATMULT(R,NEXPK,L,NK,L,DELPAR,1,1,DUMNK1)
      CALL MATADD(Q,DUMNK1,NEXPK,1,NK,1,1,DUMNK2)
      CALL MATMULT(D,NEXPK,NEXPK,NK,NK,DUMNK2,1,1,DELX)
      CALL MATNEG(DELX,NEXPK,1,NK,1)

C     Calculate delta Z.

      CALL MATMULT(GXGYFYFX,NEXP,NEXPK,N,NK,DELX,1,1,
     #             DUMN1)
      CALL MATMULT(GPGYFYFP,NEXP,L,N,L,DELPAR,1,1,DUMN2)
      CALL MATADD(GRGYFYFR,DUMN1,NEXP,1,N,1,1,DELZ)
      CALL MATADD(DELZ,DUMN2,NEXP,1,N,1,1,DUMN1)
      CALL MATMULT(GZGYFYFZ,NEXP,NEXP,N,N,DUMN1,1,1,DELZ)
      CALL MATNEG(DELZ,NEXP,1,N,1)

C     Calculate delta Y.

      CALL MATMULT(GXGZFZFX,NEXP,NEXPK,N,NK,DELX,1,1,
     #             DUMN1)
      CALL MATMULT(GPGZFZFP,NEXP,L,N,L,DELPAR,1,1,DUMN2)
      CALL MATADD(GRGZFZFR,DUMN1,NEXP,1,N,1,1,DELY)
      CALL MATADD(DELY,DUMN2,NEXP,1,N,1,1,DUMN1)
      CALL MATMULT(GYGZFZFY,NEXP,NEXP,N,N,DUMN1,1,1,DELY)
      CALL MATNEG(DELY,NEXP,1,N,1)

C     Calculate new values for the variables and the sum
C     of squared deviations between calculated and
C     experimental values.

      SUMSQN = 0.0
      DO I = 1,NEXP
         YR(I) = FRACT*DELY(I) + YR(I)
         ZR(I) = FRACT*DELZ(I) + ZR(I)
         SUMSQN = SUMSQN + (ZR(I) - ZM(I))**2*DELTA(I,I) +
     #            (YR(I) - YM(I))**2*GAMMA(I,I)
      ENDDO
      DO I = 1,NEXPK
         XR(I) = FRACT*DELX(I) + XR(I)
         SUMSQN = SUMSQN + (XR(I) - XM(I))**2*LAMBDA(I,I)
      ENDDO
```

```
C       Check for nonconvergence.

        IF (ITER .GT. ITERMAX) THEN
           WRITE (6,100) ITERMAX
100        FORMAT (1X,'NO CONVERGENCE IN',I3,' ITERATIONS.')
           GO TO 999
        ENDIF

C       Calculate new values for the parameters.

        IF (ITER .LT. 3) THEN
           FRACTPAR = FRACT/3.0
        ELSEIF (ITER .GE. 3 .AND. ITER .LT. 5) THEN
           FRACTPAR = FRACT/2.0
        ELSE
           FRACTPAR = FRACT
        ENDIF
        DO I = 1,L
           PARAM(I) = FRACTPAR*DELPAR(I) + PARAM(I)
        ENDDO

C       Check for convergence.

        DIFF = DABS(SUMSQN - SUMSQ)/SUMSQN
        WRITE (6,*) 'SUMSQN,DIFF  ',SUMSQN,DIFF
        IF (DIFF .GT. EPS) THEN
           IF (ITER .LT. 7) FRACT = (1. - FRACT)*.5 + FRACT
           IF (ITER .EQ. 8) FRACT = 1.0
           SUMSQ = SUMSQN
           GO TO 30
        ENDIF

C       End calculational loop
C  ***************************************************************

        S = SUMSQN/(NEXP - L)

C       Output results.

        DO I = 1,NEXP
           DI = 100.*(XR(2*I-1) - XM(2*I-1))/XM(2*I-1)
           WRITE (6,*) 'TCALC,TMEAS,PERCENT DIFFERENCE '
           WRITE (6,*) XR(2*I-1),XM(2*I-1),DI
           DI = 100.*(ZR(I) - ZM(I))/ZM(I)
           WRITE (6,*) 'PCALC,PMEAS,PERCENT DIFFERENCE '
           WRITE (6,*) ZR(I),ZM(I),DI
           DI = DABS(XR(2*I) - XM(2*I))
           WRITE (6,*) 'XCALC,XMEAS,ABSOLUTE DIFFERENCE '
```

```
            WRITE (6,*) XR(2*I),XM(2*I),DI
            DI = DABS(YR(I) - YM(I))
            WRITE (6,*) 'YCALC,YMEAS,ABSOLUTE DIFFERENCE '
            WRITE (6,*) YR(I),YM(I),DI
            WRITE (6,*)
         ENDDO
         WRITE (6,*) 'PARAMETERS',(PARAM(I), I = 1,L)
         WRITE (6,*) 'STANDARD DEVIATION = ', S
999      END


C        This subroutine uses a five point difference formula
C        two calculates the derivatives of the two
C        constraints.  It also calculates the values of the
C        two constraint functions.

         SUBROUTINE FUNCTIONS(XR,YR,ZR,NMIX,NEQ,N,K,L,NK,NEXP
     #                       ,PARAM,TC,PC,W,PARA,ZC,FR,DFDX,
     #                       DFDY,DFDZ,DFDPAR,GR,DGDX,DGDY,
     #                       DGDZ,DGDPAR)
         PARAMETER NP = 1
         IMPLICIT REAL*8 (A-H,O-Z)
         REAL*8 XR(NK),YR(N),ZR(N),PARAM(L),TC(2),PC(2),W(2),
     #          FR(N),DFDX(N,NK),DFDY(N,N),DFDPAR(N,L),GR(N),
     #          DGDX(N,NK),DGDY(N,N),DGDZ(N,N),DFDZ(N,N),
     #          DGDPAR(N,L),X(2),Y(2),KV(2),DUMPAR(NP),
     #          DUMX(2),DUMY(2),PARA(2),ZC(2)
         NEXPK = NEXP*K
         DO I = 1,NEXP
            T = XR(2*I-1)
            P = ZR(I)
            X(1) = XR(2*I)
            X(2) = 1.0 - X(1)
            Y(1) = YR(I)
            Y(2) = 1.0 - Y(1)

C        Calculate the values of the constraint functions.

            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,T,P,X,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                     PARAM,KV)
            ENDIF
```

```
            FR(I) = Y(1) - KV(1)*X(1)
            GR(I) = Y(2) - KV(2)*X(2)

C       Calculate the derivative of each constraint with
C       respect to each parameter.

            DO J = 1,L
               DELPAR = 0.001*PARAM(J)
               IF (DABS(PARAM(J)) .LT. 0.001) DELPAR = 0.0001
               DO KK = 1,L
                  IF (KK .EQ. J) THEN
                     DUMPAR(KK) = PARAM(KK) - 2.*DELPAR
                  ELSE
                     DUMPAR(KK) = PARAM(KK)
                  ENDIF
               ENDDO
               IF (NMIX .EQ. 1) THEN
                  CALL MANSOORI(TC,PC,W,T,P,X,Y,2,DUMPAR,KV)
               ELSEIF (NMIX .EQ. 2) THEN
                  CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                         DUMPAR,KV)
               ELSE
                  CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                        DUMPAR,KV)
               ENDIF
               FN2 = Y(1) - KV(1)*X(1)
               GN2 = Y(2) - KV(2)*X(2)
               DUMPAR(J) = PARAM(J) - DELPAR
               IF (NMIX .EQ. 1) THEN
                  CALL MANSOORI(TC,PC,W,T,P,X,Y,2,DUMPAR,KV)
               ELSEIF (NMIX .EQ. 2) THEN
                  CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                         DUMPAR,KV)
               ELSE
                  CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                        DUMPAR,KV)
               ENDIF
               FN1 = Y(1) - KV(1)*X(1)
               GN1 = Y(2) - KV(2)*X(2)
               DUMPAR(J) = PARAM(J) + DELPAR
               IF (NMIX .EQ. 1) THEN
                  CALL MANSOORI(TC,PC,W,T,P,X,Y,2,DUMPAR,KV)
               ELSEIF (NMIX .EQ. 2) THEN
                  CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                         DUMPAR,KV)
               ELSE
                  CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                        DUMPAR,KV)
```

```
            ENDIF
            FP1 = Y(1) - KV(1)*X(1)
            GP1 = Y(2) - KV(2)*X(2)
            DUMPAR(J) = PARAM(J) + 2.*DELPAR
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,T,P,X,Y,2,DUMPAR,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                      DUMPAR,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,2,
     #                     DUMPAR,KV)
            ENDIF
            FP2 = Y(1) - KV(1)*X(1)
            GP2 = Y(2) - KV(2)*X(2)
            DFDPAR(I,J) = (2.*FN2 - 16.*FN1 + 16.*FP1 -
     #                     2.*FP2)/(24.*DELPAR)
            DGDPAR(I,J) = (2.*GN2 - 16.*GN1 + 16.*GP1 -
     #                     2.*GP2)/(24.*DELPAR)
         ENDDO

C        Calculate the derivative of the constraints with
C        respect to temperature.

            DELT = T*0.0001
            DUMT = T - 2.*DELT
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,DUMT,P,X,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                     PARAM,KV)
            ENDIF
            FN2 = Y(1) - KV(1)*X(1)
            GN2 = Y(2) - KV(2)*X(2)
            DUMT = T - DELT
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,DUMT,P,X,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                     PARAM,KV)
            ENDIF
            FN1 = Y(1) - KV(1)*X(1)
```

```
            GN1 = Y(2) - KV(2)*X(2)
            DUMT = T + DELT
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,DUMT,P,X,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                     PARAM,KV)
            ENDIF
            FP1 = Y(1) - KV(1)*X(1)
            GP1 = Y(2) - KV(2)*X(2)
            DUMT = T + 2.*DELT
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,DUMT,P,X,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,DUMT,P,X,Y,2,
     #                     PARAM,KV)
            ENDIF
            FP2 = Y(1) - KV(1)*X(1)
            GP2 = Y(2) - KV(2)*X(2)
            DFDX(I,2*I-1) = (2.*FN2 - 16.*FN1 + 16.*FP1 -
     #                       2.*FP2)/(24.*DELT)
            DGDX(I,2*I-1) = (2.*GN2 - 16.*GN1 + 16.*GP1 -
     #                       2.*GP2)/(24.*DELT)

C           Calculate the derivative of the constraints with
C           respect to liquid mole fraction.

            DELX = 0.0001
            IF (X(1) .LE. 0.0003) DELX = 0.1*X(1)
            IF (X(2) .LE. 0.0003) DELX = 0.1*X(2)
            DUMX(1) = X(1) - 2.*DELX
            DUMX(2) = 1.0 - DUMX(1)
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,T,P,DUMX,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                     PARAM,KV)
            ENDIF
            FN2 = Y(1) - KV(1)*DUMX(1)
```

```
            GN2 = Y(2) - KV(2)*DUMX(2)
            DUMX(1) = X(1) - DELX
            DUMX(2) = 1.0 - DUMX(1)
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,T,P,DUMX,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                     PARAM,KV)
            ENDIF
            FN1 = Y(1) - KV(1)*DUMX(1)
            GN1 = Y(2) - KV(2)*DUMX(2)
            DUMX(1) = X(1) + DELX
            DUMX(2) = 1.0 - DUMX(1)
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,T,P,DUMX,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                     PARAM,KV)
            ENDIF
            FP1 = Y(1) - KV(1)*DUMX(1)
            GP1 = Y(2) - KV(2)*DUMX(2)
            DUMX(1) = X(1) + 2.*DELX
            DUMX(2) = 1.0 - DUMX(1)
            IF (NMIX .EQ. 1) THEN
               CALL MANSOORI(TC,PC,W,T,P,DUMX,Y,2,PARAM,KV)
            ELSEIF (NMIX .EQ. 2) THEN
               CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                      PARAM,KV)
            ELSE
               CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,DUMX,Y,2,
     #                     PARAM,KV)
            ENDIF
            FP2 = Y(1) - KV(1)*DUMX(1)
            GP2 = Y(2) - KV(2)*DUMX(2)
            DFDX(I,2*I) = (2.*FN2 - 16.*FN1 + 16.*FP1 -
     #                     2.*FP2)/(24.*DELX)
            DGDX(I,2*I) = (2.*GN2 - 16.*GN1 + 16.*GP1 -
     #                     2.*GP2)/(24.*DELX)

C           Calculate the derivative of the constraints with
C           respect to vapor mole fraction.
```

```
      DELY = 0.0001
      IF (Y(1) .LE. 0.0003) DELY = 0.1*Y(1)
      IF (Y(2) .LE. 0.0003) DELY = 0.1*Y(2)
      DUMY(1) = Y(1) - 2.*DELY
      DUMY(2) = 1.0 - DUMY(1)
      IF (NMIX .EQ. 1) THEN
         CALL MANSOORI(TC,PC,W,T,P,X,DUMY,2,PARAM,KV)
      ELSEIF (NMIX .EQ. 2) THEN
         CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
     #                 PARAM,KV)
      ELSE
         CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
     #                PARAM,KV)
      ENDIF
      FN2 = DUMY(1) - KV(1)*X(1)
      GN2 = DUMY(2) - KV(2)*X(2)
      DUMY(1) = Y(1) - DELY
      DUMY(2) = 1.0 - DUMY(1)
      IF (NMIX .EQ. 1) THEN
         CALL MANSOORI(TC,PC,W,T,P,X,DUMY,2,PARAM,KV)
      ELSEIF (NMIX .EQ. 2) THEN
         CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
     #                 PARAM,KV)
      ELSE
         CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
     #                PARAM,KV)
      ENDIF
      FN1 = DUMY(1) - KV(1)*X(1)
      GN1 = DUMY(2) - KV(2)*X(2)
      DUMY(1) = Y(1) + DELY
      DUMY(2) = 1.0 - DUMY(1)
      IF (NMIX .EQ. 1) THEN
         CALL MANSOORI(TC,PC,W,T,P,X,DUMY,2,PARAM,KV)
      ELSEIF (NMIX .EQ. 2) THEN
         CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
     #                 PARAM,KV)
      ELSE
         CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
     #                PARAM,KV)
      ENDIF
      FP1 = DUMY(1) - KV(1)*X(1)
      GP1 = DUMY(2) - KV(2)*X(2)
      DUMY(1) = Y(1) + 2.*DELY
      DUMY(2) = 1.0 - DUMY(1)
      IF (NMIX .EQ. 1) THEN
         CALL MANSOORI(TC,PC,W,T,P,X,DUMY,2,PARAM,KV)
      ELSEIF (NMIX .EQ. 2) THEN
         CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
```

```
     #                     PARAM,KV)
           ELSE
              CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,DUMY,2,
     #                    PARAM,KV)
           ENDIF
           FP2 = DUMY(1) - KV(1)*X(1)
           GP2 = DUMY(2) - KV(2)*X(2)
           DFDY(I,I) = (2.*FN2 - 16.*FN1 + 16.*FP1 -
     #                 2.*FP2)/(24.*DELY)
           DGDY(I,I) = (2.*GN2 - 16.*GN1 + 16.*GP1 -
     #                 2.*GP2)/(24.*DELY)

C          Calculate the derivative of the constraints with
C          respect to pressure.

           DELP = P*0.001
           DUMP = P - 2.*DELP
           IF (NMIX .EQ. 1) THEN
              CALL MANSOORI(TC,PC,W,T,DUMP,X,Y,2,PARAM,KV)
           ELSEIF (NMIX .EQ. 2) THEN
              CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
     #                     PARAM,KV)
           ELSE
              CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
     #                    PARAM,KV)
           ENDIF
           FN2 = Y(1) - KV(1)*X(1)
           GN2 = Y(2) - KV(2)*X(2)
           DUMP = P - DELP
           IF (NMIX .EQ. 1) THEN
              CALL MANSOORI(TC,PC,W,T,DUMP,X,Y,2,PARAM,KV)
           ELSEIF (NMIX .EQ. 2) THEN
              CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
     #                     PARAM,KV)
           ELSE
              CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
     #                    PARAM,KV)
           ENDIF
           FN1 = Y(1) - KV(1)*X(1)
           GN1 = Y(2) - KV(2)*X(2)
           DUMP = P + DELP
           IF (NMIX .EQ. 1) THEN
              CALL MANSOORI(TC,PC,W,T,DUMP,X,Y,2,PARAM,KV)
           ELSEIF (NMIX .EQ. 2) THEN
              CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
     #                     PARAM,KV)
           ELSE
              CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
```

```
     #                     PARAM,KV)
           ENDIF
           FP1 = Y(1) - KV(1)*X(1)
           GP1 = Y(2) - KV(2)*X(2)
           DUMP = P + 2.*DELP
           IF (NMIX .EQ. 1) THEN
              CALL MANSOORI(TC,PC,W,T,DUMP,X,Y,2,PARAM,KV)
           ELSEIF (NMIX .EQ. 2) THEN
              CALL STANDKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
     #                      PARAM,KV)
           ELSE
              CALL TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,DUMP,X,Y,2,
     #                     PARAM,KV)
           ENDIF
           FP2 = Y(1) - KV(1)*X(1)
           GP2 = Y(2) - KV(2)*X(2)
           DFDZ(I,I) = (2.*FN2 - 16.*FN1 + 16.*FP1 -
     #                 2.*FP2)/(24.*DELP)
           DGDZ(I,I) = (2.*GN2 - 16.*GN1 + 16.*GP1 -
     #                 2.*GP2)/(24.*DELP)
        ENDDO
        RETURN
        END


C       This subroutine is used to set the interaction
C       matrix, and call any one of three equations of state
C       to calculate K-values for the simple mixing rule
C       with one binary interaction parameter.

        SUBROUTINE STANDKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,N,
     #                     K12,KV)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 TC(N),PC(N),W(N),X(N),Y(N),KV(N),KP(2,2),
     #         K12(1),PARA(N),ZC(N)
        KP(1,1) = 0.0
        KP(1,2) = K12(1)
        KP(2,1) = K12(1)
        KP(2,2) = 0.0
        IF (NEQ .EQ. 1) THEN
           CALL PRKV(TC,PC,W,T,P,X,Y,N,KP,KV)
        ELSEIF (NEQ .EQ. 2) THEN
           CALL SRKKV(TC,PC,W,T,P,X,Y,N,KP,KV)
        ELSE
           CALL SRKFKV(TC,PC,W,ZC,PARA,T,P,X,Y,N,KP,KV)
        ENDIF
        RETURN
        END
```

```
C       This subroutine is used to set the interaction
C       matrix, and call any one of three equations of state
C       to calculate K-values for the simple mixing rule
C       with a temperature dependent binary interaction
C       parameter.

        SUBROUTINE TEMPKV(NEQ,TC,PC,W,PARA,ZC,T,P,X,Y,N,
     #                    PAR,KV)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 TC(N),PC(N),W(N),X(N),Y(N),KV(N),KP(2,2)
        REAL*8 K12,PAR(2)
        K12 = PAR(1) + PAR(2)/T
        KP(1,1) = 0.0
        KP(1,2) = K12
        KP(2,1) = K12
        KP(2,2) = 0.0
        IF (NEQ .EQ. 1) THEN
           CALL PRKV(TC,PC,W,T,P,X,Y,N,KP,KV)
        ELSEIF (NEQ .EQ. 2) THEN
           CALL SRKKV(TC,PC,W,T,P,X,Y,N,KP,KV)
        ELSE
           CALL SRKFKV(TC,PC,W,T,P,X,Y,N,KP,KV)
        ENDIF
        RETURN
        END
```

```
C       This subroutine is used to set the interaction
C       matrices and call the Peng-Robinson equation of
C       state to calculate K-values using the Mansoori
C       mixing rules.

        SUBROUTINE MANSOORI(TC,PC,W,T,P,X,Y,N,PARAMET,KV)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 TC(N),PC(N),W(N),X(N),Y(N),KV(N),PAR1(2,2),
     #         PAR2(2,2),PAR3(2,2),PARAMET(3)
        DO I = 1,2
           DO J = 1,2
              PAR1(I,J) = 0.0
              PAR2(I,J) = 0.0
              PAR3(I,J) = 0.0
           ENDDO
        ENDDO
        PAR1(1,2) = PARAMET(1)
        PAR1(2,1) = PARAMET(1)
        PAR2(1,2) = PARAMET(2)
        PAR2(2,1) = PARAMET(2)
        PAR3(1,2) = PARAMET(3)
        PAR3(2,1) = PARAMET(3)
        CALL PRMANSKV(TC,PC,W,T,P,X,Y,2,PAR1,PAR2,PAR3,KV)
        RETURN
        END
```

```
C       This subroutine calculates K-values for a mixture
C       with the Peng-Robinson equation of state and the
C       standard quadratic mixing rule for a with one
C       binary interaction parameter and linear mixing
C       rule for b.

        SUBROUTINE PRKV(TC,PC,W,T,P,X,Y,N,KP,K)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 K(N),KP(N,N),KAPPA(3)
        REAL*8 X(N),Y(N),A(3),B(3),PHIL(3),PHIV(3),
     #           AC(3),ALPHA(3),TC(N),PC(N),W(N)
        R = 82.05*14.696*0.0068947
        TWO = 2.0

C       Calculate the pure component constants.

        DO I = 1,N
           B(I) = 0.0778*R*TC(I)/PC(I)
           AC(I) = 0.45724*(R*TC(I))**2/PC(I)
           KAPPA(I) = 0.37464 + 1.54226*W(I)
     #                - 0.26992*W(I)**2
           ALPHA(I) = (1.0 + KAPPA(I)*(1.0 -
     #                DSQRT(T/TC(I))))**2
           A(I) = AC(I)*ALPHA(I)
        ENDDO

C       Calculate the mixture constants for the liquid
C       phase.

        BMIX = 0.0
        AMIX = 0.0
        DO I = 1,N
           BMIX = BMIX + X(I)*B(I)
           DO J = 1,N
              AMIX = AMIX + X(I)*X(J)*DSQRT(A(I)*A(J))*(1.0
     #               - KP(I,J))
           ENDDO
        ENDDO

C       Solve the cubic equation of state for the
C       compressibility factor of the liquid.

        CAPA = AMIX*P/(R*T)**2
        CAPB = BMIX*P/(R*T)
        D = CAPB - 1.0
        E = CAPA - 3.0*CAPB**2 - 2.0*CAPB
        F = CAPB**3 + CAPB**2 - CAPA*CAPB
        ID = 1
```

```
      CALL VCUB(D,E,F,ID,Z)

C     Calculate the liquid fugacity coefficient.

      DO I = 1,N
         Q = 0.0
         DO J = 1,N
            Q = Q + 2.0*X(J)*DSQRT(A(I)*A(J))*(1.0
     #           - KP(I,J))
         ENDDO
         Q1 = B(I)*(Z - 1.0)/BMIX - DLOG(Z - CAPB)
         Q2 = CAPA*(Q/AMIX - B(I)/BMIX)/
     #        (2.0*CAPB*DSQRT(TWO))
         Q3 = DLOG((Z + CAPB*(1.0 + DSQRT(TWO)))/
     #        (Z - CAPB*(DSQRT(TWO) - 1.0)))
         PHIL(I) = DEXP(Q1 - Q2*Q3)
      ENDDO

C     Calculate the mixture constants for the vapor phase.

      BMIX = 0.0
      AMIX = 0.0
      DO I = 1,N
         BMIX = BMIX + Y(I)*B(I)
         DO J = 1,N
            AMIX = AMIX + Y(I)*Y(J)*DSQRT(A(I)*A(J))*
     #           (1.0 - KP(I,J))
         ENDDO
      ENDDO

C     Solve the cubic equation of state for the
C     compressibility factor of the vapor.

      CAPA = AMIX*P/(R*T)**2
      CAPB = BMIX*P/(R*T)
      D = CAPB - 1.0
      E = CAPA - 3.0*CAPB**2 - 2.0*CAPB
      F = CAPB**3 + CAPB**2 - CAPA*CAPB
      ID = -1
      CALL VCUB(D,E,F,ID,Z)

C     Calculate the vapor fugacity coefficient.

      DO I = 1,N
         Q = 0.0
         DO J = 1,N
            Q = Q + 2.0*Y(J)*DSQRT(A(I)*A(J))*
     #           (1.0 - KP(I,J))
```

```
            ENDDO
            Q1 = B(I)*(Z - 1.0)/BMIX - DLOG(Z - CAPB)
            Q2 = CAPA*(Q/AMIX - B(I)/BMIX)/
     #           (2.0*CAPB*DSQRT(TWO))
            Q3 = DLOG((Z + CAPB*(1.0 + DSQRT(TWO)))/
     #           (Z - CAPB*(DSQRT(TWO) - 1.0)))
            PHIV(I) = DEXP(Q1 - Q2*Q3)
         ENDDO

C        Calculate the K-values.

         DO I = 1,N
            K(I) = PHIL(I)/PHIV(I)
         ENDDO
         RETURN
         END

C        This subroutine calculates k-values for a mixture
C        with the Soave-Redlich-Kwong equation of state and
C        the standard quadratic mixing rule for a with one
C        binary interaction parameter and linear mixing
C        rule for b.

         SUBROUTINE SRKKV(TC,PC,W,T,P,X,Y,N,KP,K)
         IMPLICIT REAL*8 (A-H,O-Z)
         REAL*8 TC(N),PC(N),W(N),X(N),Y(N),A(3),B(3),
     #          PHIV(3)
         REAL*8 KP(N,N),K(N),M
         R = 82.05*14.696*0.0068947
         DO I = 1,N
            M = 0.48 + 1.574*W(I) - 0.176*W(I)**2
            ALPHA = 1.0 + M*(1.0 - DSQRT(T/TC(I)))
            A(I) = 0.42747*(TC(I)*ALPHA*R)**2/PC(I)
            B(I) = 0.08664*TC(I)*R/PC(I)
         ENDDO
         AMIX = 0.0
         BMIX = 0.0
         DO I = 1,N
            BMIX = BMIX + Y(I)*B(I)
            DO J = 1,N
               AMIX = AMIX + Y(I)*Y(J)*DSQRT(A(I)*A(J))*
     #                (1.0 - KP(I,J))
            ENDDO
         ENDDO
         CAPA = P*AMIX/(R*T)**2
         CAPB = P*BMIX/(R*T)
         D = -1.0
         E = CAPA - CAPB - CAPB**2
```

```
      F = -CAPA*CAPB
      ID = -1
      CALL VCUB(D,E,F,ID,Z)
      DO I = 1,N
         Q = 0.0
         DO J = 1,N
            Q = Q + 2.0*Y(J)*DSQRT(A(I)*A(J))*
     #           (1.0 - KP(I,J))
         ENDDO
         Q1 = B(I)*(Z - 1.0)/BMIX - DLOG(Z - CAPB)
         Q2 = CAPA*(Q/AMIX - B(I)/BMIX)*
     #        DLOG(1. + CAPB/Z)/CAPB
         PHIV(I) = DEXP(Q1 - Q2)
      ENDDO
      AMIX = 0.0
      BMIX = 0.0
      DO I = 1,N
         BMIX = BMIX + X(I)*B(I)
         DO J = 1,N
            AMIX = AMIX + X(I)*X(J)*DSQRT(A(I)*A(J))*
     #              (1.0 - KP(I,J))
         ENDDO
      ENDDO
      CAPA = P*AMIX/(R*T)**2
      CAPB = P*BMIX/(R*T)
      D = -1.0
      E = CAPA - CAPB - CAPB**2
      F = -CAPA*CAPB
      ID = 1
      CALL VCUB(D,E,F,ID,Z)
      DO I = 1,N
         Q = 0.0
         DO J = 1,N
            Q = Q + 2.0*X(J)*DSQRT(A(I)*A(J))*
     #           (1.0 - KP(I,J))
         ENDDO
         Q1 = B(I)*(Z - 1.0)/BMIX - DLOG(Z - CAPB)
         Q2 = CAPA*(Q/AMIX - B(I)/BMIX)*
     #        DLOG(1. + CAPB/Z)/CAPB
         K(I) = DEXP(Q1 - Q2)/PHIV(I)
      ENDDO
      RETURN
      END
```

```
C       This subroutine calculates k-values for a mixture
C       with the Fuller modification of the Soave-Redlich-
C       Kwong equation of state and the standard quadratic
C       mixing rule for a with one binary interaction
C       parameter and linear mixing rule for b.

        SUBROUTINE SRKFKV(TC,PC,W,ZC,PARA,T,P,X,Y,N,KP,K)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 TC(N),PC(N),W(N),X(N),Y(N),ZC(N),PARA(N),
     #         BETA(3),BETAC(3),Q3(3),A(3),B(3),C(3),
     #         THETA(3),PHIV(3),PHIL(3)
        REAL*8 KP(N,N),K(N),M
        R = 82.05*14.696*0.0068947
        DO I = 1,N
           BETACL = 0.07
           BETACR = 0.24
           DO J = 1,12
              BETACM = (BETACL + BETACR)/2.0
              Z = F(BETACM)
              IF (Z .LT. ZC(I)) THEN
                 BETACL = BETACM
              ELSE
                 BETACR = BETACM
              ENDIF
           ENDDO
           BETAC(I) = BETACM
        ENDDO
        DO I = 1,N
           THETA(I) = 10.9356 + 0.0285*PARA(I)
           BETA0 = (7.788 - 36.8316*ZC(I) +
     #             50.7061*ZC(I)**2)*BETAC(I)
           BETA(I) = 2./(1. + DEXP(THETA(I)*
     #               (T/TC(I) - 1.))) - 1.
           BETA(I) = BETAC(I) + (BETA0 - BETAC(I))*BETA(I)
           M = 0.48 + 1.574*W(I) - 0.176*W(I)**2
           ALPHA = (1. + (BETA(I)/0.26)**0.25*M*(1. -
     #                DSQRT(T/TC(I))))**2
           C(I) = (DSQRT(1./BETA(I) - 0.75) - 1.5)/BETA(I)
           FUNCB = BETA(I)*((1. - BETA(I))*(2. + C(I)*
     #             BETA(I)) - (1. + C(I)*BETA(I)))/((2.
     #             + C(I)*BETA(I))*(1. - BETA(I))**2)
           FUNCA = (1. + C(I)*BETA(I))**2*FUNCB/(BETA(I)*
     #             (1. - BETA(I))**2*(2. + C(I)*BETA(I)))
           B(I) = FUNCB*R*TC(I)/PC(I)
           A(I) = FUNCA*R*R*TC(I)*TC(I)*ALPHA/PC(I)
        ENDDO
        AMIX = 0.0
        BMIX = 0.0
```

```
      BCMIX = 0.0
      DO I = 1,N
         Q3(I) = 0.0
         BMIX = BMIX + X(I)*B(I)
         BCMIX = BCMIX + X(I)*B(I)*C(I)
         DO J = 1,N
            Q3(I) = Q3(I) + X(J)*DSQRT(A(I)*A(J))*
     #              (1.0 - KP(I,J))
            AMIX = AMIX + X(I)*X(J)*DSQRT(A(I)*A(J))*
     #           (1.0 - KP(I,J))
         ENDDO
         Q3(I) = 2.0*Q3(I)
      ENDDO
      D = BCMIX - BMIX -R*T/P
      E = AMIX/P - R*T*BCMIX/P - BMIX*BCMIX
      G = -AMIX*BMIX/P
      ID = 1
      CALL VCUB(D,E,G,ID,V)
      Q1 = DLOG(V/(V - BMIX))
      Q2 = DLOG(V/(V + BCMIX))
      DO I = 1,N
         Q4 = AMIX*B(I)*C(I)/(R*T*BCMIX*(V + BCMIX))
         Q5 = AMIX*B(I)*C(I)/BCMIX
         PHIL(I) = DEXP(Q1 +B(I)/(V - BMIX) - Q4 + (Q3(I)
     #           - Q5)*Q2/(R*T*BCMIX) - DLOG(P*V/(R*T)))
      ENDDO
      AMIX = 0.0
      BMIX = 0.0
      BCMIX = 0.0
      DO I = 1,N
         Q3(I) = 0.0
         BMIX = BMIX + Y(I)*B(I)
         BCMIX = BCMIX + Y(I)*B(I)*C(I)
         DO J = 1,N
            Q3(I) = Q3(I) + Y(J)*DSQRT(A(I)*A(J))*
     #              (1.0 - KP(I,J))
            AMIX = AMIX + Y(I)*Y(J)*DSQRT(A(I)*A(J))*
     #           (1.0 - KP(I,J))
         ENDDO
         Q3(I) = 2.0*Q3(I)
      ENDDO
      D = BCMIX - BMIX -R*T/P
      E = AMIX/P - R*T*BCMIX/P - BMIX*BCMIX
      G = -AMIX*BMIX/P
      ID = -1
      CALL VCUB(D,E,G,ID,V)
      Q1 = DLOG(V/(V - BMIX))
      Q2 = DLOG(V/(V + BCMIX))
```

```
      DO I = 1,N
         Q4 = AMIX*B(I)*C(I)/(R*T*BCMIX*(V + BCMIX))
         Q5 = AMIX*B(I)*C(I)/BCMIX
         PHIV(I) = DEXP(Q1 +B(I)/(V - BMIX) - Q4 + (Q3(I)
     #                - Q5)*Q2/(R*T*BCMIX) - DLOG(P*V/(R*T)))
         K(I) = PHIL(I)/PHIV(I)
      ENDDO
      RETURN
      END
      REAL*8 FUNCTION F(X)
      IMPLICIT REAL*8 (A-H,O-Z)
      C = (DSQRT(1./X - 0.75) - 1.5)/X
      F = ((1. - X)*(2. + C*X) - (1. + C*X))/
     #     ((2. + C*X)*(1. - X)**2)
      RETURN
      END
```

```
C       This subroutine calculates the real roots of a cubic
C       equation of the form Z**3 + D*Z**2 + E*Z + F = 0.

        SUBROUTINE VCUB(D,E,F,ID,Z)
        IMPLICIT REAL*8 (A-H,O-Z)
        ABC = 1.0/3.0
        G = (3.0*E - D*D)/3.0
        H = -(9.0*D*E - 27.0*F - 2.0*D**3)/27.0
        IF (G**3/27.0 + H*H/4.0 .LE. 0.0) GO TO 10

C       Only one real root exists.

        S = -H/2.0 + DSQRT(G**3/27.0 + H*H/4.0)
        TT = -H/2.0 - DSQRT(G**3/27.0 +H*H/4.0)
        IF (S) 5,6,6
5       S = -((-S)**ABC)
        GO TO 7
6       S = S**ABC
7       IF (TT) 8,9,9
8       TT = -((-TT)**ABC)
        GO TO 15
9       TT = (TT)**ABC

C       Z is the value of the single real root.

15      Z = S + TT - D/3.0
        GO TO 40

C       There are three real roots.

10      THETA = (DACOS(-0.5*H/DSQRT(-G**3/27.0)))/3.0
        Z1 = 2.0*DSQRT(-G/3.0)*DCOS(THETA)
        Z2 = 2.0*DSQRT(-G/3.0)*DCOS(THETA + 2.0943951)
        Z3 = 2.0*DSQRT(-G/3.0)*DCOS(THETA + 4.1887902)

C       Take the largest root for the vapor
C       compressibility factor.

        IF (ID) 20,30,30
20      Z = DMAX1(Z1,Z2,Z3) - D/3.0
        GO TO 40

C       Take the smallest root for the liquid
C       compressibility factor.

30      Z = DMIN1(Z1,Z2,Z3) - D/3.0
40      RETURN
        END
```

```
C       Subroutine to invert a symmetric matrix.
C       This subroutine was taken from "Computer
C       Calculations for High-Pressure Vapor-Liquid
C       Equilibria" by Prausnitz and Chueh, 1968.

        SUBROUTINE MATSYMINV(A,N,ND,IRR)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 A(ND,ND),P(150),Q(150)
        INTEGER R(150)
        IRR = 0
        DO 10 I = 1,N
10         R(I) = 1
        DO 150 I = 1,N
           BIG = 0.0
           DO 40 J = 1,N
              TEST = DABS(A(J,J))
              IF (TEST-BIG) 40,40,20
20            IF (R(J)) 160,40,30
30            BIG = TEST
              K = J
40         CONTINUE
           IF (BIG .LT. 1.-19) GO TO 160
           R(K) = 0
           Q(K) = 1./A(K,K)
           P(K) = 1.0
           A(K,K) = 0.0
           KP1 = K + 1
           KM1 = K - 1
           IF (KM1) 160,80,50
50         DO 70 J = 1,KM1
              P(J) = A(J,K)
              Q(J) = A(J,K)*Q(K)
              IF (R(J)) 160,70,60
60            Q(J) = -Q(J)
70            A(J,K) = 0.0
80         IF (K-N) 90,130,160
90         DO 120 J = KP1,N
              P(J) = A(K,J)
              IF (R(J)) 160,100,110
100           P(J) = -P(J)
110           Q(J) = -A(K,J)*Q(K)
120           A(K,J) = 0.0
130        DO 140 J = 1,N
              DO 140 K = J,N
                 A(J,K) = A(J,K) + P(J)*Q(K)
140              A(K,J) = A(J,K)
150     CONTINUE
        RETURN
```

```
160     IRR = 1
        RETURN
        END


C       Subroutine to invert a diagonal matrix.

        SUBROUTINE MATDIAGINV(A,N,ND,AINV)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 A(ND,ND),AINV(ND,ND)
        DO I = 1,N
           DO J = 1,N
              IF (I .EQ. J) THEN
                 AINV(I,J) = 1.0/A(I,J)
              ELSE
                 AINV(I,J) = 0.0
              ENDIF
           ENDDO
        ENDDO
        RETURN
        END


C       Subroutine to add or subtract two matrices.  If
C       ID is greater than zero then addition is performed,
C       and if ID is less than zero then subtraction is
C       performed.

        SUBROUTINE MATADD(A,B,N,M,ND,MD,ID,SUM)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 A(ND,MD),B(ND,MD),SUM(ND,MD)
        IF (ID .GT. 0) THEN
           DO I = 1,N
              DO J = 1,M
                 SUM(I,J) = A(I,J) + B(I,J)
              ENDDO
           ENDDO
        ELSE
           DO I = 1,N
              DO J = 1,M
                 SUM(I,J) = A(I,J) - B(I,J)
              ENDDO
           ENDDO
        ENDIF
        RETURN
        END
```

```
C       Subroutine to multiply two matrices.

        SUBROUTINE MATMULT(A,N,M,ND,MD,B,L,LD,PROD)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 A(ND,MD),B(MD,LD),PROD(ND,LD)
        DO I = 1,N
           DO J = 1,L
              BEGIN = 0.0
              DO K = 1,M
                 BEGIN = A(I,K)*B(K,J) + BEGIN
              ENDDO
              PROD(I,J) = BEGIN
           ENDDO
        ENDDO
        RETURN
        END


C       Subroutine to take the negative of a matrix.

        SUBROUTINE MATNEG(A,N,M,ND,MD)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 A(ND,MD)
        DO I = 1,N
           DO J = 1,M
              A(I,J) = -A(I,J)
           ENDDO
        ENDDO
        RETURN
        END


C       Subroutine to transpose a matrix.

        SUBROUTINE MATTRANS(A,N,M,ND,MD,ATRANS)
        IMPLICIT REAL*8 (A-H,O-Z)
        REAL*8 A(ND,MD),ATRANS(MD,ND)
        DO I = 1,N
           DO J = 1,M
              ATRANS(J,I) = A(I,J)
           ENDDO
        ENDDO
        RETURN
        END
```