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EXPERIMENTAL AND CALCULATED VAPOR-LIQUID EQUILIBRIA  
FOR THE METHANE-PROPANE-CARBON DIOXIDE  
SYSTEMS AT 230 K AND 270 K

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by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical and Petroleum-Refining Engineering).

Golden, Colorado

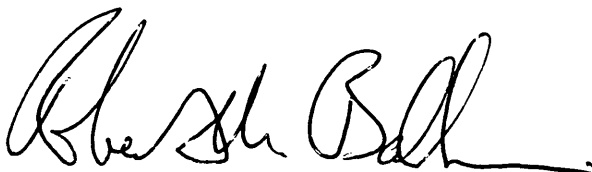
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## ABSTRACT

An apparatus for the measurement of low-temperature vapor-liquid equilibria was rebuilt with modifications to the refrigeration system and the equilibrium cell. The system was tested to insure that it could reproduce the precision of the previous apparatus by the generation of vapor pressure measurements for Coleman grade carbon dioxide.

Vapor-liquid equilibria data were measured for the binary systems methane-carbon dioxide, methane-propane, and carbon dioxide-propane at 230 K and 270 K. The ternary system methane-carbon dioxide-propane was studied at 230 K for 0.8, 4.0, and 7.0 MPa; and at 270 K for 2.8, 5.5, and 8.0 MPa.

The binary data were used to fit a single interaction coefficient for the Peng-Robinson equation of state. The interaction coefficients were then used in the equation of state to predict the ternary vapor-liquid equilibria. These predictions were compared with the experimental data. The

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Peng-Robinson equation satisfactorily predicts the ternary data except near the critical region of the mixture.

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## INTRODUCTION

Natural gas is becoming an increasingly important fuel source in the United States. Over time fields which were deemed uneconomical to process will be needed to meet demands. Many of these fields have high carbon dioxide content. Phase equilibria is important in the design of gas processing unit operations. The behavior of alkanes and carbon dioxide will be especially needed for the design and optimization of future thermal separation units. There is also a need for experimental data for vapor-liquid equilibrium of the heavier alkanes in natural gas, C<sub>3</sub>+. The processing of gases for ethane recovery requires cryogenic processes at high pressures. The behavior of the C<sub>3</sub>+ components are difficult to model under these conditions.

Furthermore, the widespread implementation of computer simulators for the design, control and optimization of gas processing facilities has made the use of equations of state to model vapor-liquid equilibria indispensable. All such equations in use in the industry today require vapor-liquid equilibria data to fit at least one adjustable parameter.

It has been the goal of this laboratory since 1972 to establish a base of accurate phase equilibria data to be used not only to determine interaction parameters but also to evaluate current equations and mixing rules, and to develop better models.

## LITERATURE REVIEW

Table 1 lists all of the published binary data with the explored temperature range.

CH<sub>4</sub>-CO<sub>2</sub> Binary System

A large quantity of data has been published on the CH<sub>4</sub>-CO<sub>2</sub> system. In this laboratory four experimentalists have included low-temperature data on this system in their thesis work. For the 270 K isotherm direct comparisons were made with the data of Al-Sahhaf (1983) and Somait (1978).

CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> Binary System

Comparisons were made with four of the twenty-two published references. Comparisons were made by graphing calculated Henry's law constants versus temperature. These data sets were chosen because they were generated at subambient temperatures and included data for the liquid phase in the dilute region for which Henry's Law applies. Three groups of investigators published data on the CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub>

binary system in the 1950s: Akers, Burns, and Fairchild (1954); Reamer, Sage, and Lacey (1950); and, Price and Kobayashi (1959). The other investigation was published more recently by Wichterle & Kobayashi (1972).

#### CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> Binary System

The CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> binary system has the least amount of published data of the three binaries. Only six groups of experimentalists have published data on this system. Four of the data sets are at subambient temperatures. Comparisons were made by graphing calculated Henry's law constants versus temperature with the data sets of Nagahama et al. (1974); Reamer, Sage, and Lacey (1951); and Hamam and Lu (1976).

#### CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> Ternary System

No data have been published for the CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> ternary system.

Table 1  
Summary of Previous Experimental Data

| <u>System</u>                                  | <u>References</u>                   | <u>Temperature(K)</u> |
|--|-------------------------------------|-----------------------|
| CH <sub>4</sub> -CO <sub>2</sub>               | Al-Sahhaf, Kidnay, and Sloan, 1983  | 219,240,270           |
|  | Arai, Kaminishi, and Saito, 1971    | 253,273,288           |
|  | Davalos et al., 1976                | 230,250,270           |
|  | Donnelly and Katz, 1954             | 219 to 272            |
|  | Hwang et al., 1976                  | 153 to 219            |
|  | Kaminishi and Toriumi, 1968         | 233,253,273           |
|  | Kaminishi et al., 1968              | 233,253,273,283       |
|  | Mathot, 1963                        | 90                    |
|  | Mraw, Hwang, and Kobayashi, 1978    | 153 to 219            |
|  | Neumann and Walch, 1968             | 208.5,208.8,220       |
|  | Phelps, 1989                        | 270                   |
|  | Pikaar, 1959                        | 160 to 220            |
|  | Somait and Kidnay, 1978             | 270                   |
|  | Wei, Brown, Kidnay, and Sloan, 1995 | 230,250,270           |
|  | Xu, et al., 1992                    | 288,293               |
| CH <sub>4</sub> -C <sub>3</sub> H <sub>8</sub> | Ahland, 1966                        | 271-274               |
|  | Akers, Burns, and Fairchild, 1954   | 158-273               |

Table 1 (continued)  
 Summary of Previous Experimental Data

| <u>System</u>                                  | <u>References</u>                  | <u>Temperature(K)</u> |
|--|------------------------------------|-----------------------|
| CH <sub>4</sub> -C <sub>3</sub> H <sub>8</sub> | Calado, Garcia, and Staveley, 1974 | 116,135               |
|  | Cheung and Wang, 1964              | 92 to 128             |
|  | Cutler and Morrison, 1965          | 90 to 110             |
|  | Frolich et al., 1931               | 298                   |
|  | Kalra and Robinson, 1975           | 214                   |
|  | Poon and Lu, 1974                  | 114,118,122           |
|  | Price and Kobayashi, 1959          | 144-283               |
|  | Reamer and Sage, 1957              | 278 to 376            |
|  | Reamer, Sage, and Lacey, 1950      | 278 to 361            |
|  | Roof and Baron, 1967               | 305 to 356            |
|  | Rutherford, 1962                   | 316                   |
|  | Sage, Lacey, and Schaafsma, 1934   | 293-363               |
|  | Skripa, et al., 1970               | 123 to 153            |
|  | Stoeckli and Staveley, 1970        | 91                    |
|  | Wichterle and Kobayashi, 1972      | 130-214               |
|  | Wiese, Jacobs, and Sage, 1970      | 278 to 344            |
| Wiese, Reamer, and Sage, 1970                  | 278, 311                           |                       |

Table 1 (continued)  
 Summary of Previous Experimental Data

| <u>System</u>                                  | <u>References</u>                 | <u>Temperature(K)</u> |
|--|-----------------------------------|-----------------------|
|  | Wilson, 1975                      | 111                   |
|  | Yesavage, Katz, and Powers, 1969  | 210-350               |
|  | Yesavage, Katz, and Powers, 1970  | 180-329               |
| CO <sub>2</sub> -C <sub>3</sub> H <sub>8</sub> | Akers, Kelley, and Lipscomb, 1954 | 233,253,273           |
|  | Hamam and Lu, 1976                | 244,267               |
|  | Nagahama et al., 1974             | 253,273               |
|  | Poettman and Katz, 1945           | 300,311,333,355       |
|  | Reamer, Sage, and Lacey, 1951     | 232,253,273           |
|  | Roof and Baron, 1967              | 305 to 361            |

## EXPERIMENTAL APPARATUS

The apparatus which was used by Brown (1990) was rebuilt with modifications to the refrigeration system and the equilibrium cell. The original designer of the cryogenic apparatus was Duston (1970). Duston's description of the system and list of equipment suppliers were aids in the building and controlling of the new apparatus as were the theses of Al-Sahhaf (1981) and Somait (1976).

The phase equilibria system was of the vapor recirculation type; see Figure 1. A brass equilibrium cell with a sapphire window was suspended in a cryostat containing 67 wt% technical grade, ethylene glycol solution. This solution has an approximate freezing point of 220 K; the lower operating limit of the system was found to be 230 K. The cryostat used was a 23 liter glass dewar. The equilibrium cell is shown in Figure 2. The cell was modified from that used by Brown (1990) because of repeated leaking of the cell. The primary o-ring seal was changed

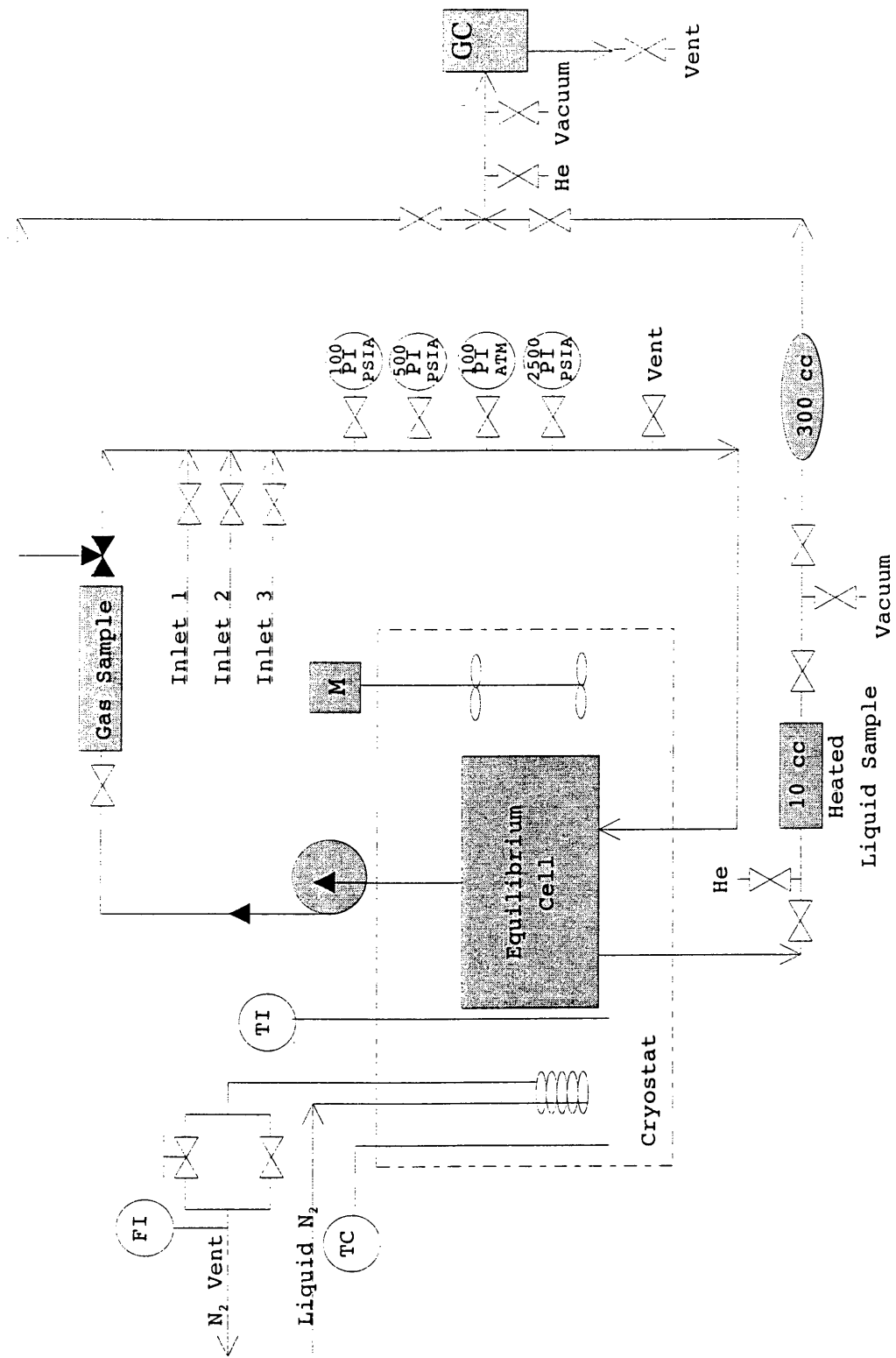


Figure 1. Experimental Apparatus.

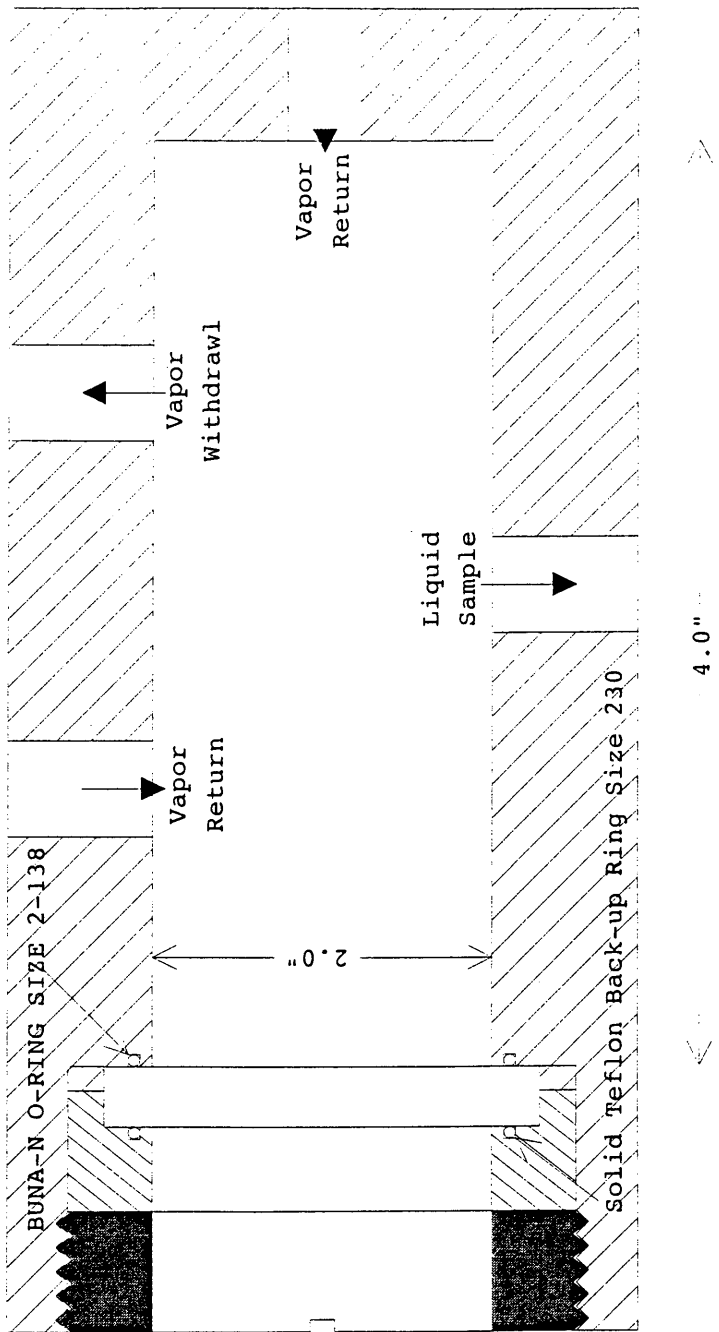


Figure 2. Equilibrium Cell

from a solid Teflon o-ring size 230 to a nitrile rubber (BUNA-N) size 2-138. Nitrile rubber does not embrittle in a cryogenic apparatus and has high chemical resistance to hydrocarbons. To hold the o-ring in place the cell was machined to add a groove. The o-ring on the sapphire side was not changed from a solid Teflon back-up ring size 139. Note this ring only serves to cushion the sapphire window and is not a sealing surface; the nitrile rubber o-ring is the only seal.

The bath is cooled via liquid nitrogen in a 1/4" copper coil heat exchanger of 20 Feet in length. The bath is well-mixed with a two-propeller, variable-speed stirrer. Excess refrigeration is balanced with one 225 watt Omega immersible heater. The heater is controlled by a Bayley Model 121 proportional temperature controller. The setting for the two control points used in this study are as follows:

Bayley Settings 230 K

Gross Control: 75.7 between 3&2 (closer to 3)

Fine Control: 2.8 (note this varies)

PBand: 4.2

Gain: 6.0

Nitrogen vent: 45 SCFH

Bayley Settings 270 K

Gross Control: 77.8 just past 5

Fine Control: 4.8 (note this varies)

PBand: 4.2

Gain: 5.8  
Nitrogen vent: 35 SCFH

The temperature was measured to  $\pm 0.001$  K with a calibrated IPTS-68 platinum resistance thermometer (#1169) connected to a Mueller bridge and a Keithley null detector. The temperature in the bath was controlled to  $\pm 0.01$ K. The pressure was measured with a series of Heise bourdon tube gauges with the following pressure ranges: 0-100 PSIA, 0-500 PSIA, 0-100 ATM, 0-2500 PSIA. Each gauge has an accuracy of  $\pm 0.1\%$  of the full-scale reading. The calibrations for the Mueller bridge and the pressure gauges are given in Appendix A.

A Pulsafeeder diaphragm metering pump, model L20-S-E was used to circulate the vapor. Vapor samples were taken from a 15 cc sample cylinder in the recirculation loop. Liquid samples were taken directly from the cell through a stainless steel, capillary line into a 10cc sample cylinder and in some cases expanded into a 300 cc cylinder. Samples were analyzed in a Hewlett-Packard 5890 Series II gas chromatograph equipped with a Valco gas sample valve with a 15 microliter sample loop and a thermal conductivity detector. Note the valve was of type 18900F and has a

maximum operating temperature of 175°C. The column and chromatograph settings which were used to obtain good separation of methane, carbon dioxide and propane at retention times of 0.75, 1.19, and 4.53 min., respectively, are as follows:

Column: Manufacturer=Alltech, Catalog No.=C-5000  
Length=9', O.D.=1/8", Material=Stainless Steel  
Mesh=80/100, Support=Porapak N, Tmax= 190°C  
Oven/Sample valve Temperature=100°C  
Thermal Conductivity Detector Temperature=125°C  
Thermal Conductivity Detector Sensitivity=low  
Helium Flow Rate=25 ml/min with 60 PSIG at regulator

Peak area counts were calculated with a Hewlett-Packard

3392A integrator with the following settings:

Zero = 0  
Attenuation = 5  
Chart Speed = 0.6  
Peak Width = 0.04  
Threshold = 4  
Integration Option 4 at Time=0  
(no test for solvent peaks)

The peak area counts were related to compositions through the use of calibration curves determined from pure components injected at known pressures. The calibration curves are shown in Figure 3. The sample loop size in the gas sampling valve was decreased until the response of all three curves was linear. The calibrations were checked with

## GAS CHROMATOGRAPH CALIBRATION

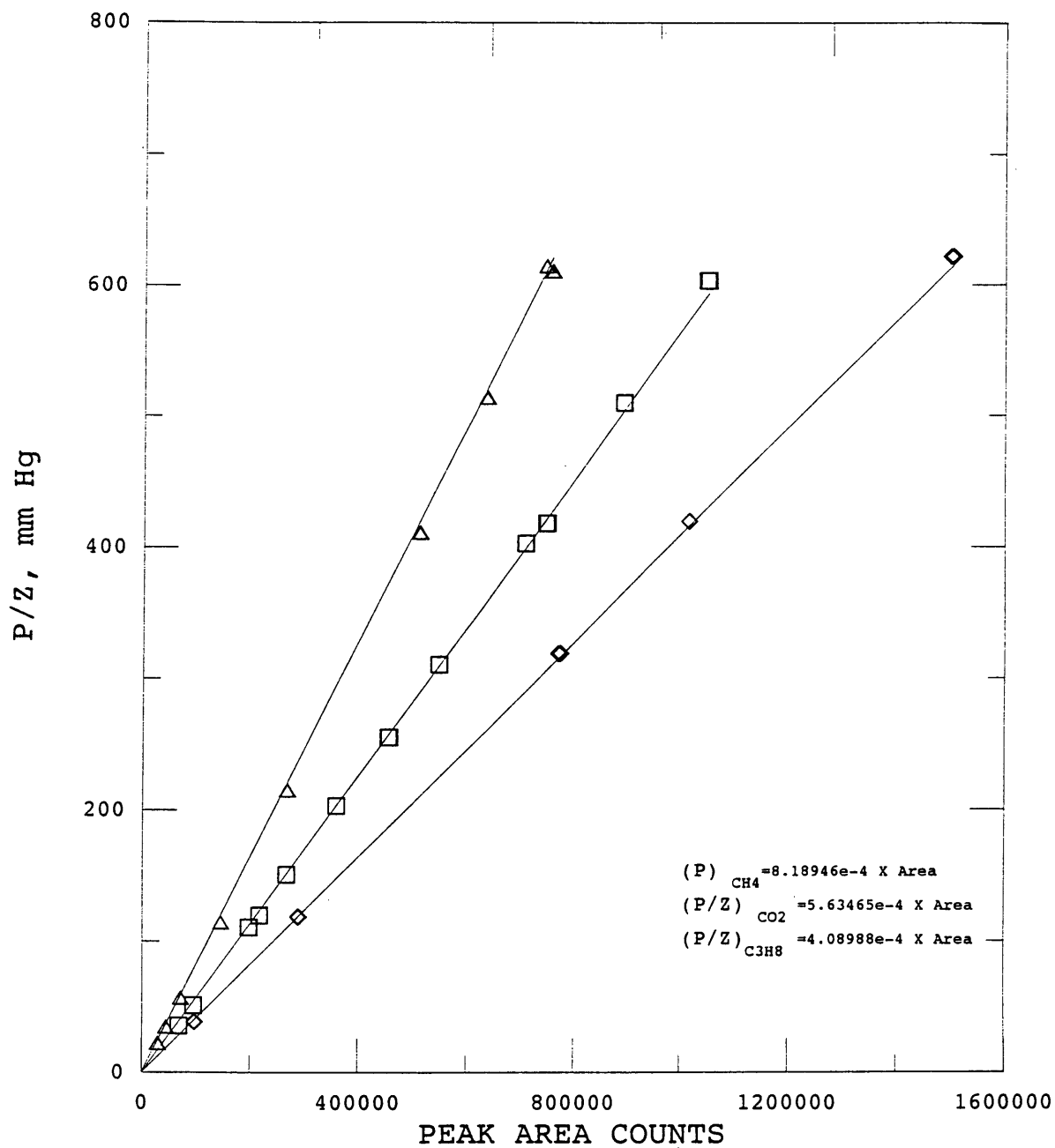


Figure 3. Gas Chromatograph Calibration:  $\Delta$  Methane,  $\square$  Carbon Dioxide,  $\diamond$  Propane.

gravimetric mixtures prepared in the laboratory. The estimated error in the calculated mole fractions using these calibration curves is  $\pm 0.002$  in the mole fraction. See Appendix A for a detailed account of the GC calibration procedure and calibration verification.

The sample tubing is shown in Figure 1. It consists of three tubing sections: the liquid tubing with sample cylinders, the vapor tubing, and the GC tubing with sample loop. The vapor sample cylinder is integral to the recirculation loop and joins the vapor sample tubing by a three-way valve. The liquid sample capillary line is open to the equilibrium cell up to a valve at the 10cc sample cylinder. The liquid sample tubing can include the 300 cc sample cylinder. Both liquid sampling cylinders are heated with heating tape connected to a variac for heat modulation. Both vapor and liquid sample tubing join the GC tubing.

The 300 cc liquid sample cylinder was added after the binary  $\text{CH}_4\text{-CO}_2$  systems were complete. The addition of propane, which has a low volatility relative to carbon dioxide and methane caused a significant problem in the liquid sampling. Normally fractionation of the liquid

sample occurs but resolves itself in the 10 cc heated sampling cylinder. As Brown (1990, pg. 10) observed with a butane system, liquid samples did not become well-mixed with time and heat. This was indicated by decreasing concentrations of the lighter component in successive gas chromatograph runs. To achieve a well-mixed liquid sample the sample was flushed with helium from the 10 cc cylinder to the 300 cc cylinder. This modified sample line worked well for all subsequent systems except the carbon dioxide-propane system at 230 K. For this low pressure isotherm the modified sample line lowered the sample size at the GC to such an extent that solute peaks below 0.3 mole fraction were not seen. For this system the 300 cc cylinder was replaced with 1/8" copper tubing.

The carbon dioxide and methane were supplied by General Air and had minimum purities of 99.995(Coleman Grade) and 99.99 mole percent, respectively. The propane was supplied by Scott Specialty Gas with a minimum purity of 99.5(Instrument Grade) mole percent. The gases were used without further purification. All gases were determined to be chromatographically pure, producing no extraneous peaks,

at the low sensitivity thermal conductivity detector  
setting.

## EXPERIMENTAL PROCEDURE

Start-up

1. Load the cell.
  - a) Turn on the vacuum pump. Close the vacuum manifold vent and open the vacuum pump to the low temperature VLE system.
  - b) Lower the dewar so that in the event of a equilibrium cell leak the bath fluid will not be sucked into the cell during evacuation.
  - c) Check valve positions. Vent valve is closed, liquid sample valve is closed, 3-way vapor sample valve is switched to the recirculation system and the vapor sample valves are open, pressure gauges are all fully open, and the inlet valves are closed.
  - d) Evacuate system for five minutes. Add the heavy system component (in this case propane) to just over atmospheric pressure, @12PSIA. Repeat two more times. Note: on the final evacuation zero the Heise gauges.

e) Take a vapor sample and analyze for impurities.

Note: when attaching inlet gases for the first time steps (d) and (e) will be carried out for each inlet gas with the heavy component completed last.

f) Raise dewar.

2. Chill the cell.

a) Turn on stirrer with speed at 2.5.

b) Turn on Bayley Temperature controller with either predetermined settings or with gross temperature dial at zero. The settings determined for this experiment are listed in the apparatus description.

c) Open liquid withdrawal valve on the liquid nitrogen dewar fully.

d) Open nitrogen vent valve fully. Note: vent valve should never be closed during idle periods because liquid nitrogen left in exchanger coil will vaporize and expand.

e) Set Mueller bridge resistors to the goal resistance, as read from the calibration for the

thermometer, plus the zero adjustment (0.0007 ohms). Turn on 1 amp power source and the null detector at approximately the 3 millivolt scale. Note: the Mueller bridge temperature controller should remain on even when the VLE system is not running. This maintains the resistors at a temperature of 35°C.

- f) As the null detector nears zero on a microvolt scale, close down on the nitrogen vent valve. For 270 K, close the main vent and the metering vent so that the rotameter reads @ 35 SCFH. For 230 K, the rotameter should read @ 45 SCFH.
- g) Charge cell with heavy component until liquid level is half of the cell.
- h) Start recirculation pump at 100% metering stroke. Note: at start-up it is sometimes necessary to bleed the air vent behind the diaphragm of the pump (see PULSAfeeder manual).
- i) If the Bayley control settings have not been determined, follow these guidelines for finding the control point. When the null detector nears

zero on the 3 microvolt scale slowly increase the gross temperature dial until the control heat indicator needle flips to 100%. Back off the gross control slowly until the needle returns to zero. This is the gross temperature range. Adjust the nitrogen vent flow so that the control heat needle stays between 3-20%, i.e., does not rest on zero or go up to 100%. The bath temperature should be coming into control as indicated by the null detector needle remaining steady on the 3 microvolt scale. Read the Mueller bridge; see thesis of Duston (1970, pg. 18). Do not forget to subtract the zero (see Calibrations Appendix A). To control the temperature at the desired setting tweak the fine temperature control setting on the Bayley and/or adjust the metering vent valve. Read Mueller bridge between adjustments. The Pband and Gain control can be adjusted to tighten control; however settings between 4-6 for both are found to be optimal.

### Vapor Pressure Measurements

1. Check that the cell is half full of the pure component. Verify purity by sampling the vapor phase and analyzing in the GC. Measure the temperature to verify it is controlled to  $\pm 0.001$  ohms of the goal resistance.
2. Monitor cell pressure. Periodically stop recirculation pump to read pressure. Note: the recirculating vapor is an important element of the heat balance on the system so although it is not needed for mixing during vapor pressure measurements it is important in the temperature control balance.
3. After the pressure has remained unchanged for at least 30 minutes, stop the pump and read the pressure gauges.

### Binary Measurements

1. Verify the experimental vapor pressure agrees with the literature value within accepted error. The acceptable error is the error in reading the Heise gauges,  $\pm 0.1\%$  of the full-scale reading of the gauge.

2. Stop recirculation pump and add the light component to desired pressure. Start pump. Repeat until desired pressure has been reached.
3. At equilibrium the pressure should remain unchanged for at least 30 minutes during which the temperature has been in good control. Read and record Mueller Bridge. Stop pump and record pressure gauges. Sample vapor and liquid.
4. Add light component to next pressure point. Start pump.

#### Ternary Measurements

1. Complete vapor pressure measurement.
2. Complete binary measurement of the heaviest and lightest component at goal pressure. Pressure should be within goal pressure by  $\pm 0.1\%$  of the full-scale reading of the Heise gauge.
3. After the binary measurement has been checked with the previously completed binary graphs add the medium weight component to goal pressure. Start pump. Recirculate. Monitor the temperature; adjustments to the Bayley fine control or the nitrogen metering vent

- might be needed to keep system in control. Start pump. Repeat until goal pressure is maintained or until mole fraction for the medium component is at the target point. In the latter case add the lightest component until the pressure remains at the goal pressure.
4. Pressure and temperature must be in control for at least 30 minutes. Read and record Mueller bridge. Stop pump and record pressure reading. Sample vapor and liquid.
  5. Repeat above steps until the ternary graph is completed as much as possible. If the plot intersects more than one binary system, binary points must be taken at the goal pressure by following the binary procedure.

#### Sampling and Sample Analysis

Sampling introduces the greatest error into the VLE measurements. The liquid sample has the most variability because of the need to purge the capillary to get a representative sample. The following procedure is only a guideline to sampling the equilibrium cell. Minor changes in technique are required as pressures and composition of

the equilibrium cell change. These are obtained through practice and are not quantifiable.

1. Sampling procedure

- a) Verify the sample valve is in the off position, i.e., the sample loop is open to the apparatus. Flush lines to the GC with helium. Evacuate one minute. Repeat two more times.
- b) Ready the sampling system by closing all valves on the sampling system except for the vacuum line valve after the 10cc liquid sample cylinder. The 10 cc will need to be evacuated during the sampling procedure.
- c) After temperature and pressure measurements have been recorded and the recirculation pump is still stopped, the following procedure is used to collect the samples:
  - i) Close the two valves on either side of the vapor sample. This isolates the vapor sample from the recirculation loop.
  - ii) In a quick motion open and then close the liquid sample valve before the 10 cc sample

cylinder. Open the valve on the outlet of the sample cylinder which is under vacuum. Evacuate the 10 cc cylinder (approximately 30 seconds). Close valve on the outlet of the sample cylinder. This is the first flush of the capillary line to remove the non-equilibrium material.

- iii) Turn 3-way vapor valve to the previously evacuated vapor sample line.
  - iv) Repeat liquid sample cylinder flush.
  - v) Take the liquid sample by again opening and closing the inlet valve to the sample cylinder in a quick but firm motion.
  - vi) Return the 3-way vapor valve to the recirculation position. Open the valves on either side to the vapor sample cylinder. Start recirculation pump. Note it is best for good temperature control to get the pump back on line as soon as possible.
- d) First the vapor sample is analyzed in the GC. Verify the GC sample line is evacuated and the

sample loop is open to the apparatus, i.e., the valve is off.

- i) Open fully the vapor sample valve to the GC sample line. Note the pressure of the sample.
- ii) Wait 3 minutes for the sample temperature to equilibrate. The sample loop and column are maintained at 100°C and the calibration curves use this temperature to determine the compressibility of each pure fluid.
- iii) Start the integrator.
- iv) Turn on the GC gas sample valve. This allows helium to sweep the sample into the chromatograph column.
- v) After the first peak has been drawn on the chromatogram, turn GC gas sample valve off. The next sample can now be readied.
- vi) If the vapor sample is above atmospheric pressure the following procedure is used to obtain the next analysis sample. Close the vapor sample valve to the GC sample line.

Open the vent valve on the GC sample line and vent out some sample to move the helium out of the gas sample valve sample loop. Close the vent and again fully open the vapor sample valve to the GC sample line. After 3 minutes this sample can be analyzed.

- vii) If the vapor sample is below atmospheric pressure the following procedure is used to obtain the next analysis sample. Close the vapor sample valve to the GC sample line. Open the vacuum valve and evacuate approximately 0.3 psi of the gas mixture. Close the vacuum valve. Again fully open the vapor sample valve to the GC sample line. After 3 minutes this sample can be analyzed.
- viii) The area counts for each component must be recorded and then multiplied by the appropriate slope from the calibration line. These numbers are used to find the mole fraction of each component.

- ix) The mole fractions are averaged between the two GC runs if the deviation between them is less than 1%. If the deviation is greater than 1% the measurement is thrown out and the cause of the deviation is determined, recorded and fixed.
- e) The liquid sample is heated for approximately 15-25 minutes in the 10 cc cylinder. For methane and carbon dioxide mixtures this presented a well-mixed sample to the GC. Samples containing propane and having a total pressure above 100 PSIA showed unresolved fractionation. This is indicated by successive analysis samples having significantly decreasing amount of the light component. In this case to achieve a well mixed sample the sample must be flushed and further expanded into the 300 cc sample cylinder. The following procedure is used:
- i) The 300 cc sample cylinder and the tubing from the 10 cc sample cylinder are flushed and evacuated three times with helium. The

vacuum valve is then closed. The liquid sample valve to the GC sample line is then closed. The inlet valve to the 300 cc sample cylinder remains open.

- ii) Open the outlet to the 10 cc sample cylinder to allow the gas mixture to expand into the 300cc cylinder.
- iii) Open the helium valve at the inlet of the 10 cc cylinder 15 seconds to flush all of the liquid sample into the 300 cc cylinder.
- iv) Close the inlet valve to the 300 cc cylinder. The 10 cc cylinder can now be evacuated and flushed with helium twice more to ready it for the next sampling of the cell's liquid phase.
- v) Open fully the liquid sample valve to the GC sample line. Note the pressure of the sample. If the sample is not expanded into the 300 cc cylinder the procedure is the same as with the above vapor sample. If the sample is expanded into the 300 cc cylinder

the pressure of the sample is approximately 45 PSIA and the venting procedure is followed to obtain the second analysis as described in the vapor sampling.

- vi) Wait 3 minutes for the sample temperature to equilibrate.
- vii) Start the integrator.
- viii) Turn on the GC gas sample valve.
- ix) After the first peak has been drawn on the chromatogram, turn GC gas sample valve off. The next sample can now be readied.
- x) The area counts for each component must be recorded and then multiplied by the appropriate slope from the calibration line. These numbers are used to find the mole fraction of each component.
- xi) The mole fractions are averaged between the two GC runs if the deviation between them is less than 1%. If the deviation is greater than 1% the measurement is thrown out and the

cause of the deviation is determined,  
recorded and fixed.

## EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results for the six binary isotherms and six ternary systems are reported. Included with the binary system results are any internal and/or mutual consistency tests which were performed. To verify consistency with other data sets two techniques were employed. When isotherms were published at 230 and 270 K the data were plotted along with the data of this experiment. With data sets containing isotherms at other temperatures that had a good number of data points in the dilute solute region, Henry's Law constants were calculated using the Krichevsky-Kasarnovsky equation (Prausnitz et al., 1986) and were plotted versus temperature. A smooth curve is expected. See Appendix C for a description of the procedure used and tabulated results.

To verify the internal consistency of the data the following tests were performed on the binary systems:

- 1) For the liquid phase a plot of  $(P - P^{\circ}_{\text{solvent}})$  versus  $X_{\text{solute}}$  must extrapolate to the origin as  $X_{\text{solute}}$  approaches zero;

i.e., the system should extrapolate smoothly to the vapor pressure of the condensable component.

- 2) The plot of  $K_{\text{solvent}}P$  versus  $(P - P^{\circ}_{\text{solvent}})$  should be a smooth curve extrapolating to the vapor pressure of the condensable component at the ordinate. This checks the consistency of both the liquid and vapor compositions.
- 3) A plot of system pressure versus  $(Y_{\text{solute}} - X_{\text{solute}})^2$  must be a smooth curve extrapolating to the critical pressure of the mixture or the vapor pressure of the solute if both components are condensable.

#### Vapor Pressure Measurements

The accuracy of the temperature and pressure measurements was established by measuring the vapor pressure of pure, Coleman grade carbon dioxide over a range of temperatures and comparing the results with the literature data of Angus, et al. (1976) which is published by the International Union of Pure and Applied Chemistry. The comparison of the results and literature values is shown in Table 2. The maximum deviation found was to be less than the error in the Heise gauges which is  $\pm 0.1\%$  of the full-scale reading. The greatest deviation from literature

Table 2: Comparison of Experimental and Literature Vapor Pressures

| Temp (K)       | Measured Vapor Pressure (MPa) | Literature Vapor Pressure (MPa) | Deviation (MPa) | $\pm 0.1\%$ of Gauge Reading (MPa) |
|----------------|-------------------------------|---------------------------------|-----------------|------------------------------------|
| Carbon Dioxide |                               |                                 |                 |                                    |
| 230            | 0.8942                        | 0.8935                          | +0.0007         | $\pm 0.0034$                       |
| 232            | 0.9656                        | 0.9632                          | +0.0024         | $\pm 0.0034$                       |
| 240            | 1.2863                        | 1.2830                          | +0.0033         | $\pm 0.0034$                       |
| 250            | 1.7890                        | 1.7856                          | +0.0034         | $\pm 0.0034$                       |
| 260            | 2.4214                        | 2.4194                          | +0.0020         | $\pm 0.0034$                       |
| 270            | 3.2026                        | 3.2034                          | -0.0008         | $\pm 0.0034$                       |
| Propane        |                               |                                 |                 |                                    |
| 230            | 0.0973                        | 0.09703                         | +0.0003         | $\pm 0.0069$                       |
| 270            | 0.4308                        | 0.43042                         | +0.0004         | $\pm 0.0069$                       |

CO<sub>2</sub> Reference: Angus, et al. (1976)

C<sub>3</sub>H<sub>8</sub> Reference: Goodwin and Haynes (1982)

occurred in the middle temperature range at 240 and 250 K. This trend was also seen in the work of Al-Sahhaf (Thesis 1981, pg. 10), Wei (Thesis 1983, pg. 11) and Duston (Thesis 1970, pg. 31).

Furthermore, as part of standard experimental procedure the vapor pressure of the initially charged component was taken at the beginning of each isotherm studied. In this case propane and carbon dioxide were measured. The results of the propane vapor pressures as compared with the literature values of Goodwin and Haynes (1982), published by the National Bureau of Standards, are also given in Table 2. At both operating temperatures the propane vapor pressure measurements matched the literature values within the accuracy of the gauge.

#### CH<sub>4</sub>-CO<sub>2</sub> Binary System

The experimental results of the CH<sub>4</sub>-CO<sub>2</sub> binary system at 270 K were compared with the results of Al-Sahhaf, et al. (1983) and Somait and Kidnay (1978). As can be seen in Figure 4 the agreement with these previous investigations was good.

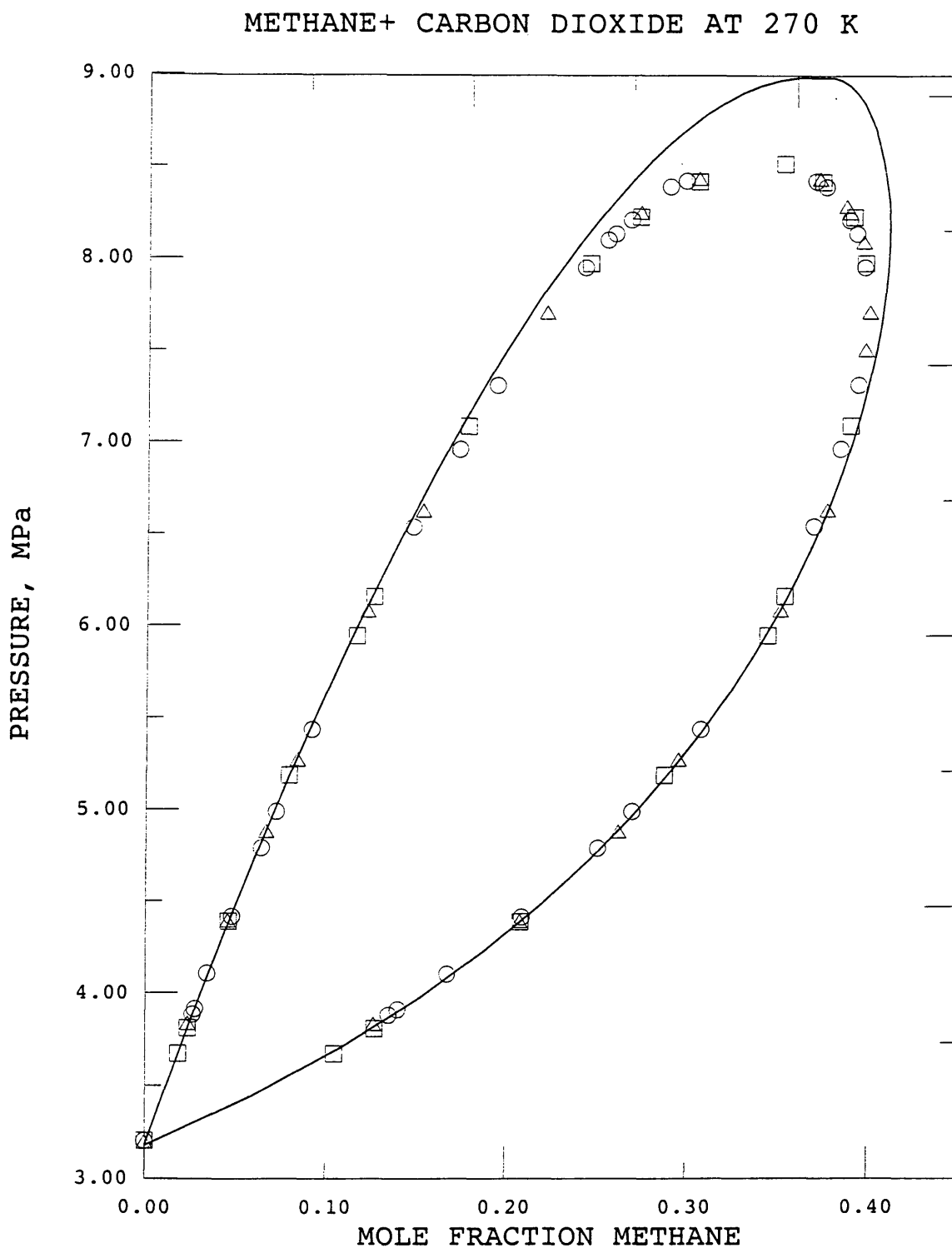


Figure 4. Methane-Carbon Dioxide at 270 K: ○ THIS STUDY, □ AL-SAHHAF, et al. (1983), △ SOMAIT AND KIDNAY (1978), — PR PREDICTION.

This system was also measured at 230 K. The  $\text{CH}_4\text{-CO}_2$  binary was previously measured in this laboratory by Wei at 230 K. Wei's work was completed in 1983 and published in 1995. The comparison is favorable up to the critical region. This region was explored more thoroughly in the present study. The results are shown in Figure 5.

The three internal consistency tests were applied to both data sets. The results appear in Figures 6-11 and indicated good internal consistency of the data.

At the temperatures investigated the isotherms exhibit standard behavior for a binary system with one sub-critical and one super-critical component. As the pressure increases the compositions and densities of the vapor and liquid approach each other until at the critical point of the mixture the two-phase envelope closes.

#### $\text{CH}_4\text{-C}_3\text{H}_8$ Binary System

Vapor-liquid equilibria measurements were made for the  $\text{CH}_4\text{-C}_3\text{H}_8$  system at 270 and 230 K. The results are shown in Figures 12 and 13. The 270 K isotherm was reworked from 6 MPa up to the critical region after the equilibrium cell was

## METHANE + CARBON DIOXIDE AT 230 K

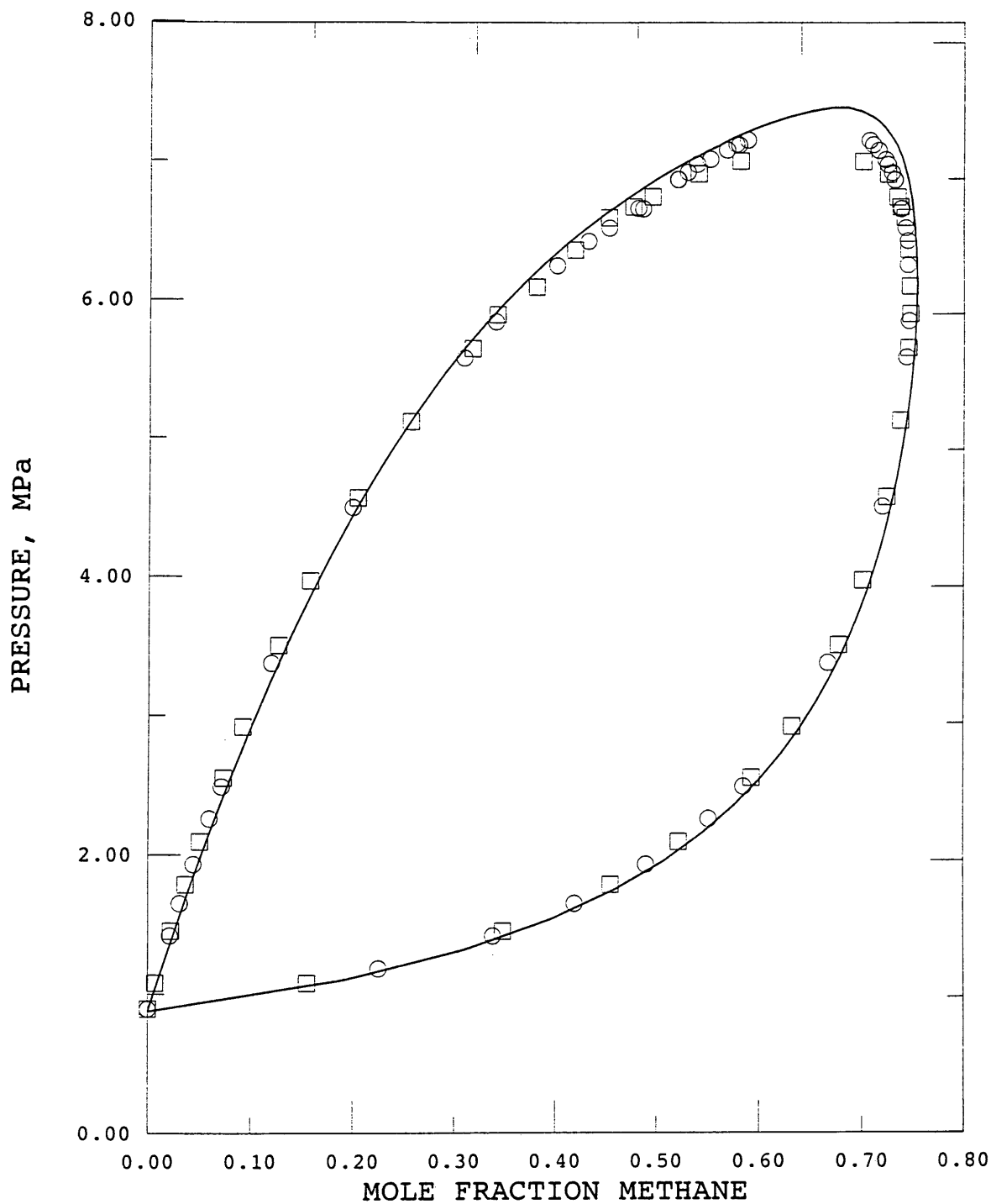


Figure 5. Methane-Carbon Dioxide at 270 K: ○ THIS STUDY, □ WEI, et al. (1995), — PR PREDICTION.

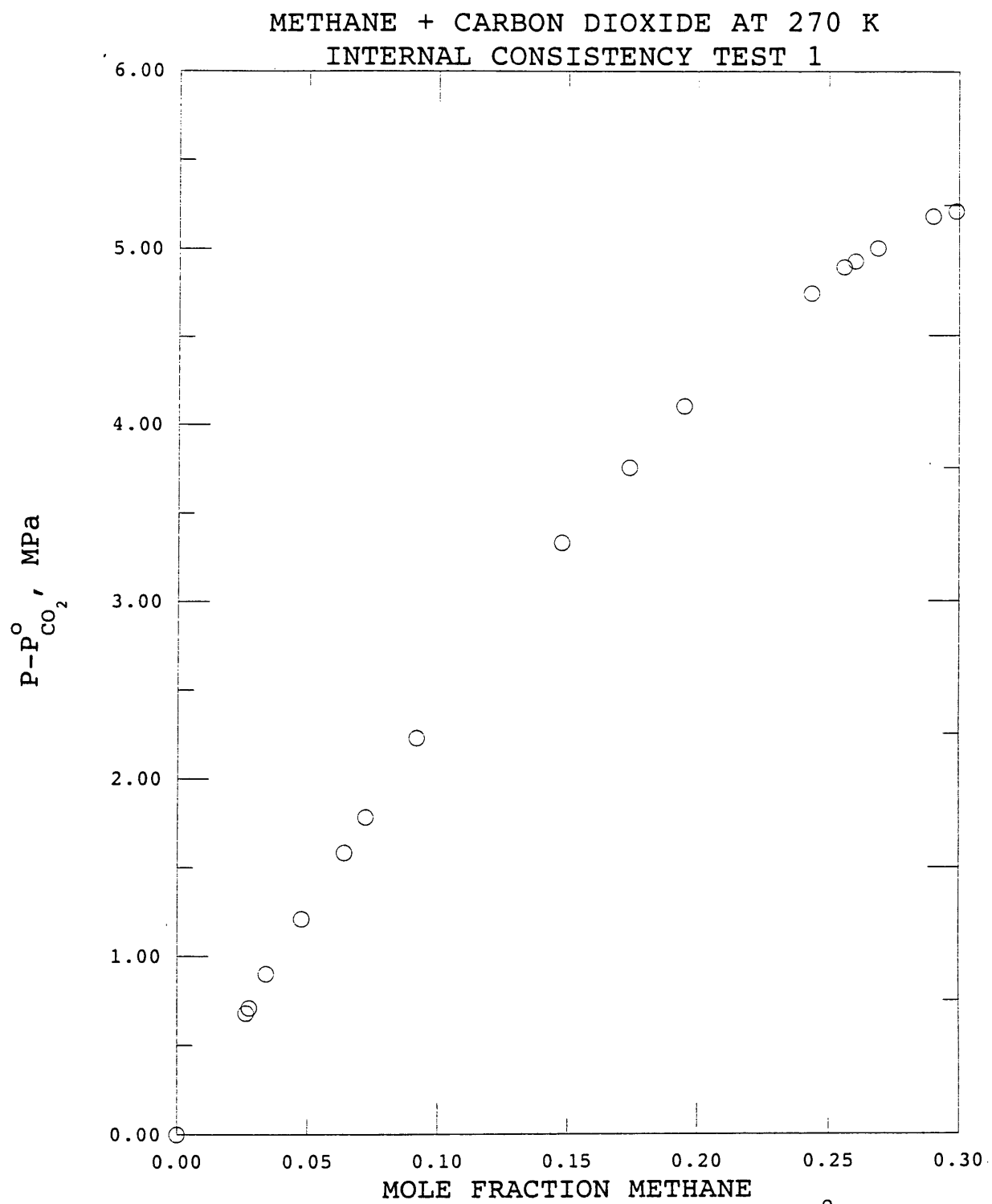


Figure 6. Methane-Carbon Dioxide at 270 K:  $P - P_{CO_2}^{\circ}$  vs.  $X_{CH_4}$ .

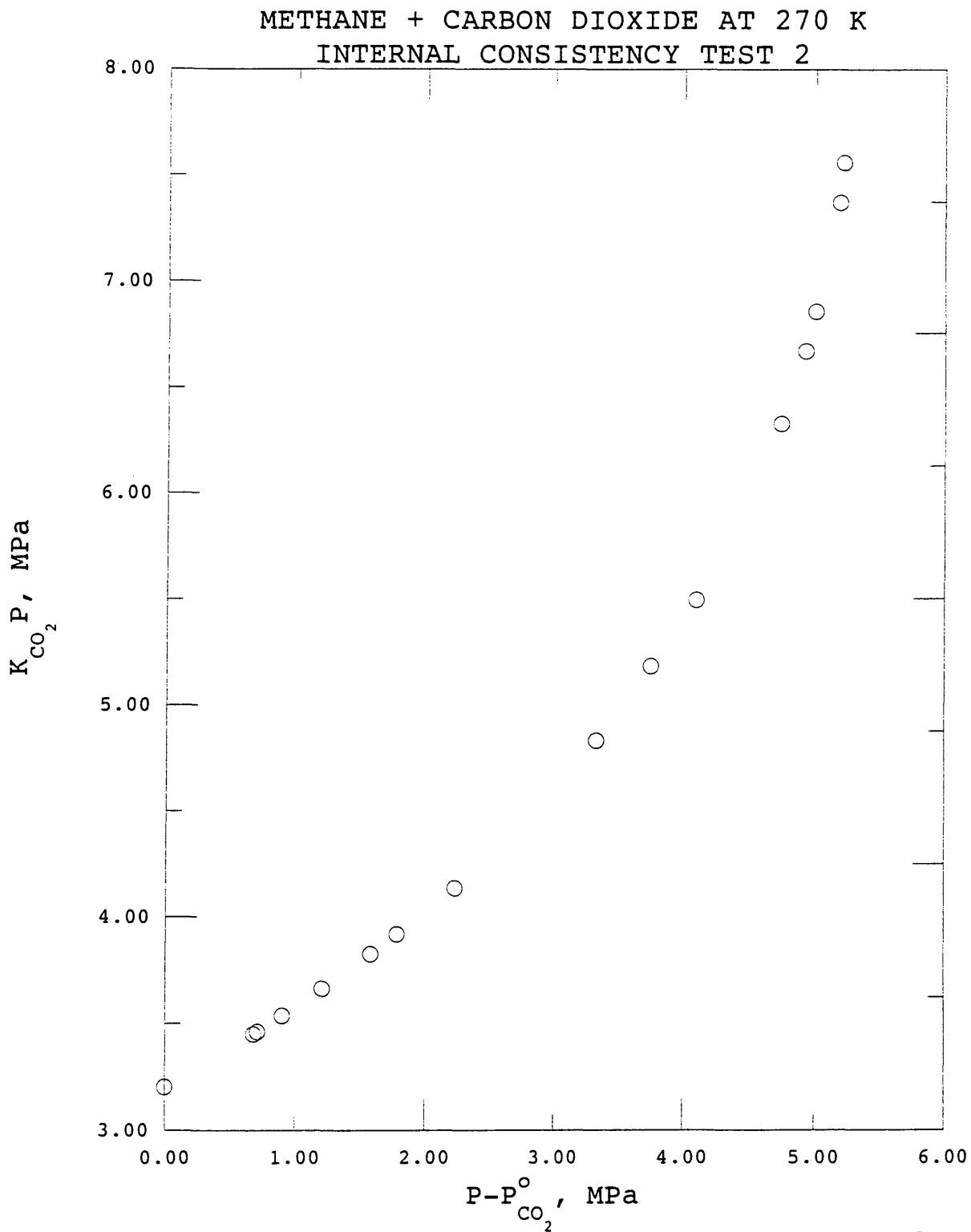


Figure 7. Methane-Carbon Dioxide at 270 K:  $K_{CO_2} P$  vs.  $P - P_{CO_2}^o$ .

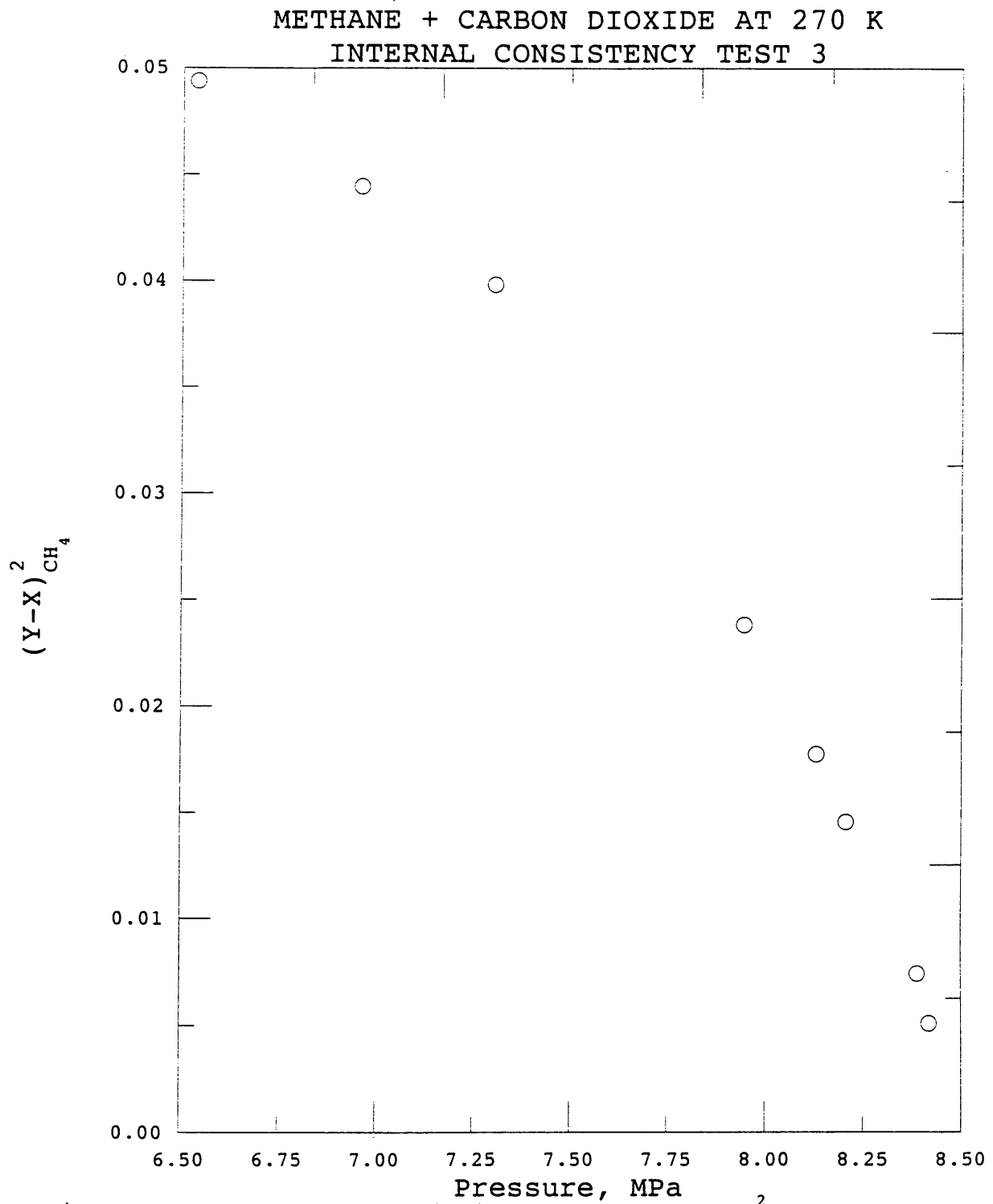


Figure 8. Methane-Carbon Dioxide at 270 K:  $(Y-X)_{\text{CH}_4}^2$  vs. Pressure.

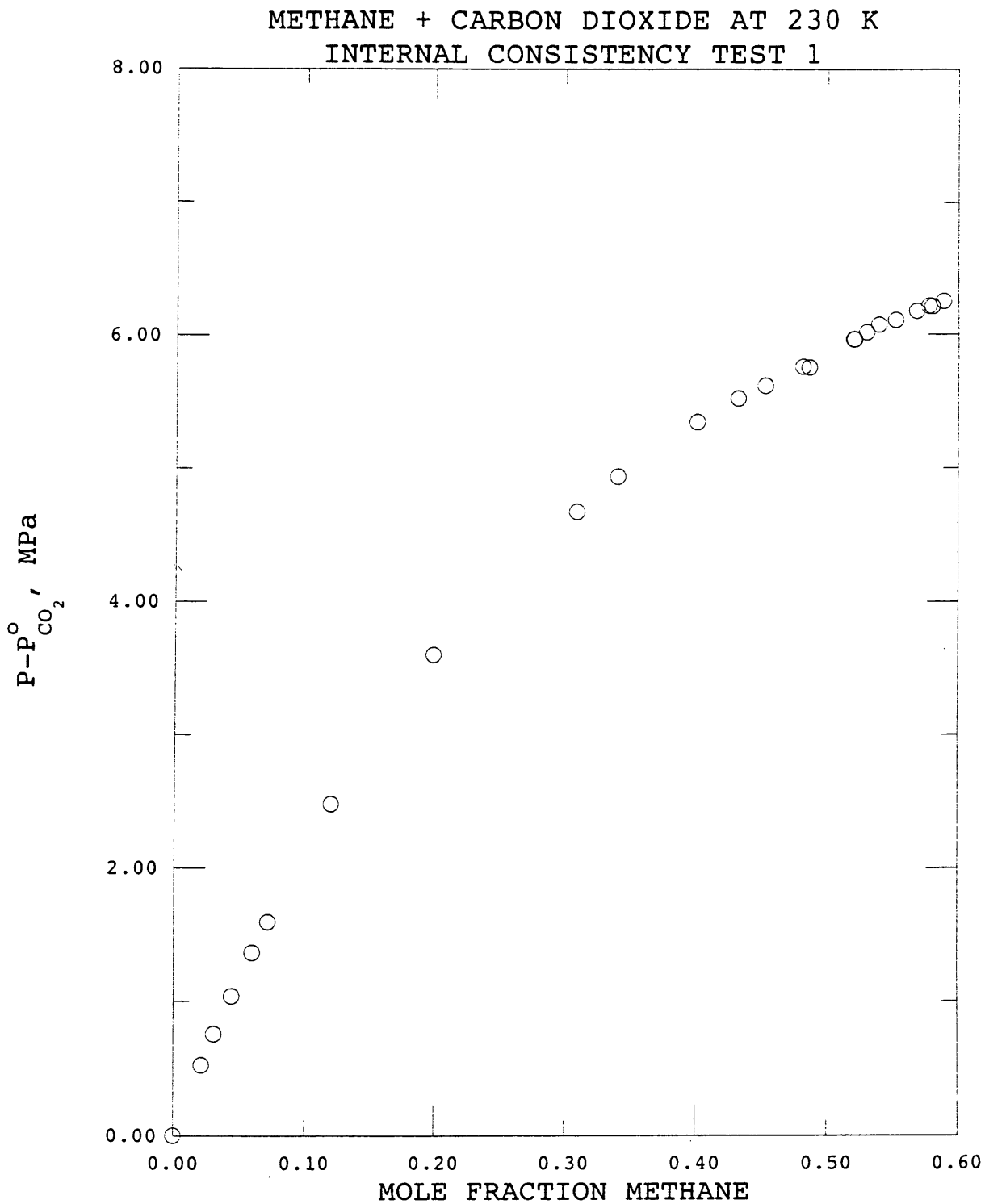


Figure 9. Methane-Carbon Dioxide at 230 K:  $P - P_{CO_2}^o$  vs.  $X_{CH_4}$ .

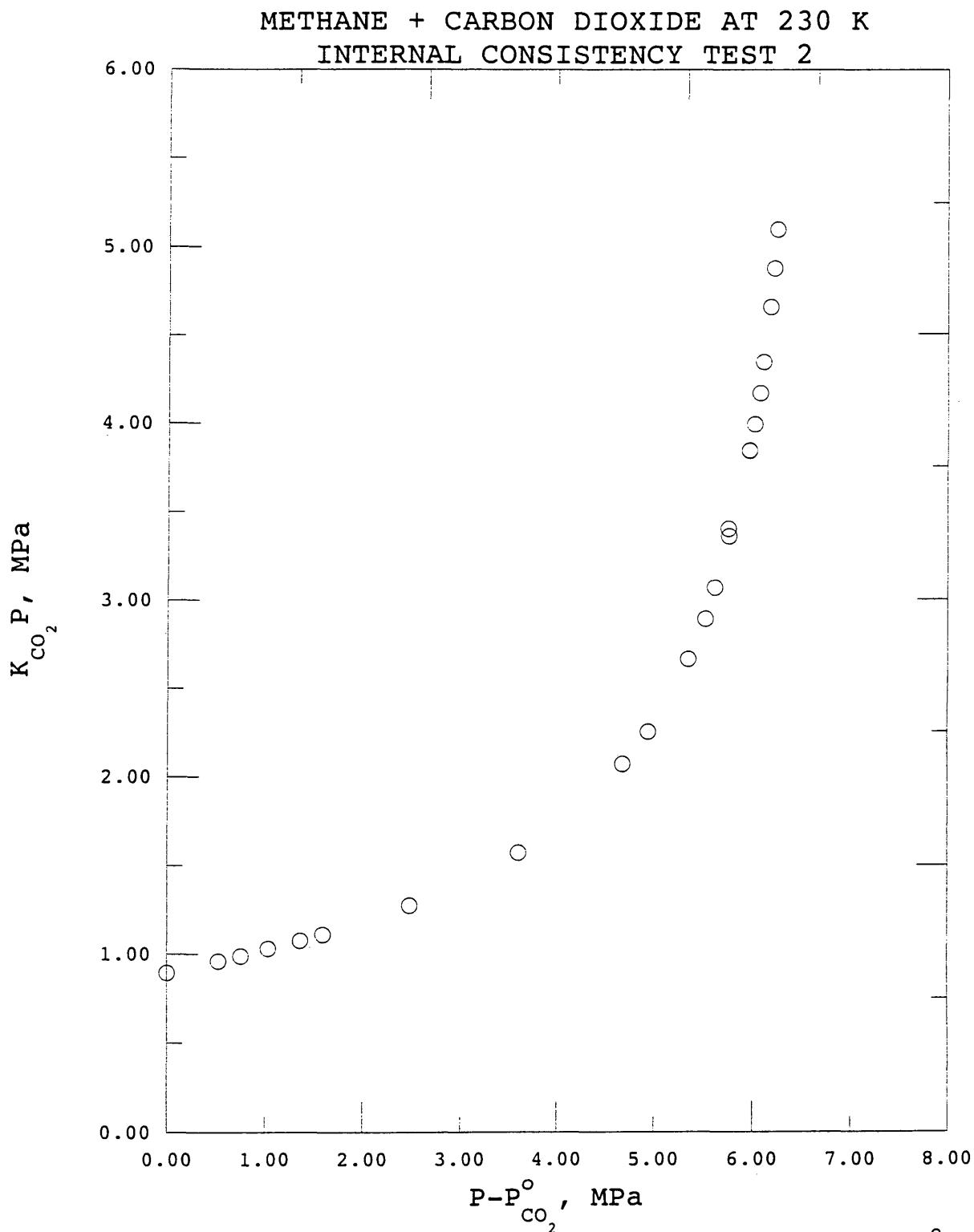


Figure 10. Methane-Carbon Dioxide at 230 K:  $K_{CO_2} P$  vs.  $P - P_{CO_2}^o$ .

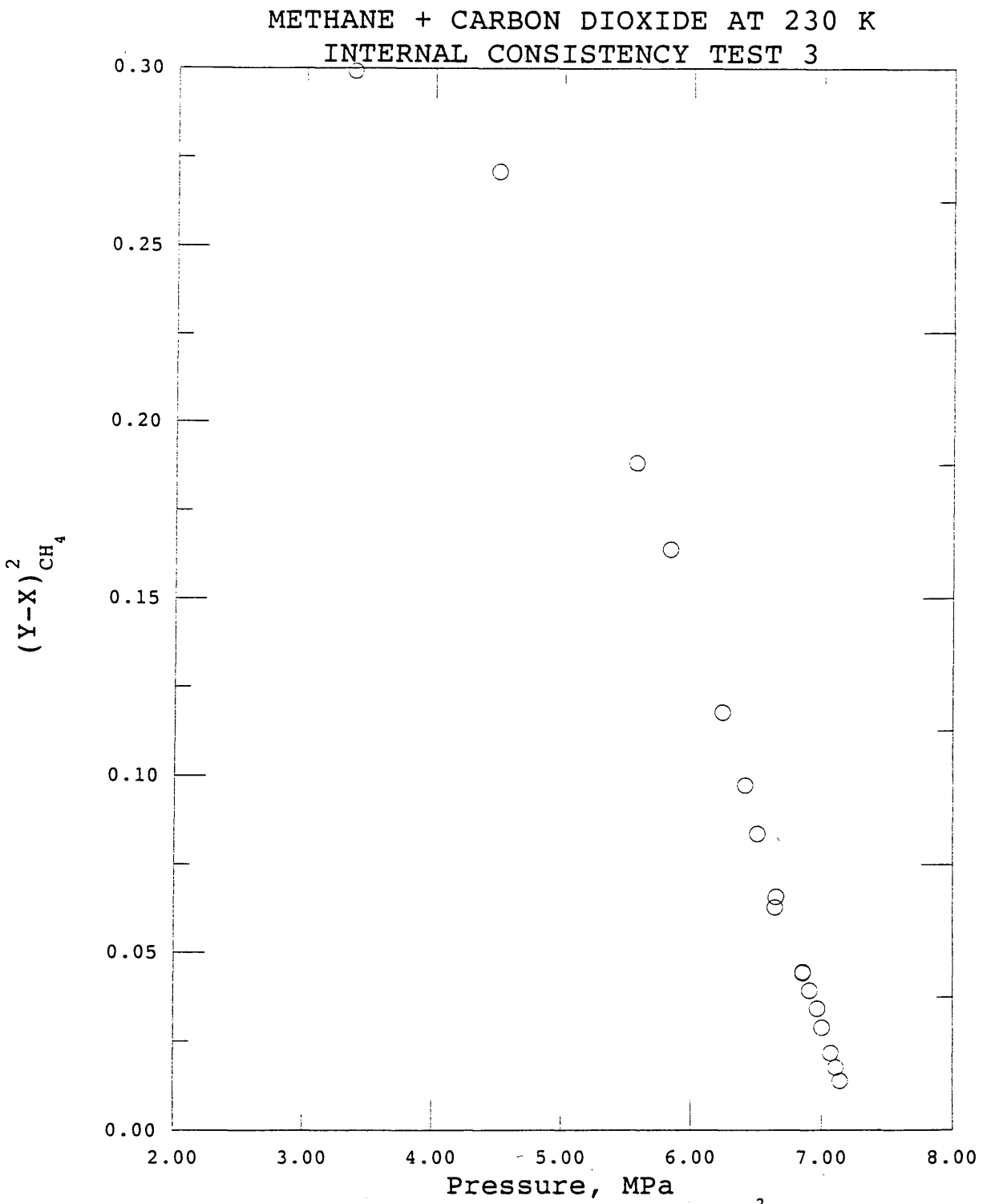
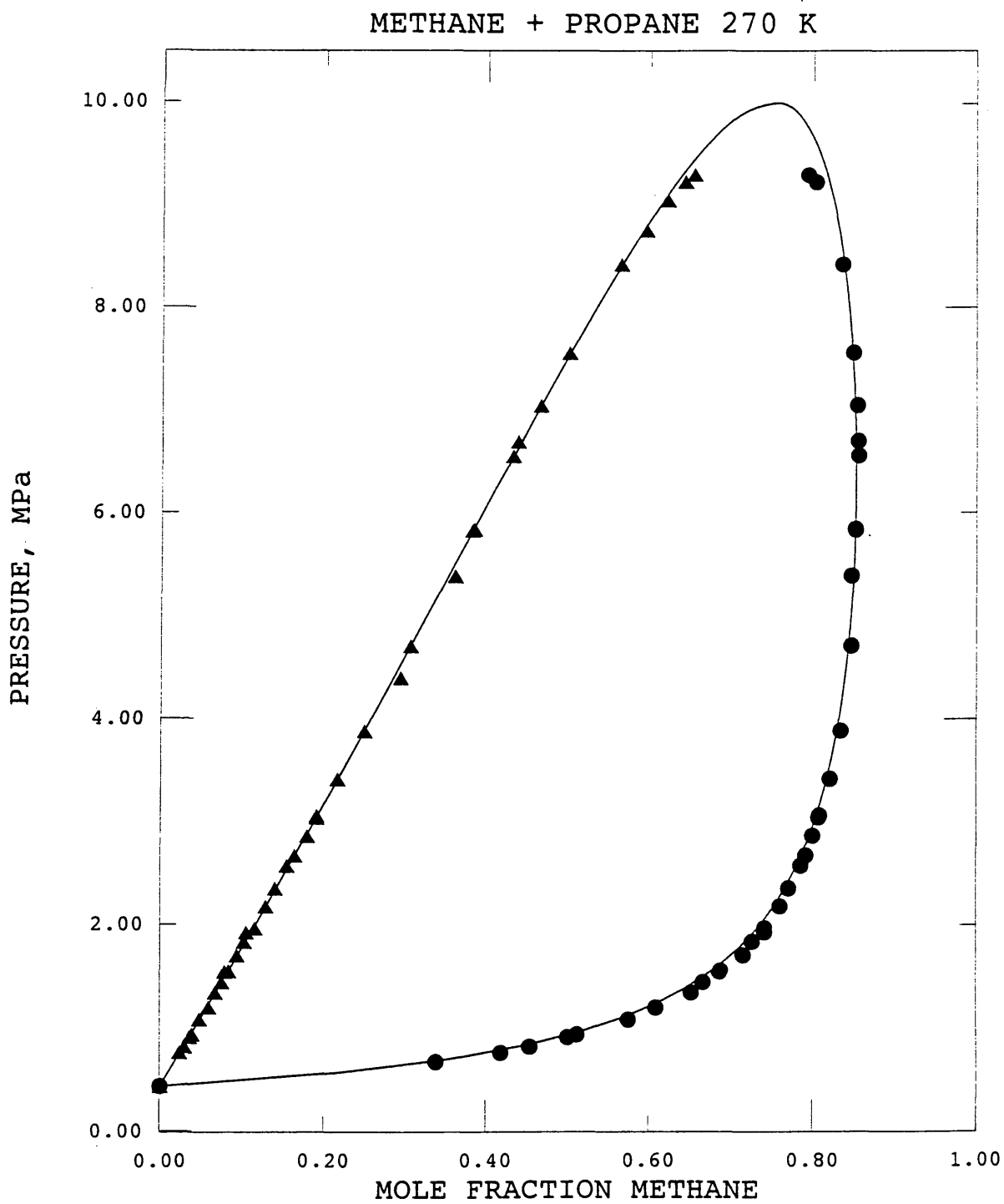


Figure 11. Methane-Carbon Dioxide at 230 K:  $(Y-X)_{\text{CH}_4}^2$  vs. Pressure.



## METHANE + PROPANE AT 230 K

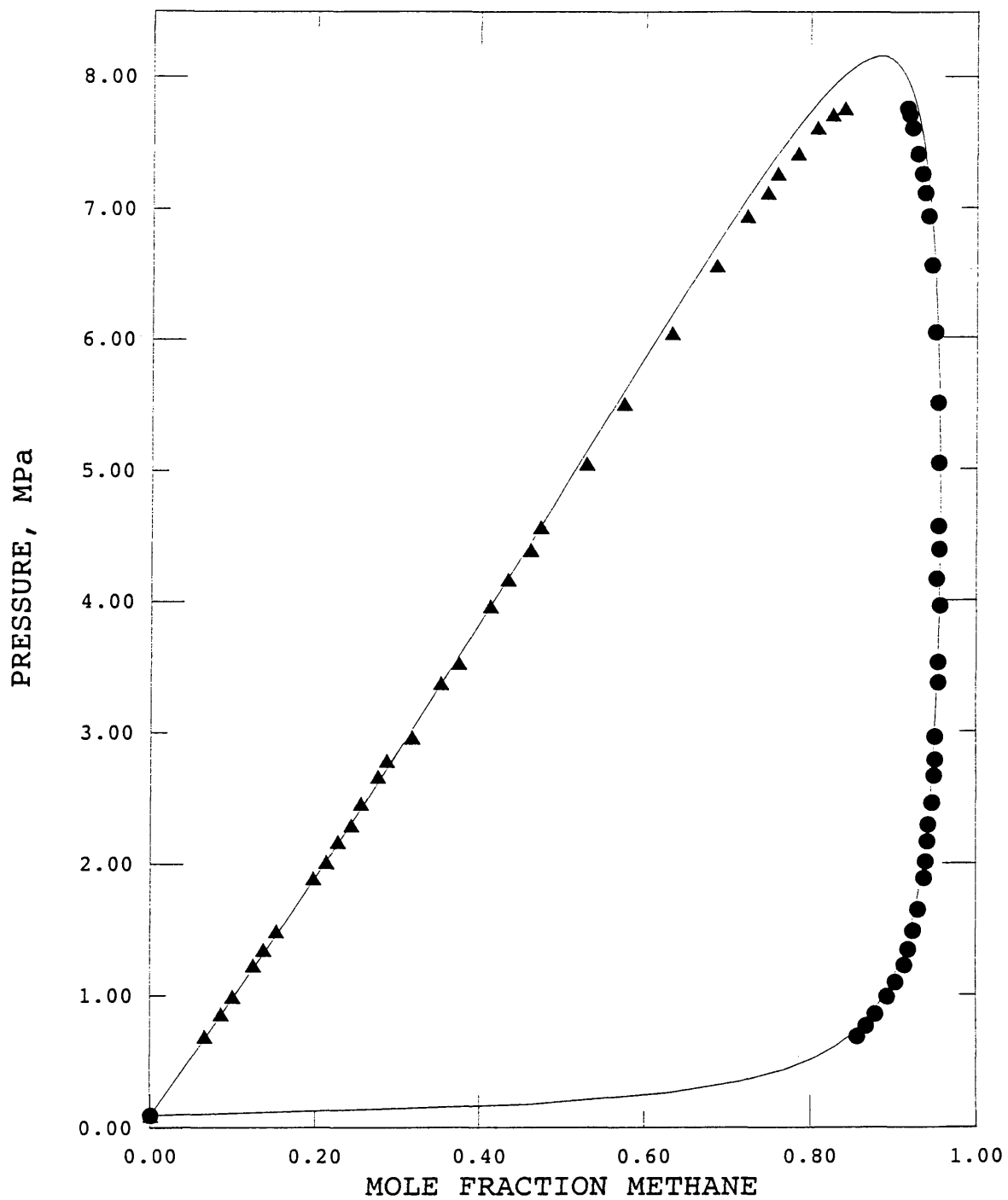


Figure 13. Methane-Propane at 230 K: ▲Liquid, ●Vapor, — PR PREDICTION.

modified. The cell leaked repeatedly in this region during the first taking of the data. For the 270 K isotherm critical opalescence with one phase appeared at 9.555 MPa.

To compare the data of other experiments done at different temperatures, calculated Henry's law constants from previous data sets which had points in this region were plotted versus temperature, see Figure 14. The present study compared very favorably with that of Wichterle and Kobayashi (1972). This work was published in 1972 and was the most recent study performed on this binary system. The Henry's constants appears to have a linear relationship in the cryogenic region studied.

The three internal consistency tests were applied to both data sets. The results appear in Figures 15-20 and indicated good internal consistency of the data.

At the temperatures investigated the isotherms exhibit standard behavior for a binary system with one sub-critical and one super-critical component. As the pressure increases the compositions and densities of the vapor and liquid approach each other until at the critical point of the mixture the two-phase envelope closes.

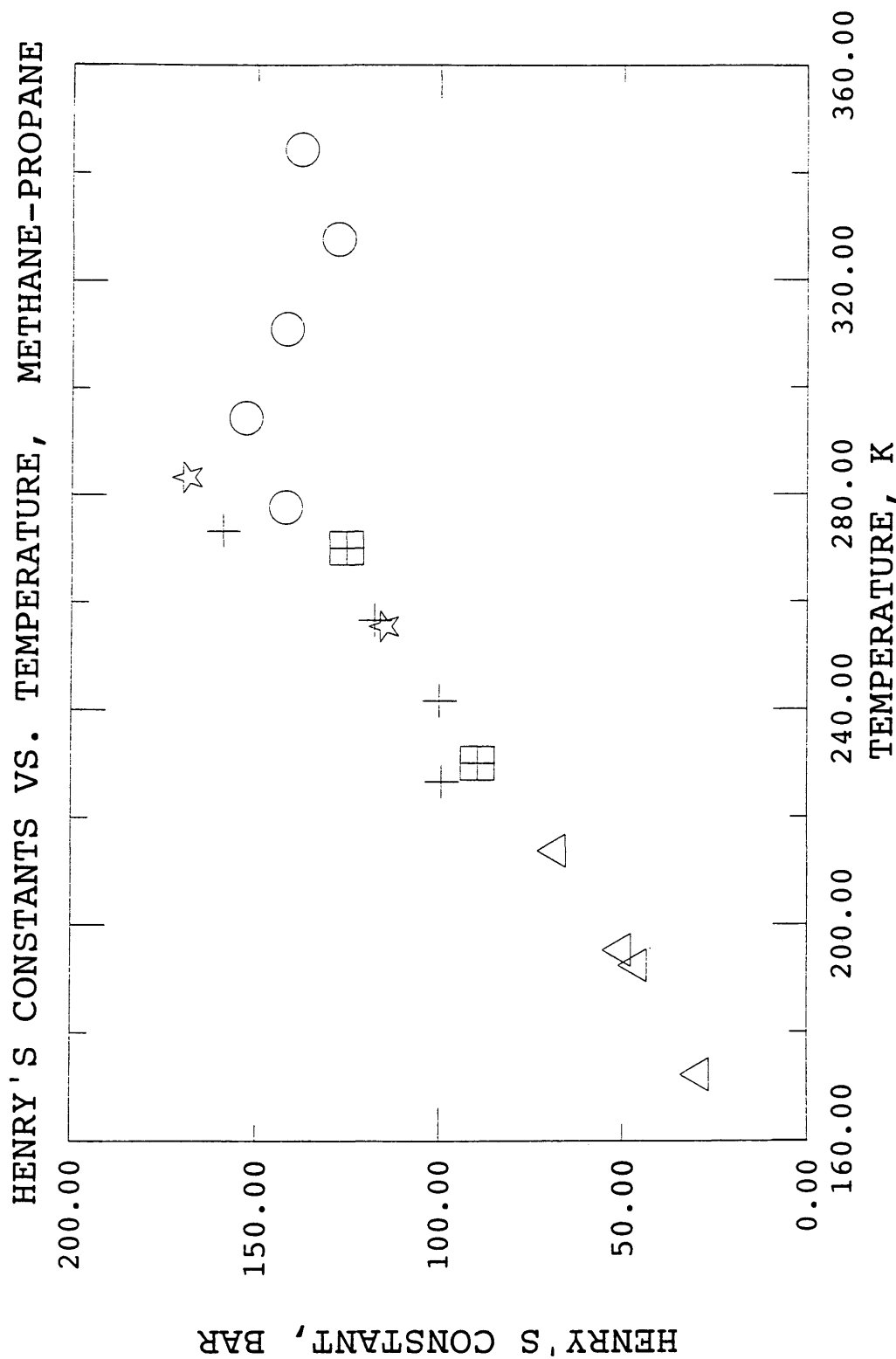
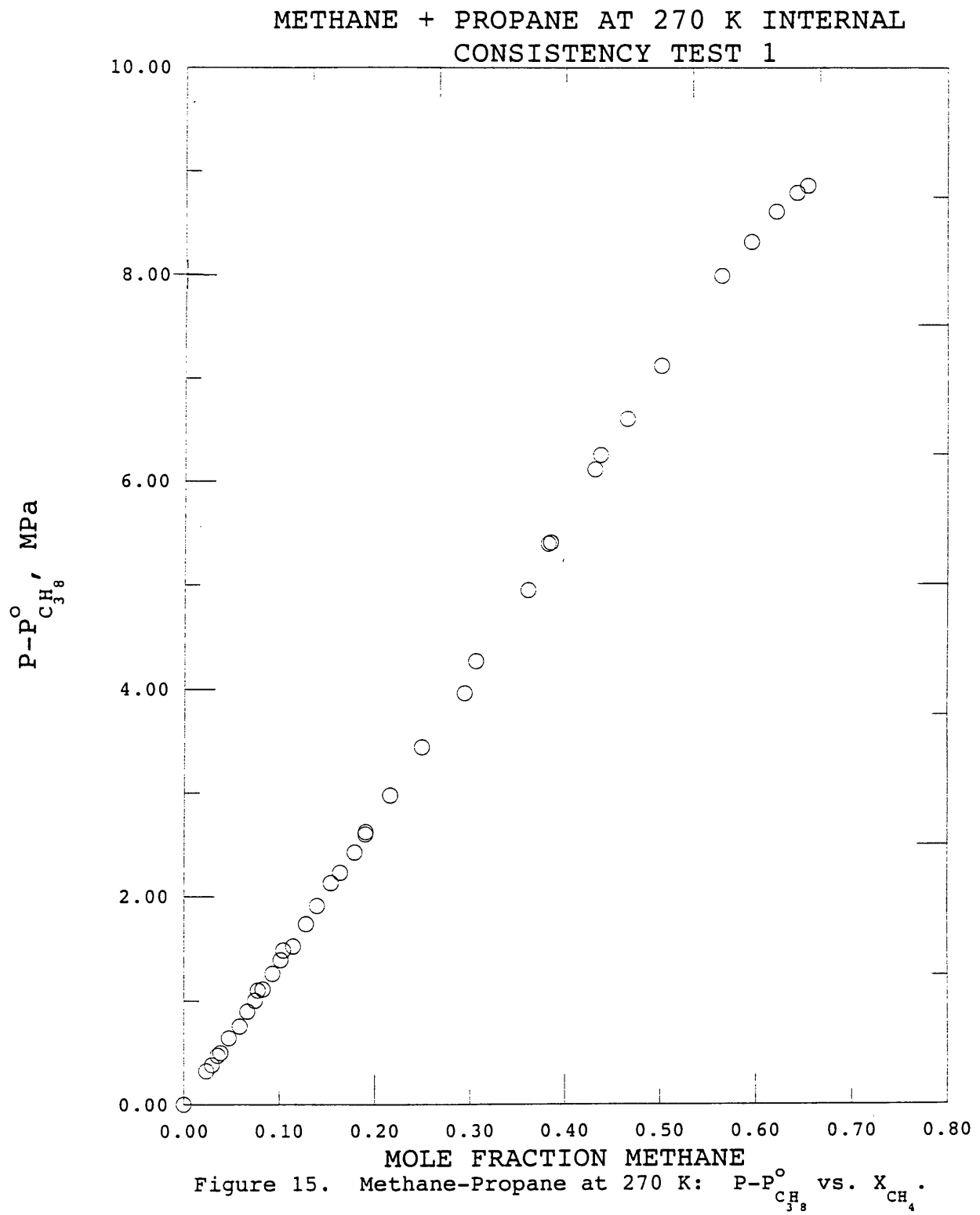


Figure 14. Henry's Constants vs. Temperature for Methane and Propane:  $\square$  This Study,  $+$  Akers, Burns, and Fairchild (1954),  $\triangle$  Wichterle and Kobayashi (1972),  $\circ$  Reamer, Sage and Lacey (1950),  $\star$  Price and Kobayashi (1959).



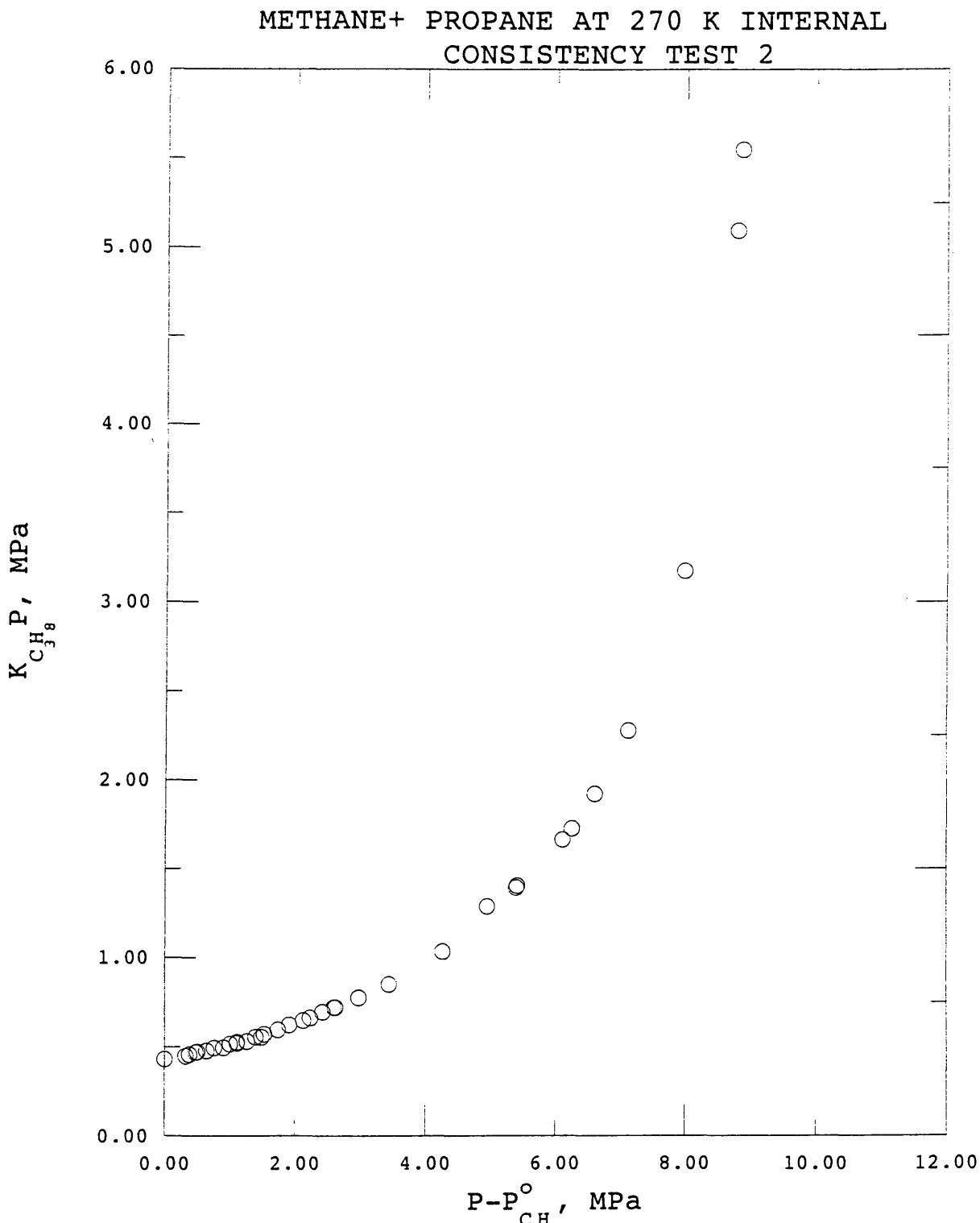


Figure 16. Methane-Propane at 270 K:  $K_{C_3H_8} P$  vs.  $P - P^{\circ}_{C_3H_8}$ .

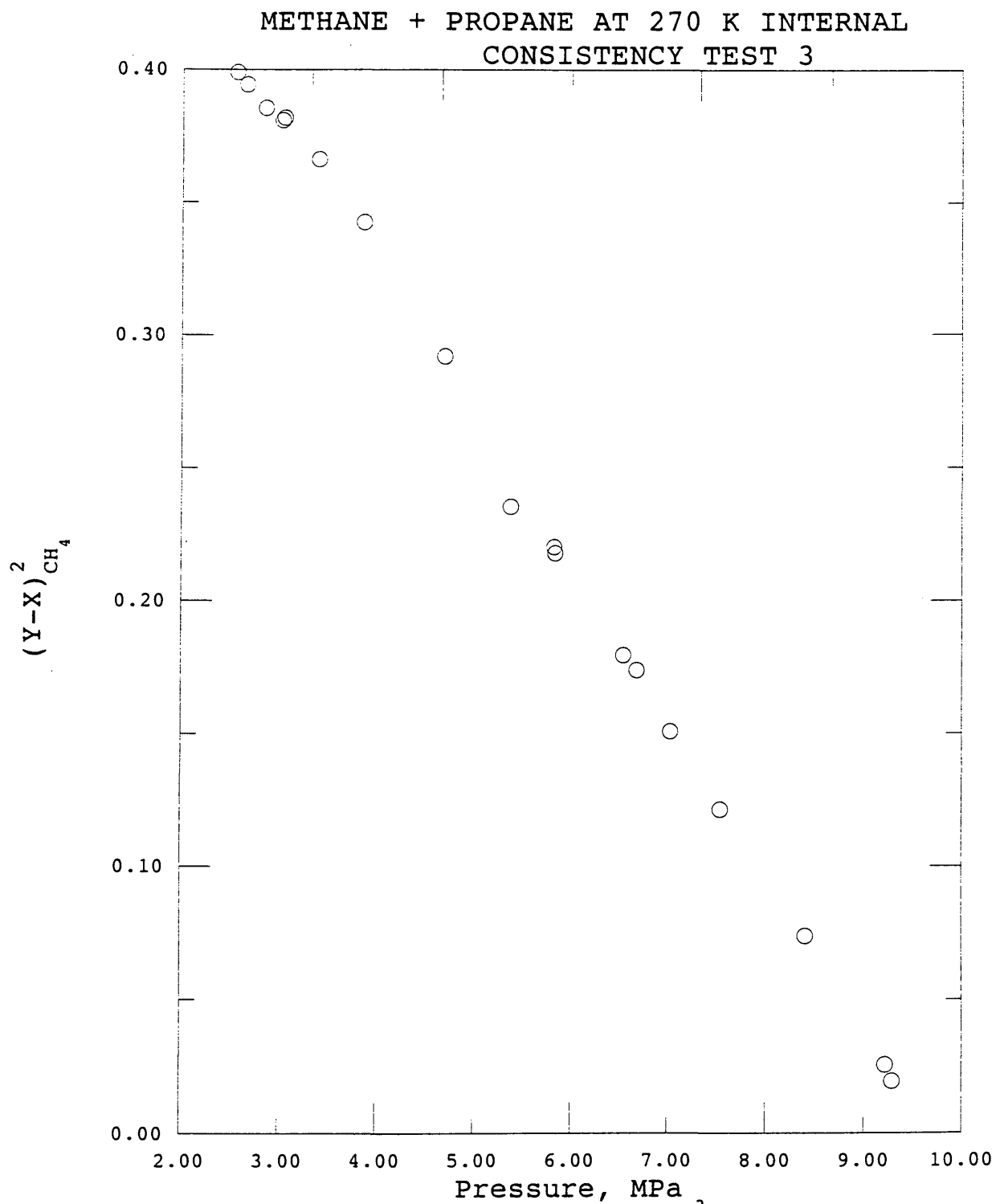


Figure 17. Methane-Propane at 270 K:  $(Y-X)_{CH_4}^2$  vs. Pressure, MPa.

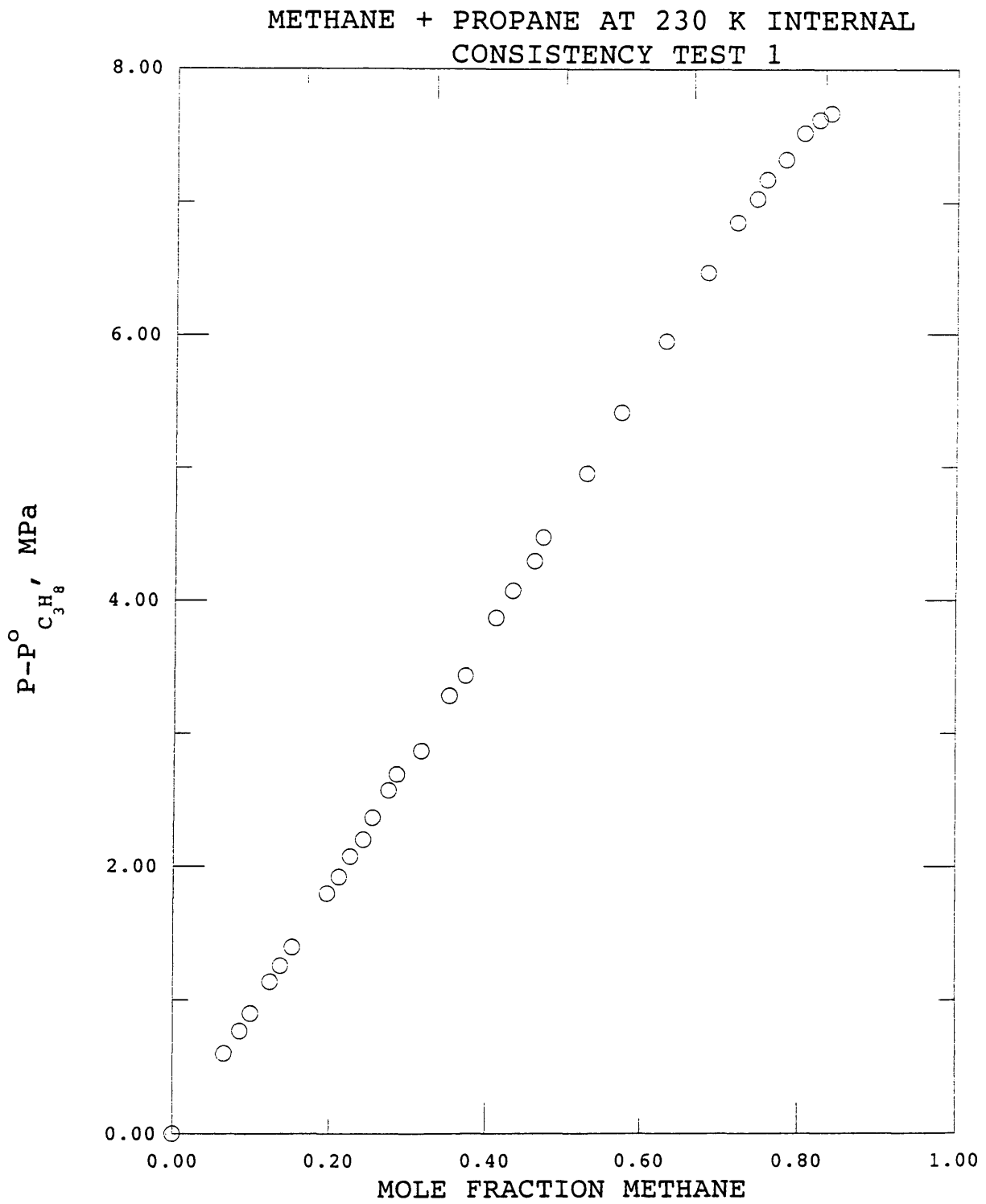
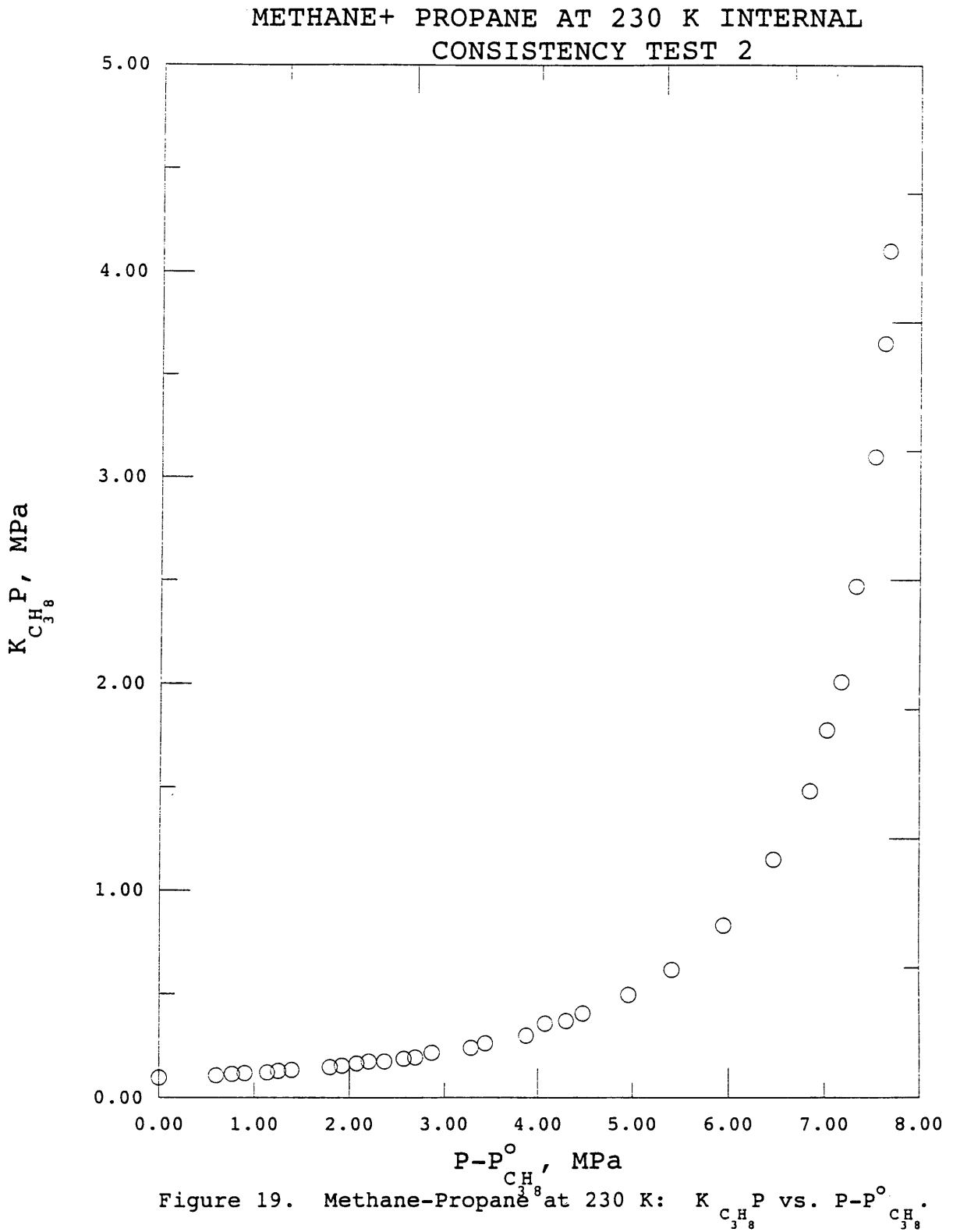


Figure 18. Methane-Propane at 230 K:  $P - P_{C_3H_8}^{\circ}$  vs.  $X_{CH_4}$ .



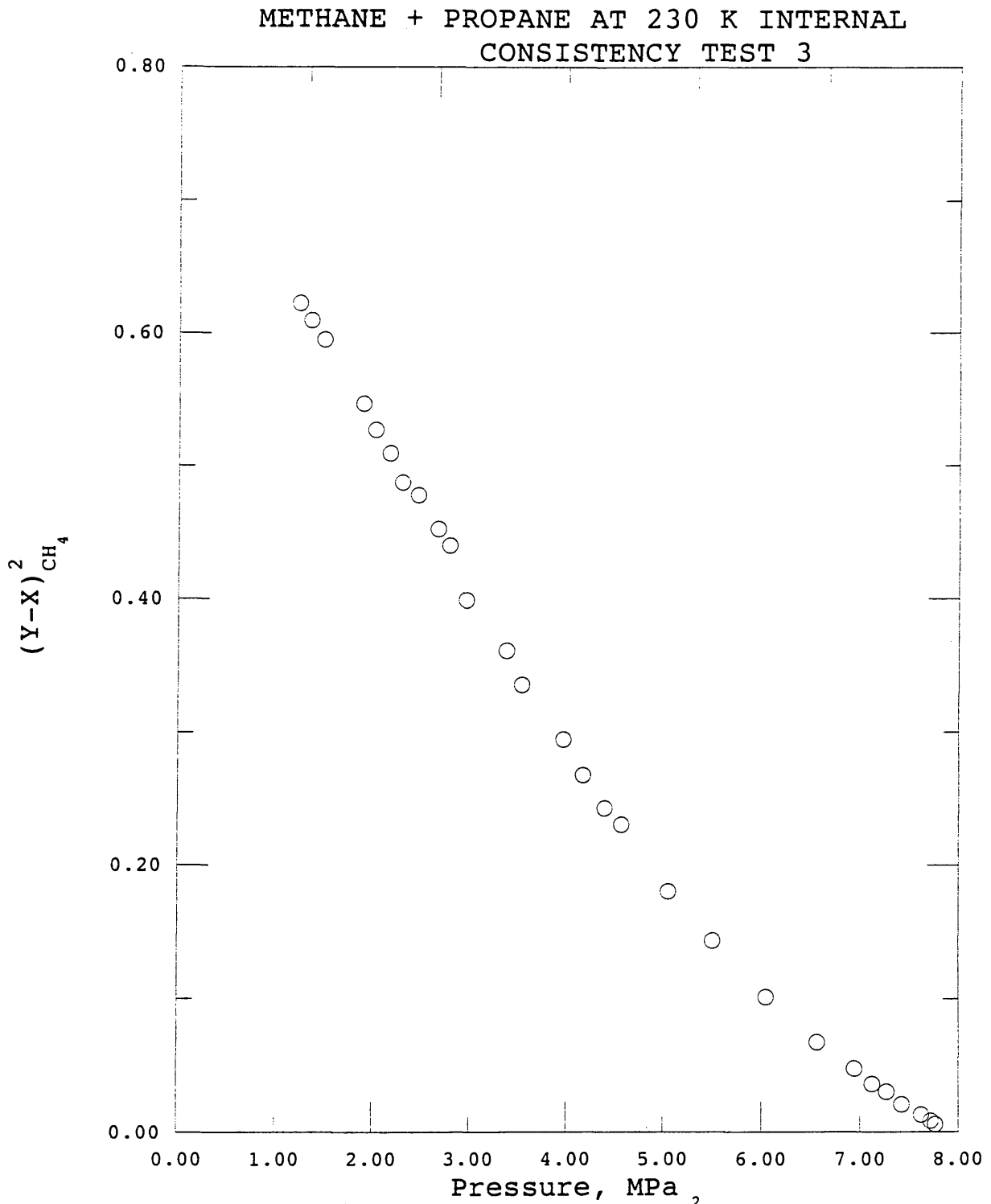


Figure 20. Methane-Propane at 230 K:  $(Y-X)_{\text{CH}_4}^2$  vs. Pressure, MPa.

CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> Binary System

Vapor-liquid equilibria measurements were made for the CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> system at 270 and 230 K. The results are shown in Figures 21 and 22. At 230 K the pressure in the cell was low; in the Henry's Law region the pressure was only 0.1-0.2 MPa. This low pressure caused problems in obtaining a large enough sample for analysis in the gas chromatograph. The liquid sampling apparatus built for the sampling of propane included flashing the sample taken from the cell into a 300 cc cylinder before analyzing in the gas chromatograph. By replacing the 300 cc cylinder with 1/8" copper tubing and following the same procedure as with other propane samples reproducible analysis were made. Previous indication of fractionating propane samples was non-reproducible GC runs.

To compare the data of other experiments done at different temperatures, calculated Henry's law constants from previous data sets which had points in this region were plotted versus temperature, see Figure 23. The constant for this study at 270 K falls in with the three other data sets published which included data in the Henry's Law region.

## CARBON DIOXIDE + PROPANE AT 270 K

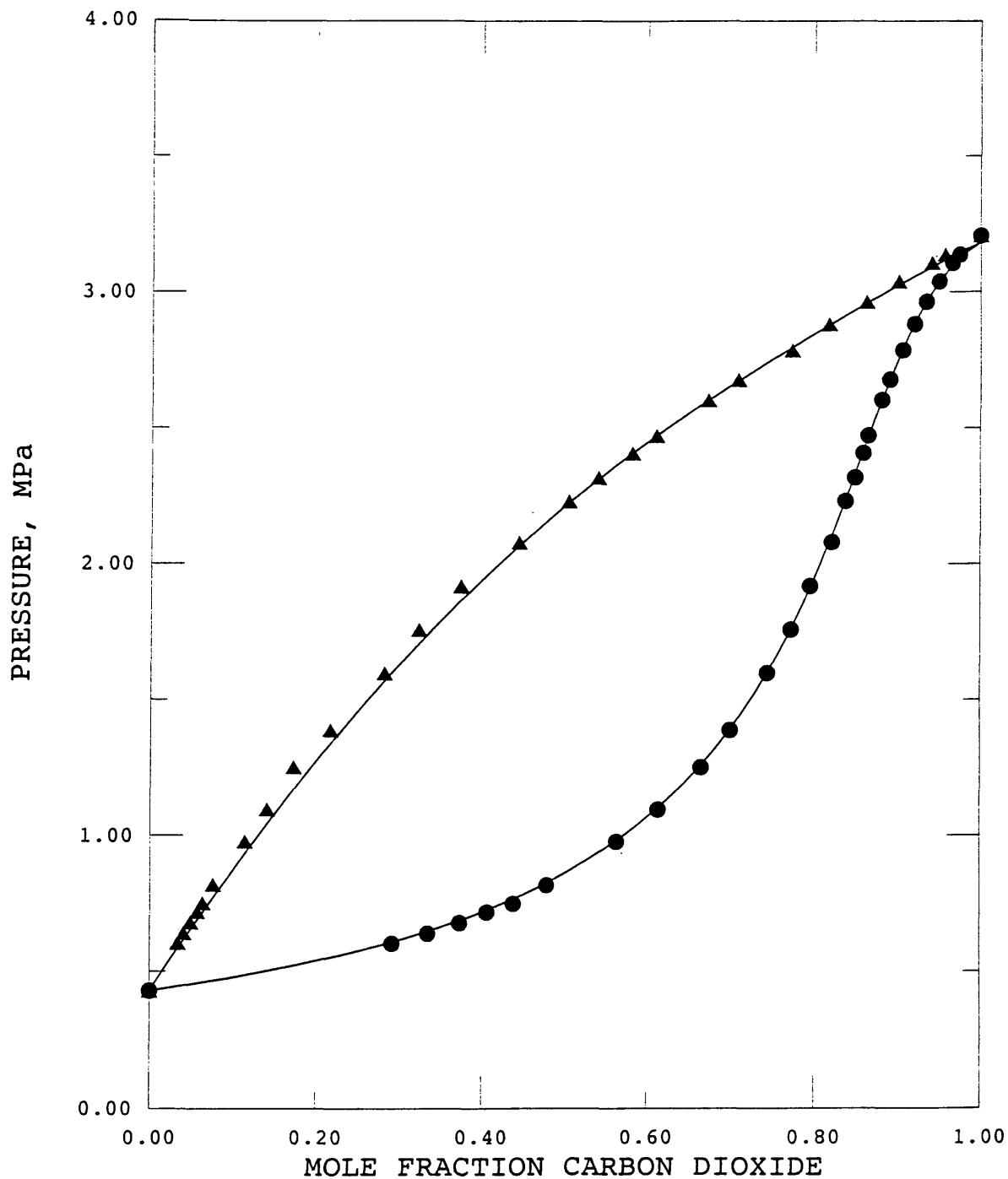


Figure 21. Carbon Dioxide-Propane at 230 K: ▲ LIQUID, ● VAPOR, — PR PREDICTION.

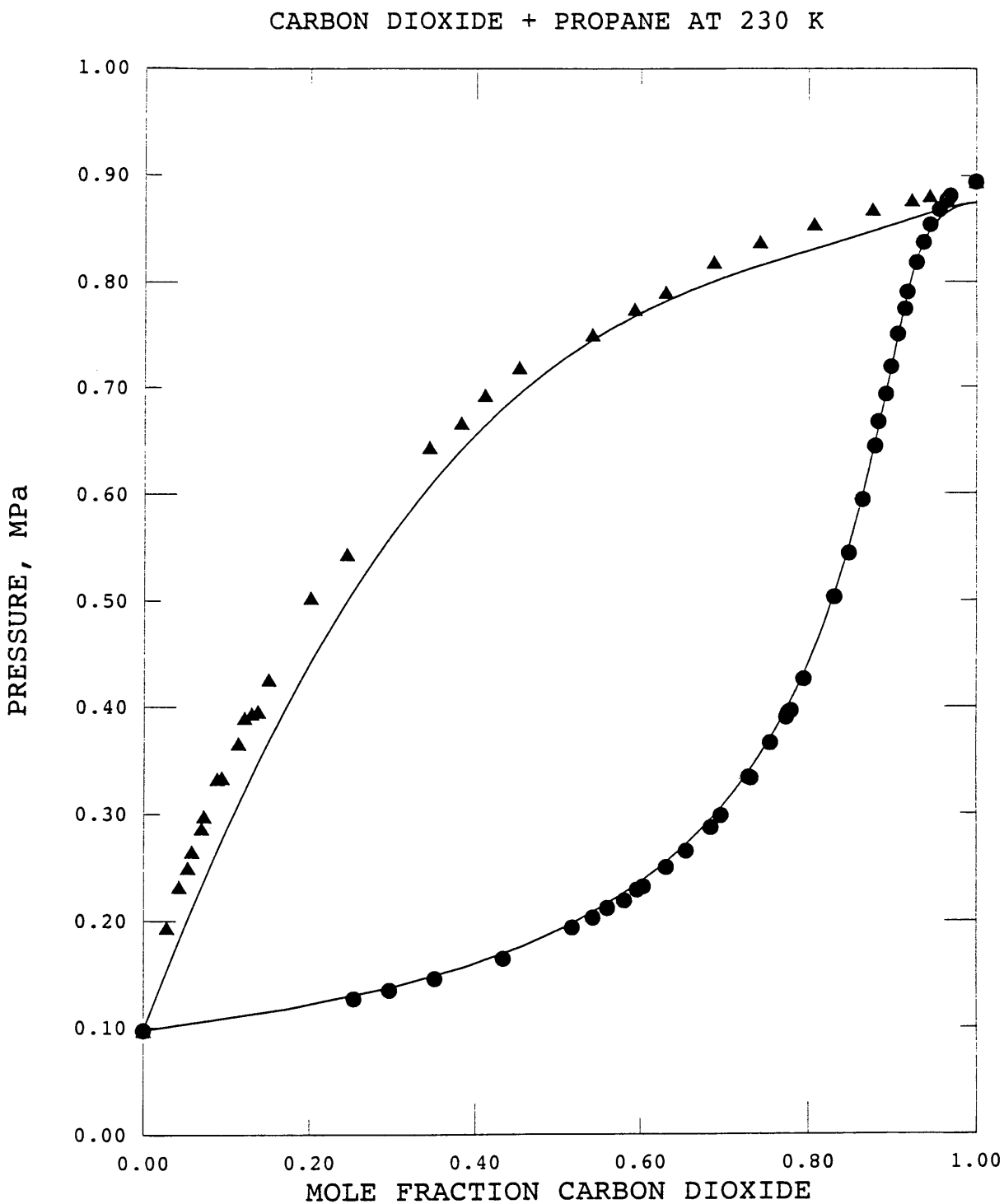


Figure 22. Carbon Dioxide - Propane at 230 K:  $\blacktriangle$  LIQUID,  $\bullet$  VAPOR, — PR PREDICTION.

HENRY'S CONSTANTS VS. TEMPERATURE, CARBON DIOXIDE-PROPANE

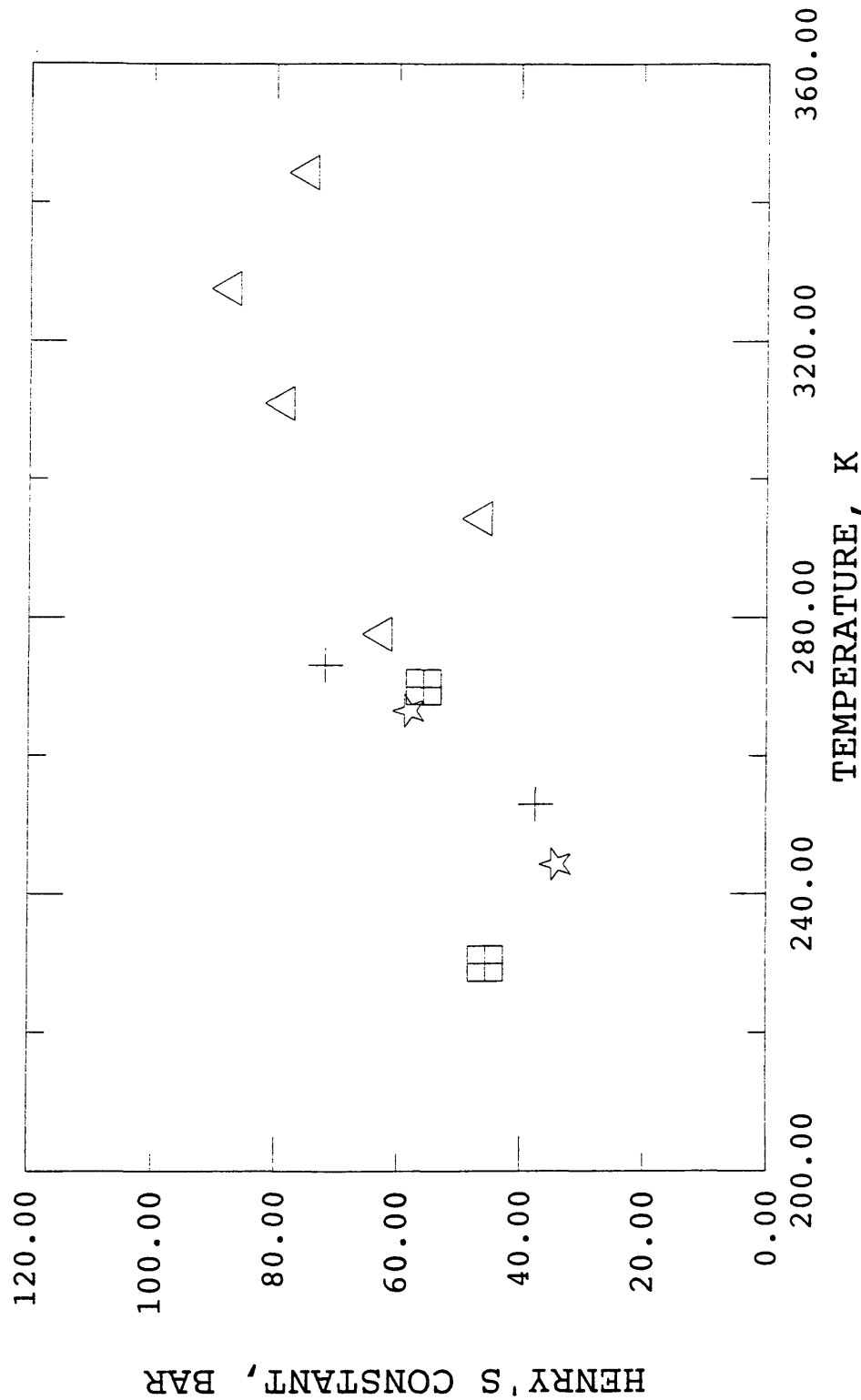


Figure 23. Henry's Constants vs. Temperature for Carbon Dioxide and Propane:   
 □ This Study, + Nagahama et al. (1974), △ Reamer, Sage, and Lacey (1951), ☆ Hamam and Lu (1976).

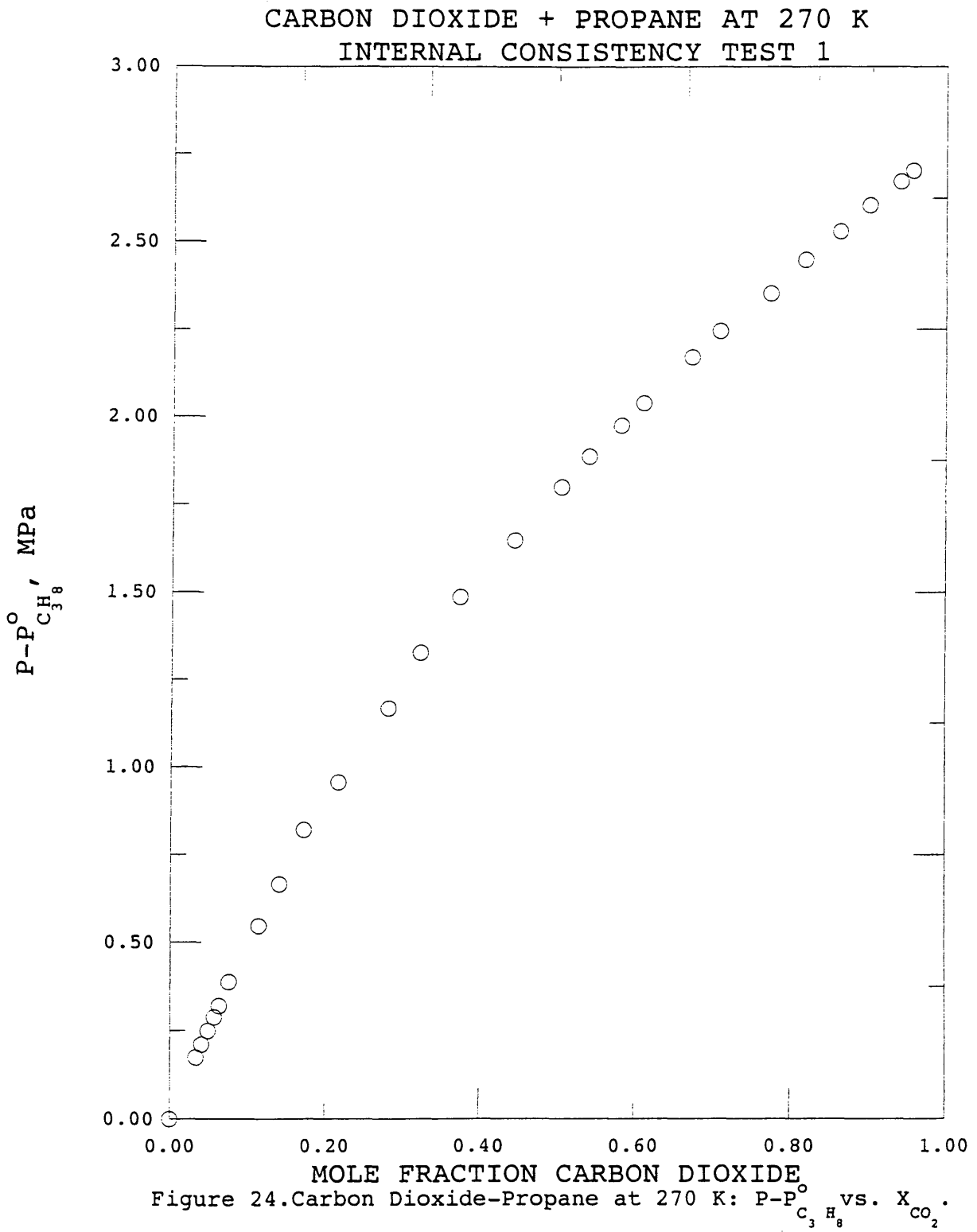
The 230 K data point agrees with the trend of Reamer, Sage, and Lacey's data published in 1951.

The three internal consistency tests were applied to both data sets. The results appear in Figures 24-29 and indicated good internal consistency of the data.

At the temperatures investigated the isotherms exhibit the standard behavior for a binary system with two sub-critical components: the isotherm extrapolates smoothly at both ends to the vapor pressure of the pure component. However, the vapor phase exhibits a reverse curvature in the carbon dioxide rich region of the isotherm. This curvature is noted in all of the literature published on this system. Poettmann and Katz (1945) attribute this behavior to the same forces which form the minimum-boiling azeotrope in the carbon dioxide-ethane system. As noted by Akers et al. (1954) and as can be seen in this study, the reverse curvature becomes more pronounced as the temperature decreases.

#### CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> Ternary System

Vapor-liquid equilibria measurements were made for the CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> system at 270 K for 2.8, 5.5, 8.0 MPa and 230 K



CARBON DIOXIDE + PROPANE AT 270 K  
INTERNAL CONSISTENCY TEST 2

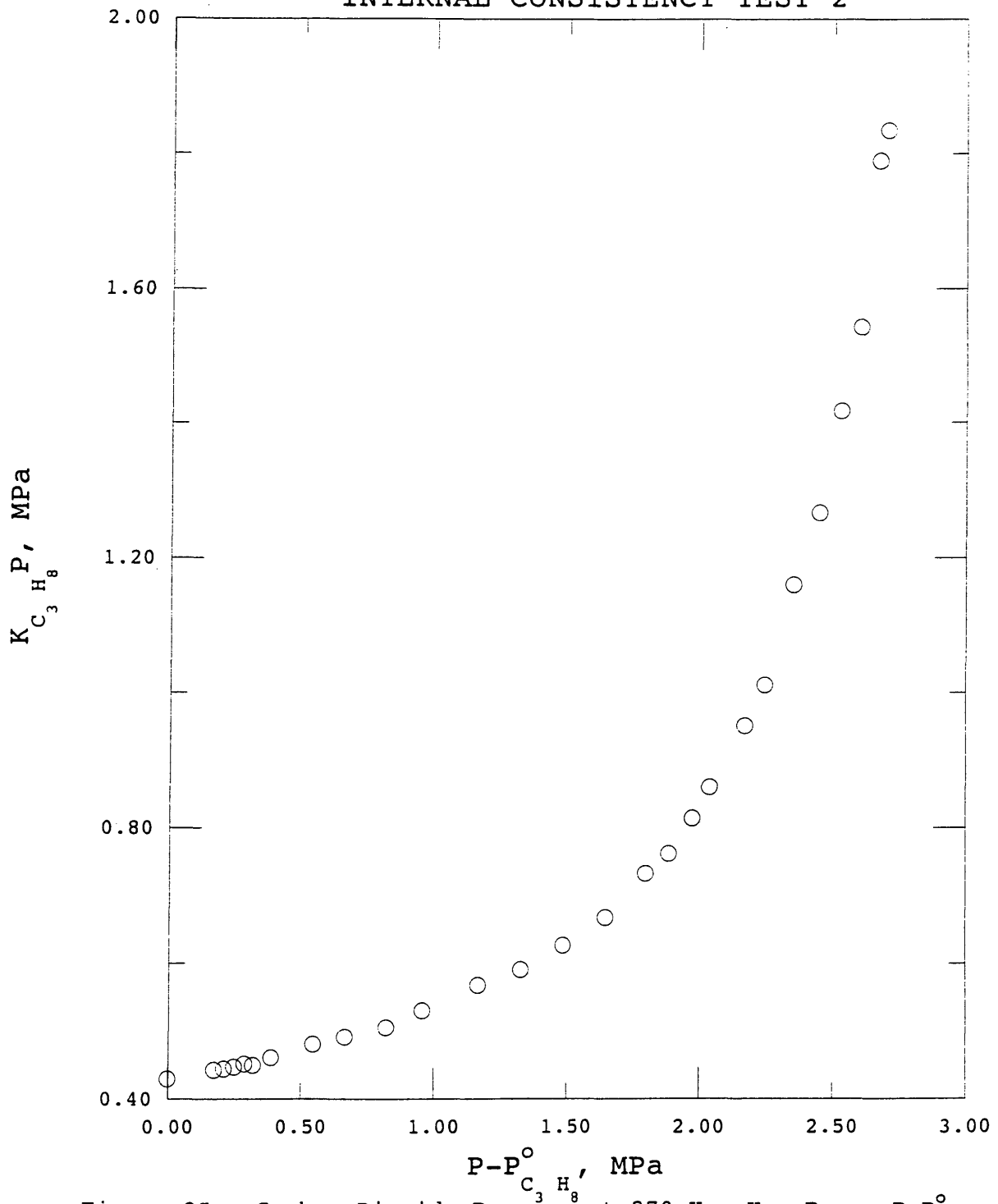


Figure 25. Carbon Dioxide-Propane at 270 K:  $K_{C_3H_8} P$  vs.  $P - P^{\circ}_{C_3H_8}$ .

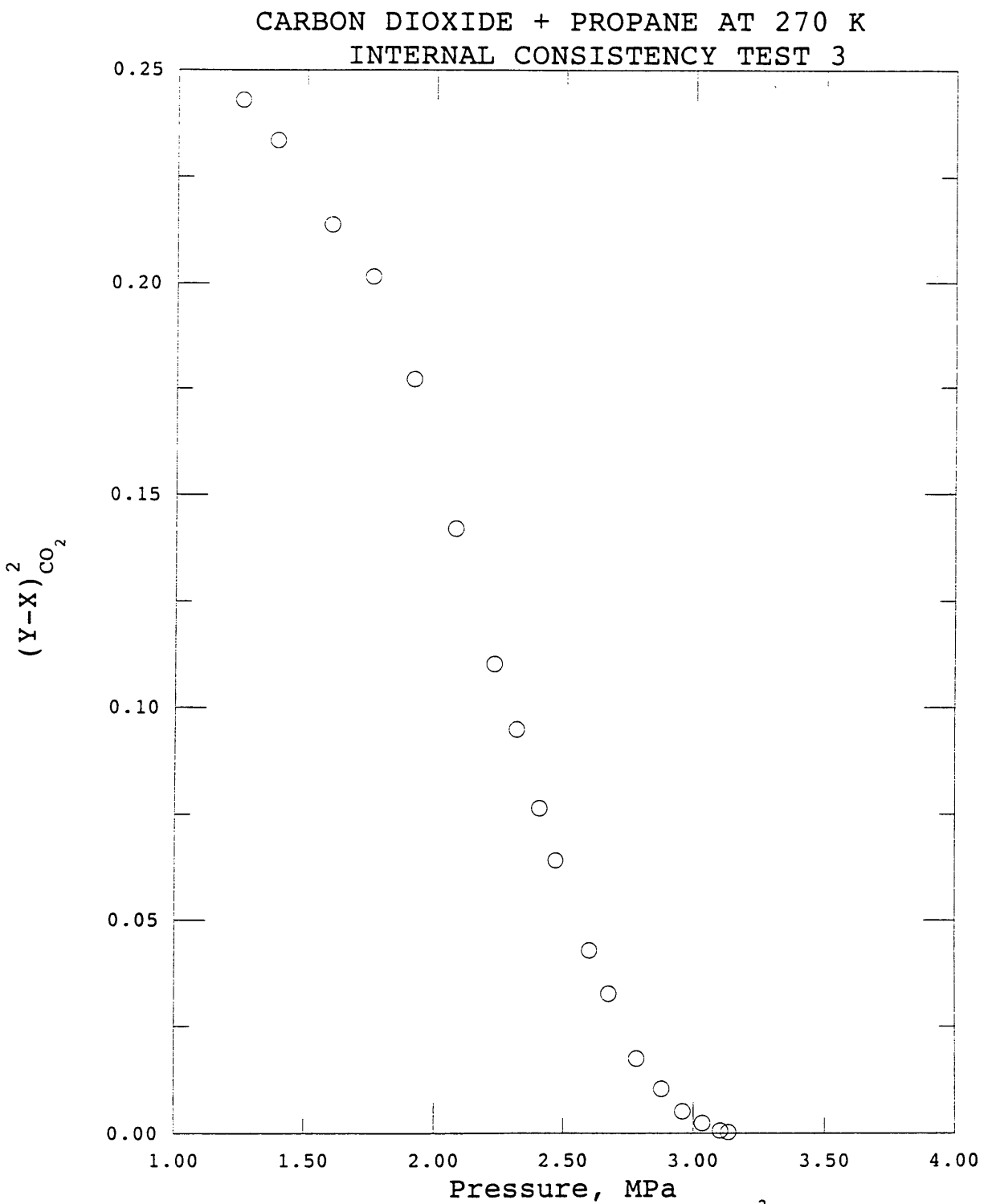


Figure 26. Carbon Dioxide-Propane at 270 K:  $(Y-X)_{\text{CO}_2}^2$  vs. Pressure.

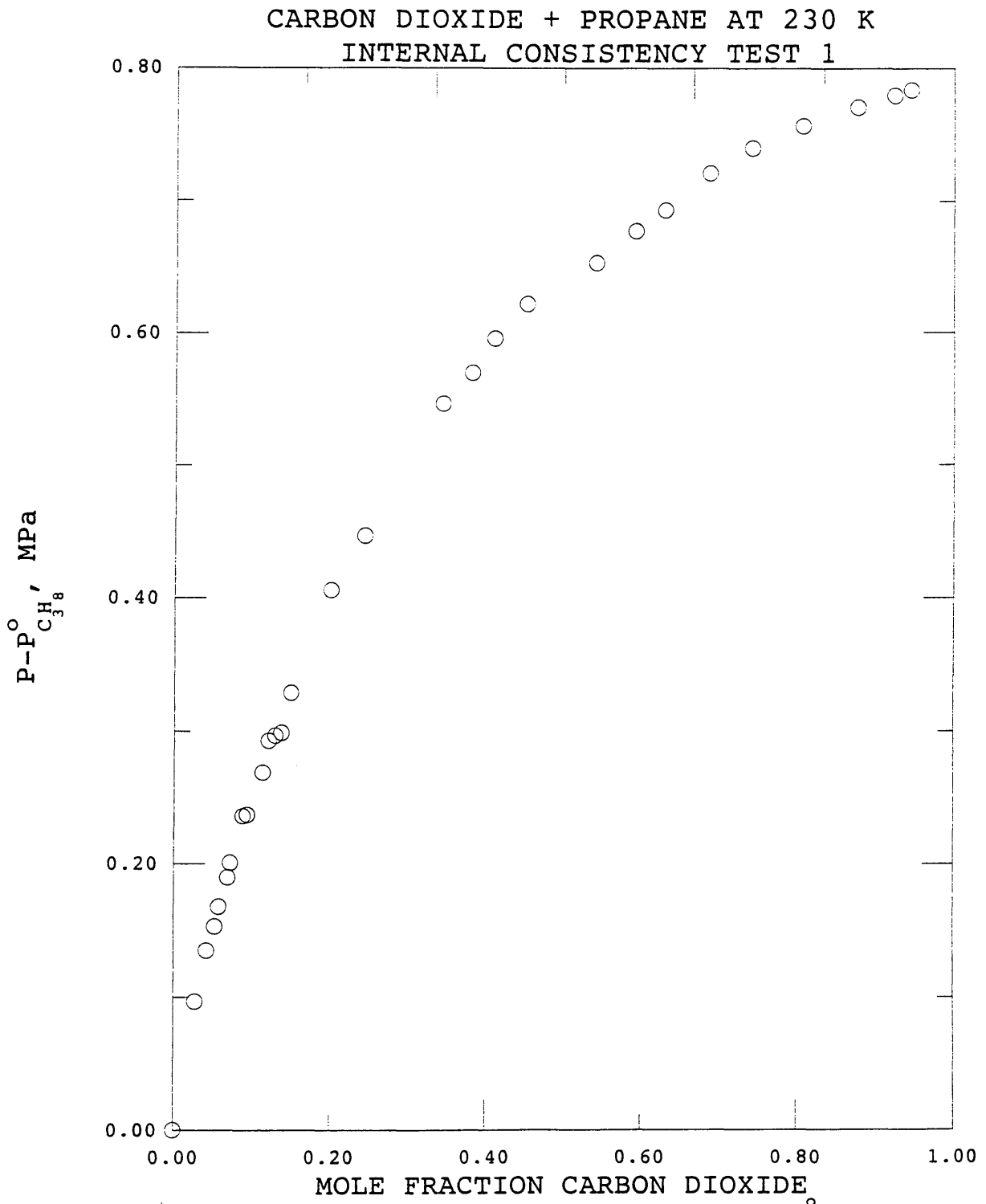


Figure 27. Carbon Dioxide-Propane at 230 K:  $P - P_{C_3H_8}^o$  vs.  $X_{CO_2}$ .

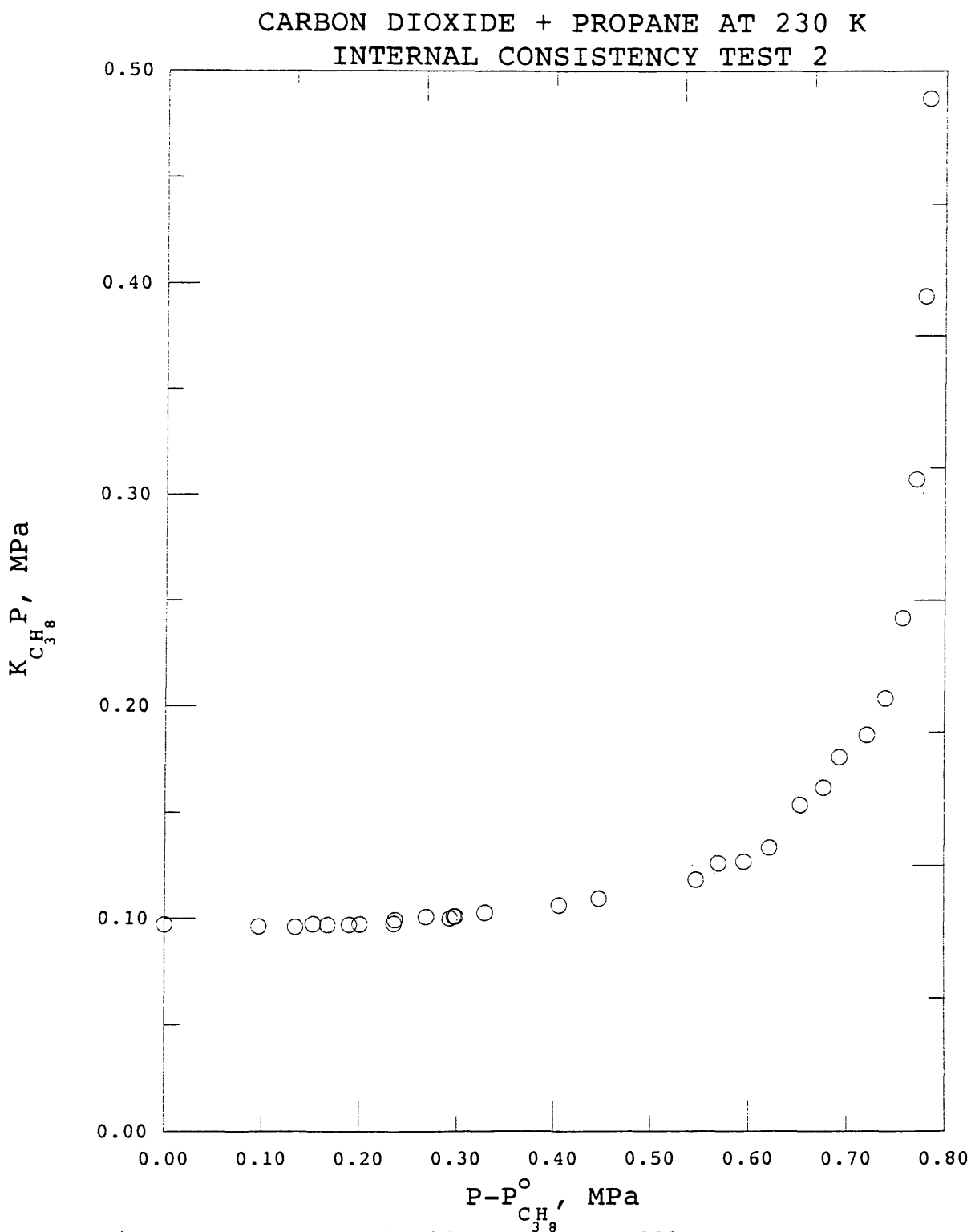


Figure 28. Carbon Dioxide-Propane at 230 K:  $K_{\text{CH}_3} P$  vs.  $P - P_{\text{CH}_3}^0$ .

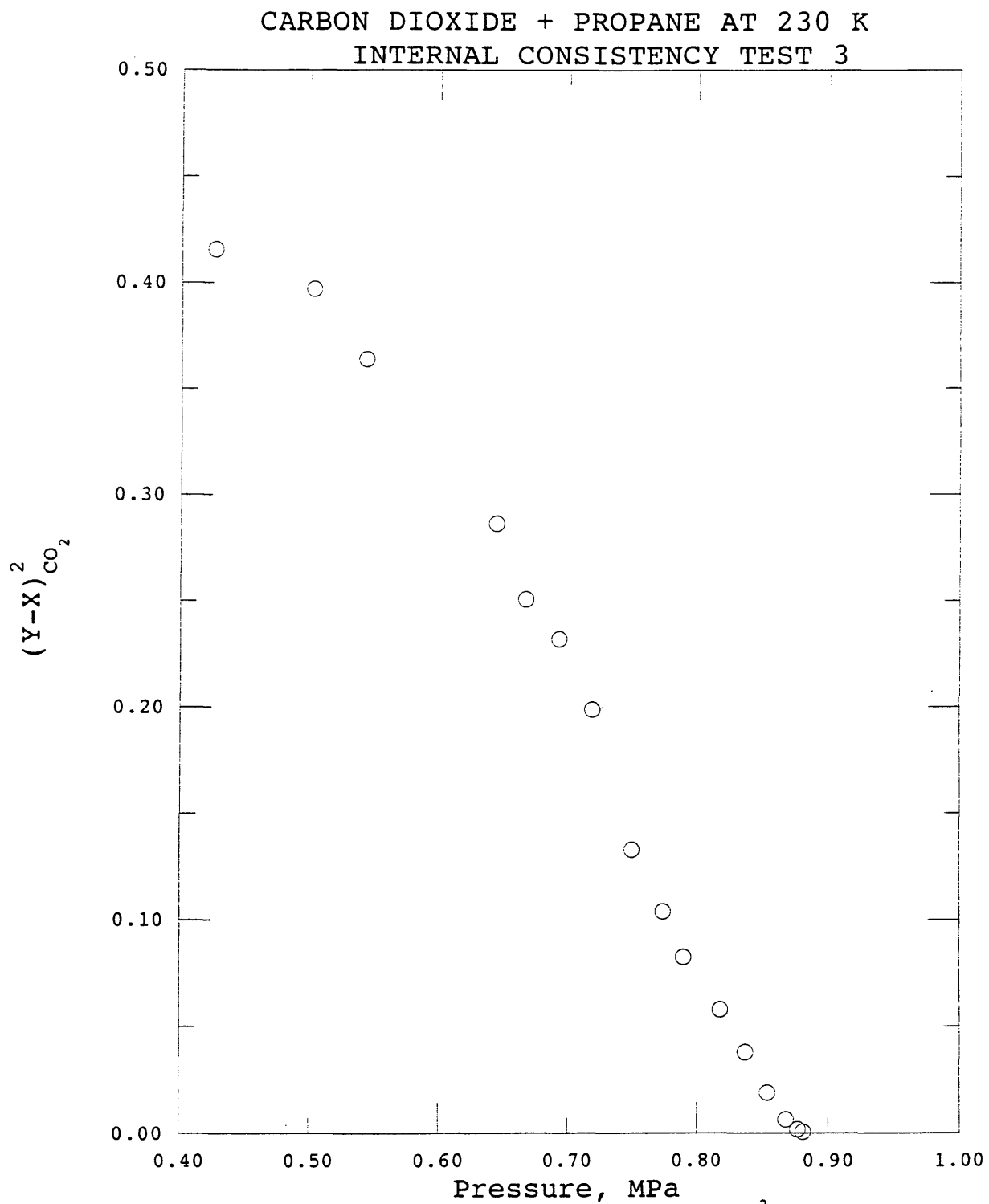


Figure 29. Carbon Dioxide-Propane at 230 K:  $(Y-X)_{\text{CO}_2}^2$  vs. Pressure.

for 0.8, 4.0, 7.0 MPa. The pressures were chosen for the same reason for both operating temperatures. They are as follows: the low pressure point is the pressure where the carbon dioxide-propane binary intercept has an inverted vapor curve, the 5.5 and 4.0 MPa are intermediate pressures, and the high pressures are near the critical region of both intercepting binaries. The results are shown in Figures 30-35. The internal consistency of each data set was checked by plotting the binary endpoint measurements against the previously generated binary curves. All 12 binary points lay within 0.002 mole fraction of the previous points.

No mutual consistency tests were performed because there are no published data on the ternary system.

CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> SYSTEM AT  
270 K AND 2.8 MPa

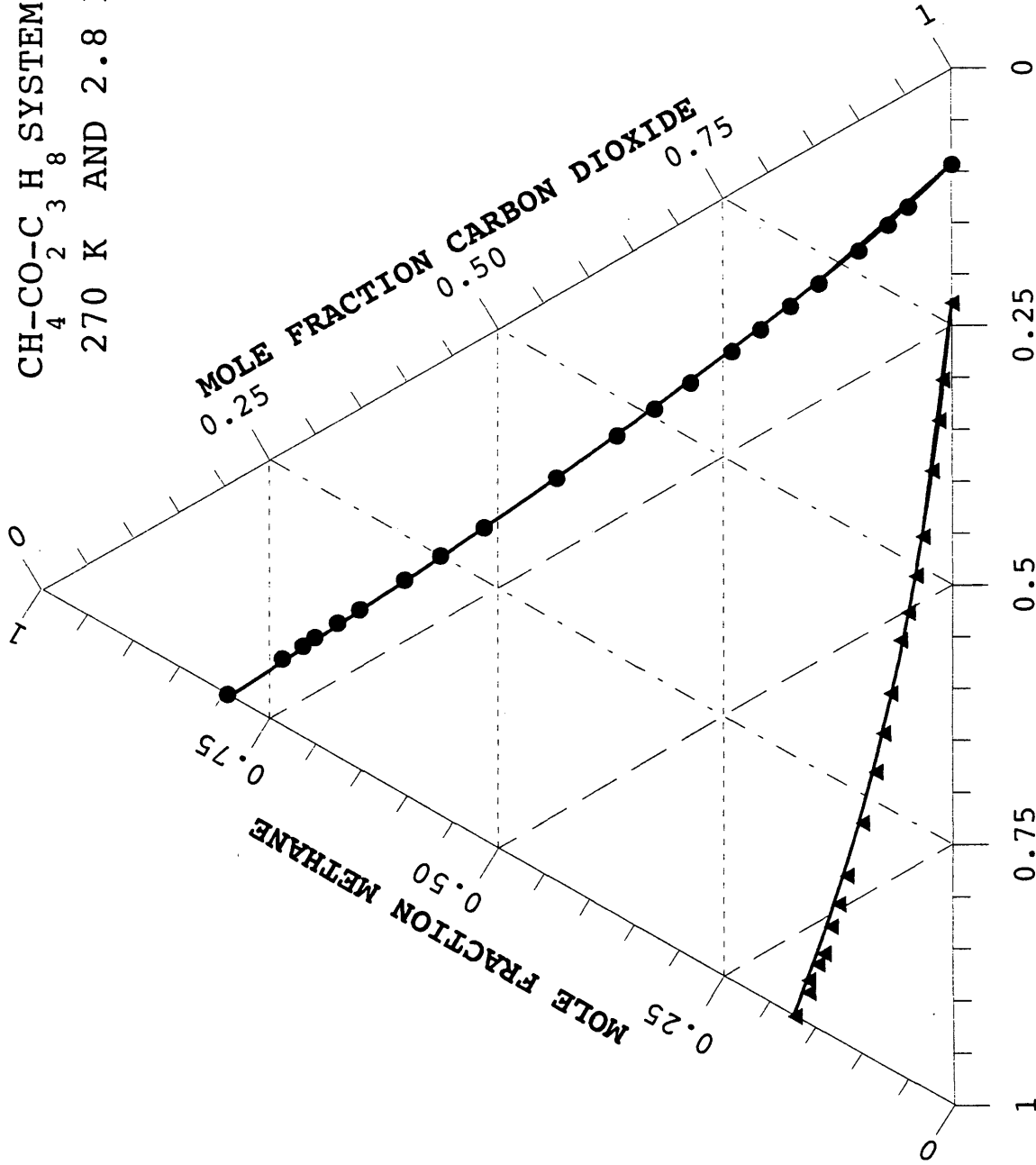
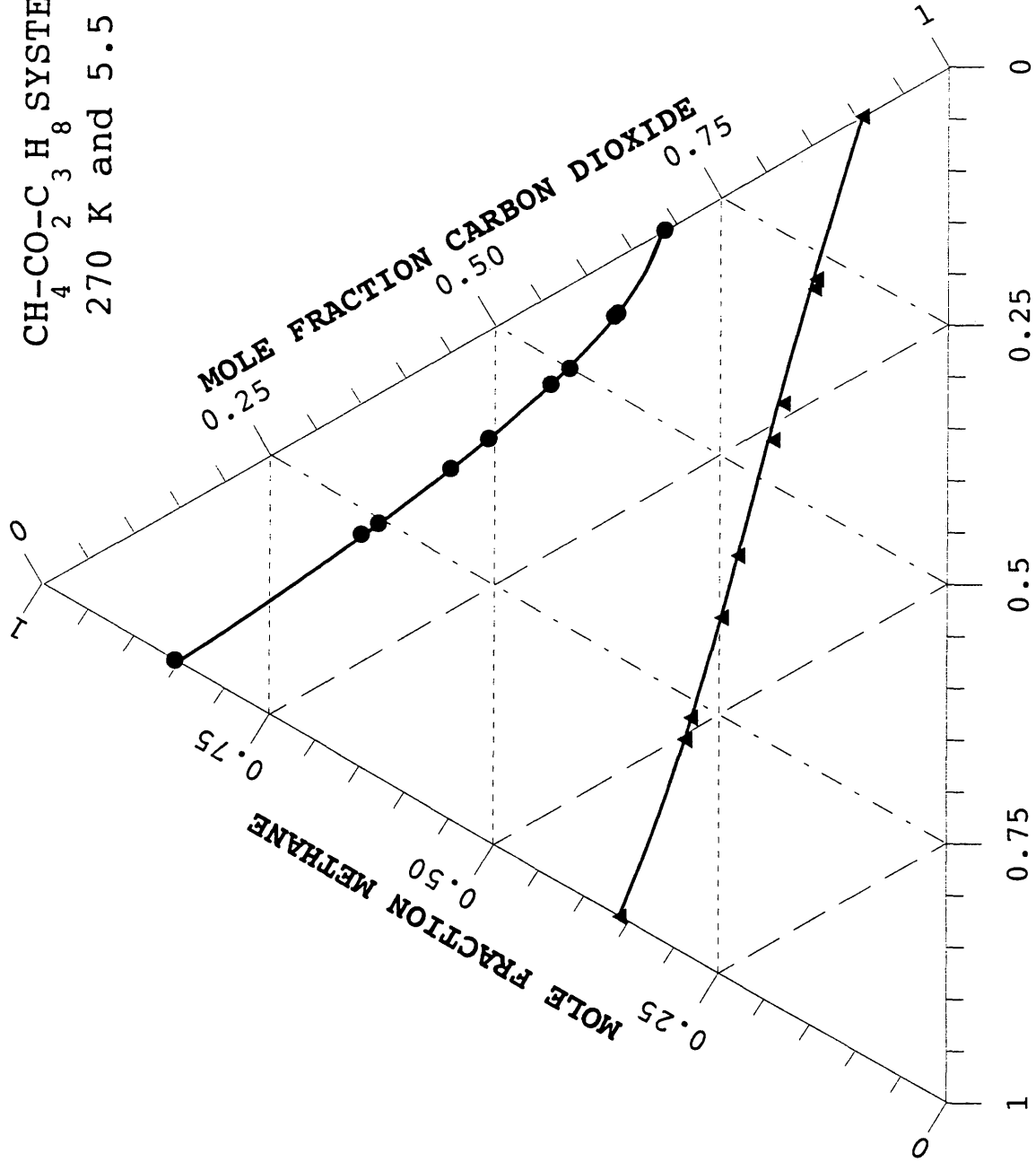


Figure 30. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System at 270 K and 2.8 MPa: ● VAPOR, ▲ LIQUID, — PR PREDICTION.

CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> SYSTEM AT  
270 K and 5.5 MPa



MOLE FRACTION PROPANE

Figure 31. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System at 270 K and 5,5 MPa:● VAPOR, ▲ LIQUID, ----- PR PREDICTION.

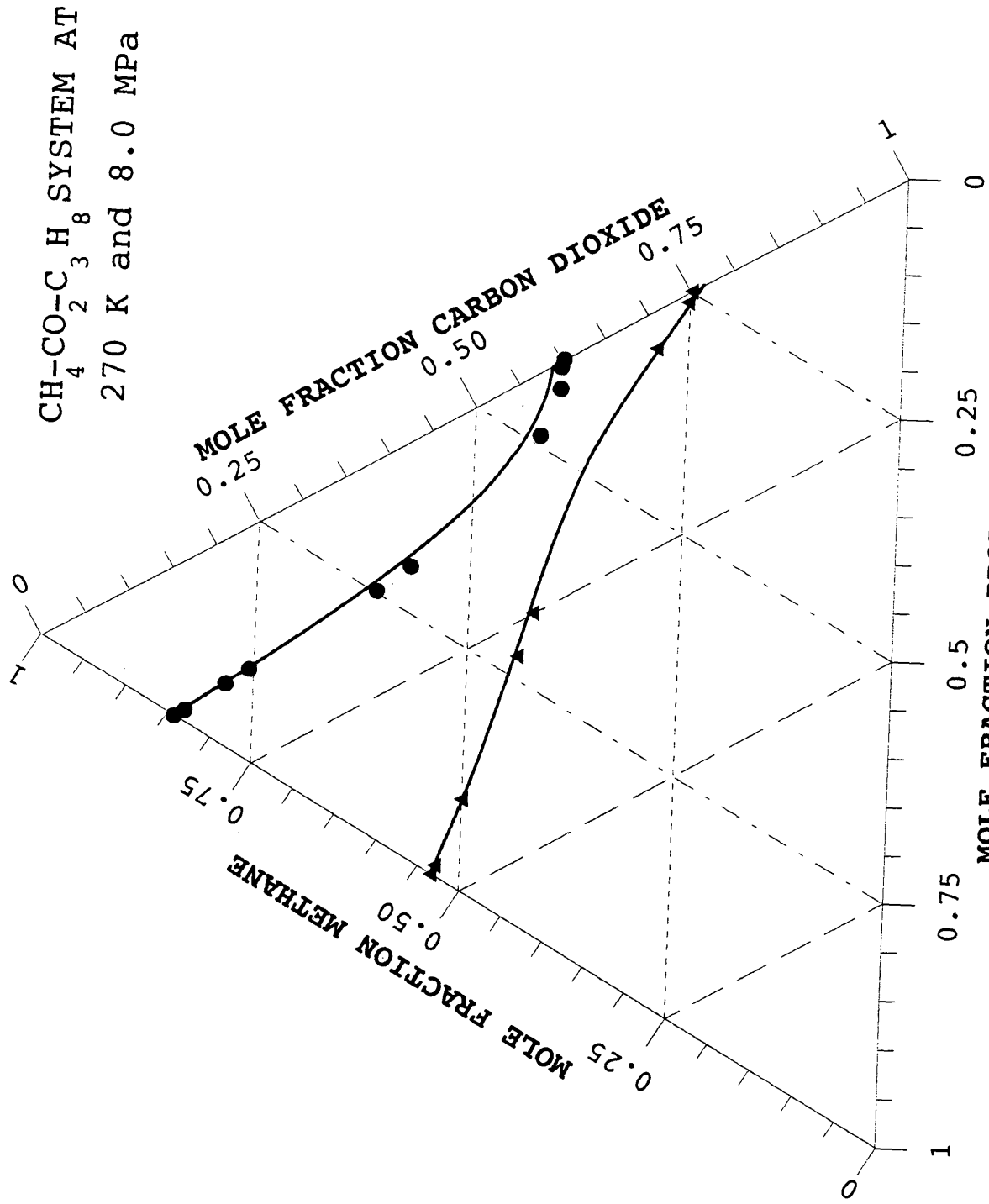


Figure 32. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System at 270 K and 8.0 MPa. ● VAPOR, ▲ LIQUID, — PR PREDICTION.

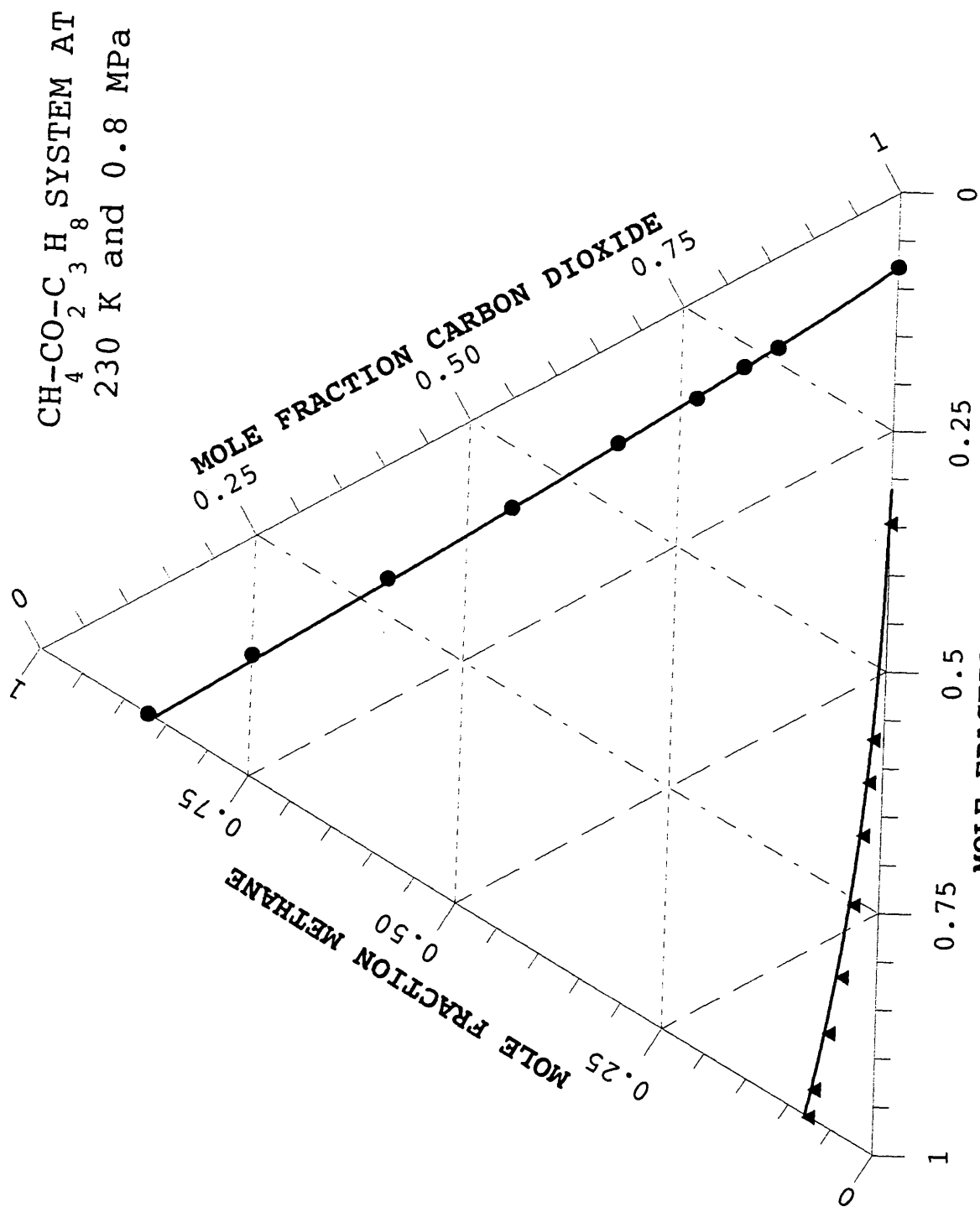


Figure 33. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System at 230 K and 0.8 MPa: ● VAPOR, ▲ LIQUID, — PR PREDICTION.

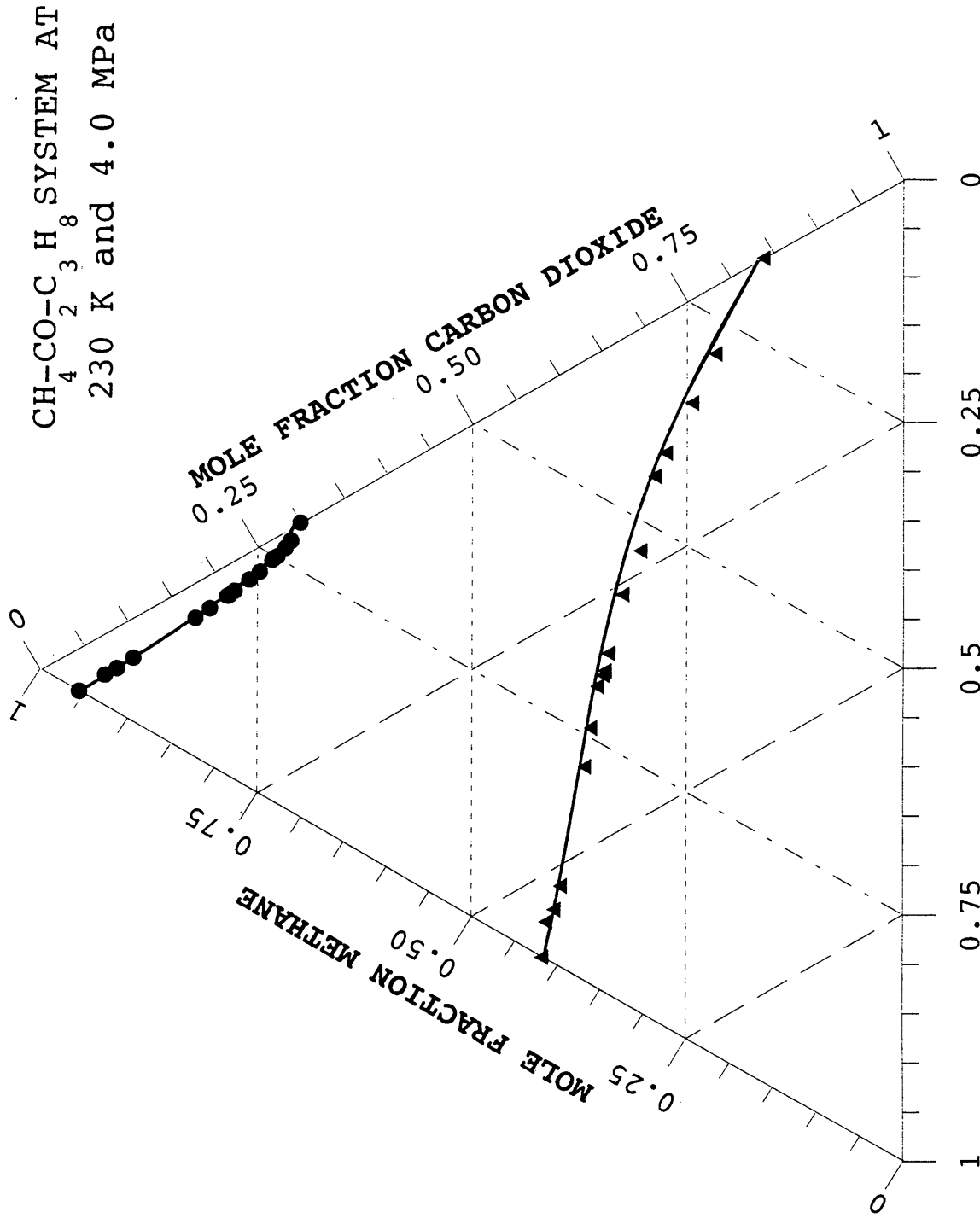


Figure 34. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System at 230 K and 4.0 MPa: ● VAPOR, ▲ LIQUID, — PR PREDICTION.

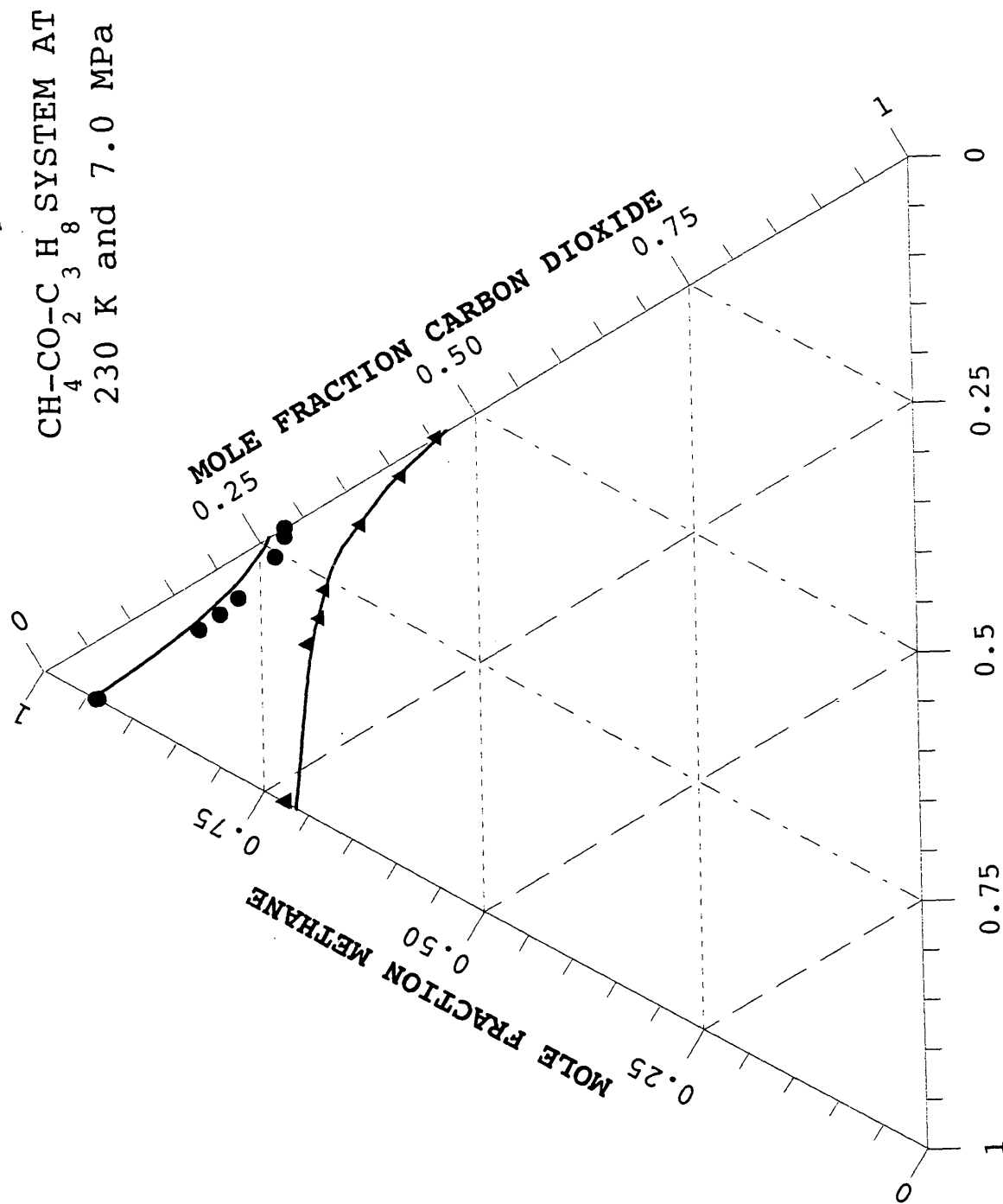


Figure 35. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> System at 230 K and 7.0 MPa: ● VAPOR, ▲ LIQUID, — PR PREDICTION.

## MODELING

The standard Peng-Robinson equation of state (Peng and Robinson, 1976) was used to model the experimental data. The equation is cubic in volume and is a modified Van der Waals Equation adapted specifically for the hydrocarbon processing industry. The equation includes one binary interaction parameter,  $k_{ij}$ , which was obtained by data regression of the binary VLE measurements. The ASPEN PLUS™ version 9.0 Data Regression System(DRS) was used to estimate  $k_{ij}$ . ASPEN employs the maximum likelihood objective function:

$$S = \sum_{i=1}^n \{ ((X_{\text{exp}} - X_{\text{cal}})_i / \sigma_{X_i})^2 + ((Y_{\text{exp}} - Y_{\text{cal}})_i / \sigma_{Y_i})^2 + ((T_{\text{exp}} - T_{\text{cal}})_i / \sigma_{T_i})^2 + ((P_{\text{exp}} - P_{\text{cal}})_i / \sigma_{P_i})^2 \} \quad (1)$$

Where the sigma values are the experimental errors; for this study they were as follows:

$$\begin{aligned} \sigma_x &= \pm 0.005 \\ \sigma_y &= \pm 0.002 \\ \sigma_T &= \pm 0.03 \text{ K} \\ \sigma_P &= \pm 0.1\% \text{ of the full-scale reading of the gauge} \end{aligned}$$

The results from ASPEN PLUS™ were compared with a program written by Dr. A. J. Kidnay which employs the simpler objective function:

$$S = \sum_{i=1}^n \{ \text{abs}(X_{\text{cal}} - X_{\text{exp}})_i + \text{abs}(Y_{\text{cal}} - Y_{\text{exp}})_i \}$$

(2)

The critical constants used in both regression programs were obtained from the ASPEN PLUS<sup>TM</sup> Pure Component Data Bank (ASPENPCD) and are as follows:

Table 3: Critical Constants Used for Calculations

| Component                     | T <sub>c</sub> (K) | P <sub>c</sub> (Bar) | Omega |
|-------------------------------|--------------------|----------------------|-------|
| CH <sub>4</sub>               | 190.6              | 46.0016              | 0.008 |
| C <sub>3</sub> H <sub>8</sub> | 369.8              | 42.4552              | 0.152 |
| CO <sub>2</sub>               | 304.2              | 73.7646              | 0.225 |

## MODELING RESULTS AND DISCUSSION

The  $k_{ij}$  results from the regression of the VLE measurements are presented in Table 4. Compared are the results from ASPEN PLUS<sup>TM</sup>, Dr. A. J. Kidnay's program (AJK), and the literature values stored in the Aspen databank EOS-LIT. The average absolute deviation (AAD) in the mole fractions of X and Y are tabulated for each regression case. Also listed in Table 4 are the regression results from the combined data sets. In all regression cases the two objective functions yielded similar results.

CH<sub>4</sub>-CO<sub>2</sub> Binary System

The Peng-Robinson correlation using AJK  $k_{ij}$ 's, 0.1 and 0.09, are plotted with the experimental data for 270 and 230 K in Figures 4 and 5 respectively. The 270 K correlation is good up to 7.0 MPa. The equation fails to predict the critical region of the mixture. Similarly the 230 K correlation is poor at pressures from 6.0 MPa to the critical point. Note in both regression cases the points in the critical region were removed in order to achieve a good fit in the low pressure regions: from the 230 K data the

Table 4: Interaction Parameters for the Peng-Robinson Equation of State

| Temp<br>(K)                                     | ASPEN<br>PLUS <sup>TM</sup><br>$k_{ij}$ | ASPEN<br>AAD<br>in X | ASPEN<br>AAD<br>in Y | AJK<br>$k_{ij}$ | AJK<br>AAD<br>in X&Y | ASPEN<br>EOSLIT<br>$k_{ij}$ |
|---|---|----------------------|----------------------|-----------------|----------------------|-----------------------------|
| CH <sub>4</sub> -C <sub>3</sub> H <sub>8</sub>  |   |                      |                      |                 |                      |                             |
| 270   | 0.0088                                  | 0.0065               | 0.0053               | 0.010           | 0.0044               | 0.014                       |
| 230   | 0.0069                                  | 0.0046               | 0.0032               | 0.007           | 0.0041               | 0.014                       |
| CH <sub>4</sub> -CO <sub>2</sub>                |   |                      |                      |                 |                      |                             |
| 270   | 0.1124                                  | 0.0012               | 0.0052               | 0.100           | 0.0067               | 0.0919                      |
| 230   | 0.0937                                  | 0.0062               | 0.0057               | 0.090           | 0.0068               | 0.0919                      |
| CO <sub>2</sub> - C <sub>3</sub> H <sub>8</sub> |   |                      |                      |                 |                      |                             |
| 270   | 0.1199                                  | 0.0065               | 0.0019               | 0.120           | 0.0046               | 0.1241                      |
| 230   | 0.1225                                  | 0.0231               | 0.0042               | 0.130           | 0.0154               | 0.1241                      |
| CH <sub>4</sub> -C <sub>3</sub> H <sub>8</sub>  |   |                      |                      |                 |                      |                             |
| 270+230   | 0.0069                                  | 0.0041               | 0.0043               |                 |                      | 0.014                       |
| CH <sub>4</sub> -CO <sub>2</sub>                |   |                      |                      |                 |                      |                             |
| 270+230   | 0.0947                                  | 0.0052               | 0.0039               |                 |                      | 0.0919                      |
| CO <sub>2</sub> - C <sub>3</sub> H <sub>8</sub> |   |                      |                      |                 |                      |                             |
| 270+230   | 0.1213                                  | 0.0153               | 0.0033               |                 |                      | 0.1241                      |

last 12 points were ignored; from the 270 K data the last 9 points were ignored.

#### CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> Binary System

The Peng-Robinson correlation using ASPEN PLUS™  $k_{ij}$ 's, 0.0088 and 0.0069 are plotted with the experimental data for 270 and 230 K in Figures 12 and 13 respectively. Both curves are a good fit of the data except in critical region. The Peng-Robinson equation over-predicts the critical pressure of the mixture at both temperatures. Note that from the 230 K data the last 4 points were ignored; from the 270 K data the last 2 points were ignored.

#### CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> Binary System

The Peng-Robinson correlation using ASPEN PLUS™  $k_{ij}$ 's, 0.1199 and 0.1225, are plotted with the experimental data for 270 and 230 K in Figures 21 and 22 respectively. The Peng-Robinson correlation is a very good fit for the propane vapor measurements at both temperatures. The liquid fit has a greater AAD than the vapor for both temperatures: at 270 K Aspen reports 0.007 in X and 0.002 in Y; and at 230 K Aspen reports 0.02 in X and 0.004 in Y. The correlation of the liquid at 230 K is clearly the greatest deviation from the measured values. The liquid correlation actually

intersects three points in the 0.7-0.8 MPa region of the binary. Internal consistency tests indicate that these three points are within acceptable deviation from the rest of the data set. The 230 K correlation also under-predicts the vapor pressure of Carbon Dioxide by 0.019 MPa. Allowing Aspen to regress the acentric factor for carbon dioxide gives  $\omega=0.2108$  and a slightly better fit of the vapor pressure, a positive deviation of 0.010 Mpa. However, this adjustment does not decrease the AAD in the liquid correlation.

#### CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> Ternary System

The Peng-Robinson prediction using AJK  $k_{ij}$ 's for the CH<sub>4</sub>-CO<sub>2</sub> system and ASPEN PLUS™  $k_{ij}$ 's for the rest are plotted with the experimental data at 270 for 2.8, 5.5, and 8.0 MPa and at 230 K for 0.8, 4.0, and 7.0 MPa in Figures 30 through 35, respectively. The Peng-Robinson predictions are most accurate at the low pressures and poorest at the high pressures of 8.0 and 7.0 MPa which are near the critical points.

## CONCLUSIONS AND RECOMMENDATIONS

The rebuilt and modified low-temperature apparatus was able to reproduce the accuracy of previous experimentalists. The very good reproduction of vapor pressures measurements and the methane-carbon dioxide isotherm at 270 K were indications of this.

An internally consistent set of binary and ternary vapor-liquid equilibria data for the methane-carbon dioxide-propane system at 230 and 270 K has been generated. Mutual consistency for the methane-carbon dioxide and the methane-propane binary systems was also confirmed. Mutual consistency in the 270 K carbon dioxide-propane system was confirmed but no conclusion was made for the 230 K isotherm. Measuring carbon dioxide-propane liquid data for temperatures between 230 and 270 K for the dilute solute region is recommended for use in the Henry's Law mutual consistency test.

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## APPENDIX A: CALIBRATIONS

This appendix contains a description of the procedure and the results of the calibrations made for the gas chromatograph, the Heise pressure gauges, and the Mueller bridge.

Gas Chromatograph

The gas chromatograph was calibrated by injecting pure gas components at known pressures and controlled temperatures using a gas sampling valve. Gauge pressure of the injected component was measured using a 30" U-tube, mercury, manometer. Atmospheric pressure was measured using a mercury barometer. The manometer was connected to the GC as described by Brown in the appendix of his Ph.D. thesis (1990). Both pressure readings were corrected for the density change of mercury due to temperature fluctuations in the lab. The correction factors were taken from Brombacher, et al. (1960). The manometer reading was also corrected for the gravitational acceleration in Golden which is  $9.79601148 \text{ m/sec}^2$ . The GC control settings and the integrator settings

were the same as those listed in the apparatus description of this thesis. The gas sampling valve was also described in the apparatus section. As was previously noted, the sample loop was decreased until a linear response from the detector was found for each component for injection pressures up to atmospheric pressure. This coincided with a range of  $0-1.5 \times 10^6$  Area counts from the integrated peaks.

The basis of this method is that the pressure, corrected for a components compressibility, is proportional to the number of moles injected since the volume and temperature are constant. Note for this study methane was assumed to be an ideal gas with  $Z=1$ . For carbon dioxide and propane the compressibility factors as a function of pressure were taken from Angus et al. (1976) and Goodwin et al. (1982), respectively.

The following are three important tips for making a good calibrations. First, good flushing must be employed to remove residual helium from the previous sample run. Three flushings with the pure component and evacuating for 2 minutes between each flush gave good results. This insures the assumption that the volume of pure component is constant

for each run is a good one. Another important assumption is that the temperature of the sample is known and the compressibility can be read from literature. The Hewlett Packard GC has a separate heating circuit which maintains the sample loop within the required temperature tolerance, but the sample will take some time to equilibrate at this temperature. In this study allowing three minutes was found to give the best results. Finally, the resulting plot of  $P_{\text{absolute}}/Z$  versus Area Counts should not only show a good fit after linear regression it should also have an intercept close to zero. The largest intercept in this study was -5 on the propane response line. All three lines were then forced through the origin to obtain the final calibration slope.

The accuracy of the calibration curves was determined to be  $\pm 0.002$  mole fraction by the analysis of gravimetric mixtures. The mixtures were weighed with a Seko balance sensitive to 1 mg. Each mixture was analyzed four times and the deviations were averaged.

#### Pressure Gauges

The Heise pressure gauges were calibrated by the manufacturer and have an accuracy of  $\pm 0.1\%$  of the full-scale reading of the gauge. The zero point of the gauges can shift after frequent cycles of pressurizing and venting; the zero was checked at the beginning of each experimental run. Two methods were used: evacuating the system for more than five minutes and checking for a zero reading and/or by comparing the vented gauge with the barometer. The accuracy of all four gauge calibrations have been verified in this laboratory with a dead weight tester.

In this study, the gauge readings were verified by measuring pure component vapor pressures and comparing them against literature values. The results from these tests are listed in Table 2.

#### Mueller Bridge

The Mueller Bridge was calibrated using a Leeds and Northrup standard 10 ohms resistor. The resistance uncertainty of the standard is 0.001%. The difference in the resistance value corrected for temperature by L&N's calibration report and the Mueller Bridge reading was found

to +0.0007 ohms. This zero value was subtracted from all  
Mueller Bridge readings.

## APPENDIX B: EXPERIMENTAL DATA

This appendix contains tables of unsmoothed, experimental vapor-liquid-equilibria data. Each data point is the averaged result of two or three gas chromatograph runs.

Table 5. CH<sub>4</sub>-CO<sub>2</sub> at 230K

| Pressure, MPa | Y <sub>CH<sub>4</sub></sub> | X <sub>CH<sub>4</sub></sub> |
|---------------|-----------------------------|-----------------------------|
| 0.894         | 0.0000                      | 0.0000                      |
| 1.187         | 0.2252                      | -                           |
| 1.420         | 0.3385                      | 0.0213                      |
| 1.651         | 0.4196                      | 0.0307                      |
| 1.931         | 0.4900                      | 0.0441                      |
| 2.257         | 0.5512                      | 0.0597                      |
| 2.488         | 0.5851                      | 0.0714                      |
| 3.375         | 0.6670                      | 0.1199                      |
| 4.497         | 0.7199                      | 0.1994                      |
| 5.573         | 0.7432                      | 0.3093                      |
| 5.836         | 0.7454                      | 0.3404                      |
| 6.241         | 0.7443                      | 0.4010                      |
| 6.417         | 0.7442                      | 0.4323                      |
| 6.512         | 0.7422                      | 0.4530                      |
| 6.649         | 0.7371                      | 0.4862                      |
| 6.654         | 0.7382                      | 0.4815                      |
| 6.859         | 0.7312                      | 0.5201                      |
| 6.859         | 0.7314                      | 0.5208                      |
| 6.912         | 0.7286                      | 0.5302                      |
| 6.970         | 0.7245                      | 0.5393                      |
| 7.004         | 0.7222                      | 0.5521                      |
| 7.072         | 0.7156                      | 0.5682                      |
| 7.108         | -                           | 0.5800                      |
| 7.112         | 0.7102                      | 0.5774                      |
| 7.145         | 0.7066                      | 0.5888                      |

Table 6. CH<sub>4</sub>-CO<sub>2</sub> at 270K

| Pressure, MPa | Y <sub>CH<sub>4</sub></sub> | X <sub>CH<sub>4</sub></sub> |
|---------------|-----------------------------|-----------------------------|
| 3.203         | 0.0000                      | 0.0000                      |
| 3.883         | 0.1352                      | 0.0264                      |
| 3.913         | 0.1402                      | 0.0276                      |
| 4.104         | 0.1680                      | 0.0342                      |
| 4.413         | 0.2093                      | 0.0477                      |
| 4.787         | 0.2517                      | 0.0640                      |
| 4.987         | 0.2706                      | 0.0723                      |
| 5.433         | 0.3085                      | 0.0919                      |
| 6.537         | 0.3702                      | 0.1479                      |
| 6.959         | 0.3847                      | 0.1739                      |
| 7.305         | 0.3945                      | 0.1949                      |
| 7.946         | 0.3977                      | 0.2435                      |
| 8.098         | -                           | 0.2559                      |
| 8.131         | 0.3934                      | 0.2602                      |
| 8.207         | 0.3894                      | 0.2688                      |
| 8.389         | 0.3762                      | 0.2901                      |
| 8.419         | 0.3704                      | 0.2991                      |

Table 7. CH<sub>4</sub> - C<sub>3</sub>H<sub>8</sub> at 230K

| Pressure, MPa | Y <sub>CH<sub>4</sub></sub> | X <sub>CH<sub>4</sub></sub> |
|---------------|-----------------------------|-----------------------------|
| 0.0973        | 0.0000                      | 0.0000                      |
| 0.697         | 0.8563                      | 0.0657                      |
| 0.776         | 0.8670                      | -                           |
| 0.865         | 0.8782                      | 0.0855                      |
| 0.997         | 0.8925                      | 0.0994                      |
| 1.104         | 0.9028                      | -                           |
| 1.234         | 0.9134                      | 0.1244                      |
| 1.353         | 0.9180                      | 0.1372                      |
| 1.493         | 0.9238                      | 0.1524                      |
| 1.655         | 0.9291                      | -                           |
| 1.895         | 0.9368                      | 0.1972                      |
| 2.020         | 0.9390                      | 0.2128                      |
| 2.174         | 0.9408                      | 0.2269                      |
| 2.301         | 0.9419                      | 0.2436                      |
| 2.466         | 0.9466                      | 0.2550                      |
| 2.672         | 0.9485                      | 0.2758                      |
| 2.792         | 0.9499                      | 0.2864                      |
| 2.969         | 0.9497                      | 0.3178                      |
| 3.382         | 0.9538                      | 0.3526                      |
| 3.537         | 0.9532                      | 0.3738                      |
| 3.971         | 0.9556                      | 0.4126                      |
| 4.174         | 0.9515                      | 0.4337                      |
| 4.399         | 0.9546                      | 0.4614                      |
| 4.575         | 0.9531                      | 0.4727                      |
| 5.057         | 0.9537                      | 0.5291                      |
| 5.513         | 0.9524                      | 0.5738                      |
| 6.050         | 0.9495                      | 0.6313                      |
| 6.566         | 0.9448                      | 0.6849                      |
| 6.946         | 0.9407                      | 0.7222                      |
| 7.125         | 0.9369                      | 0.7468                      |
| 7.270         | 0.9334                      | 0.7590                      |
| 7.422         | 0.9279                      | 0.7833                      |
| 7.621         | 0.9214                      | 0.8067                      |
| 7.720         | 0.9175                      | 0.8255                      |
| 7.767         | 0.9155                      | 0.8398                      |

Table 8. CH<sub>4</sub> - C<sub>3</sub>H<sub>8</sub> at 270K

| Pressure, MPa | Y <sub>CH<sub>4</sub></sub> | X <sub>CH<sub>4</sub></sub> |
|---------------|-----------------------------|-----------------------------|
| 0.431         | 0.0000                      | 0.0000                      |
| 0.667         | 0.3384                      | -                           |
| 0.754         | 0.4184                      | 0.0238                      |
| 0.812         | 0.4536                      | 0.0296                      |
| 0.904         | 0.5003                      | 0.0356                      |
| 0.931         | 0.5119                      | 0.0385                      |
| 1.073         | 0.5752                      | 0.0474                      |
| 1.189         | 0.6089                      | 0.0588                      |
| 1.331         | 0.6526                      | 0.0667                      |
| 1.434         | 0.6670                      | 0.0748                      |
| 1.535         | 0.6874                      | 0.0779                      |
| 1.544         | 0.6881                      | 0.0827                      |
| 1.694         | 0.7160                      | 0.0928                      |
| 1.825         | 0.7269                      | 0.1015                      |
| 1.917         | 0.7416                      | 0.1040                      |
| 1.956         | 0.7418                      | 0.1146                      |
| 2.170         | 0.7608                      | 0.1281                      |
| 2.344         | 0.7713                      | 0.1397                      |
| 2.563         | 0.7859                      | 0.1542                      |
| 2.663         | 0.7919                      | 0.1638                      |
| 2.857         | 0.7998                      | 0.1789                      |
| 3.031         | 0.8073                      | 0.1901                      |
| 3.053         | 0.8083                      | 0.1903                      |
| 3.407         | 0.8211                      | 0.2160                      |
| 3.873         | 0.8345                      | 0.2493                      |
| 4.392         | -                           | 0.2941                      |
| 4.702         | 0.8468                      | 0.3064                      |
| 5.380         | 0.8467                      | 0.3612                      |
| 5.827         | 0.8520                      | 0.3825                      |
| 5.838         | 0.8518                      | 0.3848                      |
| 6.687         | 0.8546                      | 0.4374                      |
| 6.546         | 0.8553                      | 0.4314                      |
| 7.034         | 0.8539                      | 0.4655                      |
| 7.549         | 0.8494                      | 0.5012                      |
| 8.413         | 0.8356                      | 0.5642                      |
| 8.744         | -                           | 0.5956                      |
| 9.038         | -                           | 0.6214                      |
| 9.222         | 0.8029                      | 0.6429                      |
| 9.292         | 0.7937                      | 0.6543                      |

Table 9. CO<sub>2</sub> - C<sub>3</sub>H<sub>8</sub> at 230K

| Pressure, MPa | Y <sub>CH<sub>4</sub></sub> | X <sub>CH<sub>4</sub></sub> |
|---------------|-----------------------------|-----------------------------|
| 0.0971        | 0.0000                      | 0.0000                      |
| 0.127         | 0.2533                      | -                           |
| 0.135         | 0.2964                      | -                           |
| 0.146         | 0.3510                      | -                           |
| 0.165         | 0.4335                      | -                           |
| 0.194         | 0.5170                      | 0.0275                      |
| 0.203         | 0.5425                      | -                           |
| 0.212         | 0.5603                      | -                           |
| 0.219         | 0.5807                      | -                           |
| 0.229         | 0.5961                      | -                           |
| 0.232         | 0.6032                      | 0.0420                      |
| 0.250         | 0.6313                      | 0.0528                      |
| 0.265         | 0.6549                      | 0.0577                      |
| 0.287         | 0.6847                      | 0.0690                      |
| 0.298         | 0.6965                      | 0.0720                      |
| 0.333         | 0.7322                      | 0.0879                      |
| 0.334         | 0.7296                      | 0.0935                      |
| 0.366         | 0.7554                      | 0.1135                      |
| 0.390         | 0.7740                      | 0.1208                      |
| 0.394         | 0.7762                      | 0.1292                      |
| 0.396         | 0.7796                      | 0.1371                      |
| 0.426         | 0.7946                      | 0.1499                      |
| 0.503         | 0.8310                      | 0.2009                      |
| 0.544         | 0.8480                      | 0.2447                      |
| 0.594         | 0.8646                      | -                           |
| 0.644         | 0.8795                      | 0.3442                      |
| 0.667         | 0.8833                      | 0.3825                      |
| 0.693         | 0.8922                      | 0.4107                      |
| 0.719         | 0.8984                      | 0.4524                      |
| 0.750         | 0.9062                      | 0.5415                      |
| 0.774         | 0.9149                      | 0.5925                      |
| 0.790         | 0.9177                      | 0.6303                      |
| 0.818         | 0.9290                      | 0.6880                      |
| 0.837         | 0.9374                      | 0.7426                      |
| 0.854         | 0.9453                      | 0.8068                      |
| 0.868         | 0.9563                      | 0.8766                      |
| 0.877         | 0.9656                      | 0.9234                      |
| 0.881         | 0.9694                      | 0.9447                      |

Table 10. CO<sub>2</sub> - C<sub>3</sub>H<sub>8</sub> at 270K

| Pressure, MPa | Y <sub>CH<sub>4</sub></sub> | X <sub>CH<sub>4</sub></sub> |
|---------------|-----------------------------|-----------------------------|
| 0.430         | 0.0000                      | 0.0000                      |
| 0.604         | 0.2915                      | 0.0337                      |
| 0.641         | 0.3347                      | 0.0409                      |
| 0.679         | 0.3735                      | 0.0490                      |
| 0.718         | 0.4061                      | 0.0569                      |
| 0.750         | 0.4380                      | 0.0630                      |
| 0.818         | 0.4786                      | 0.0757                      |
| 0.977         | 0.5638                      | 0.1139                      |
| 1.096         | 0.6142                      | 0.1407                      |
| 1.251         | 0.6651                      | 0.1722                      |
| 1.387         | 0.7001                      | 0.2169                      |
| 1.598         | 0.7444                      | 0.2820                      |
| 1.758         | 0.7721                      | 0.3231                      |
| 1.918         | 0.7953                      | 0.3742                      |
| 2.079         | 0.8214                      | 0.4443                      |
| 2.230         | 0.8373                      | 0.5051                      |
| 2.317         | 0.8489                      | 0.5408                      |
| 2.406         | 0.8585                      | 0.5820                      |
| 2.470         | 0.8645                      | 0.6110                      |
| 2.601         | 0.8804                      | 0.6730                      |
| 2.676         | 0.8900                      | 0.7089                      |
| 2.783         | 0.9054                      | 0.7730                      |
| 2.879         | 0.9196                      | 0.8174                      |
| 2.960         | 0.9339                      | 0.8620                      |
| 3.035         | 0.9493                      | 0.9003                      |
| 3.103         | 0.9656                      | 0.9403                      |
| 3.134         | 0.9745                      | 0.9565                      |

Table 11.  $\text{CH}_4\text{-CO}_2\text{-C}_3\text{H}_8$  at 230K and 0.8 MPa

| Pressure<br>(MPa) | $Y_{\text{CH}_4}$ | $Y_{\text{CO}_2}$ | $Y_{\text{C}_3\text{H}_8}$ | $X_{\text{CH}_4}$ | $X_{\text{CO}_2}$ | $X_{\text{C}_3\text{H}_8}$ |
|-------------------|-------------------|-------------------|----------------------------|-------------------|-------------------|----------------------------|
| 0.802             | 0.8717            | 0.0000            | 0.1283                     | 0.0759            | 0.0000            | 0.9241                     |
| 0.799             | 0.7503            | 0.1254            | 0.1243                     | 0.0695            | 0.0316            | 0.8989                     |
| 0.800             | 0.5926            | 0.2873            | 0.1201                     | 0.0544            | 0.0971            | 0.8485                     |
| 0.798             | 0.4476            | 0.4364            | 0.1160                     | 0.0405            | 0.1628            | 0.7967                     |
| 0.800             | 0.3236            | 0.5690            | 0.1074                     | 0.0294            | 0.2433            | 0.7273                     |
| 0.800             | 0.2311            | 0.6640            | 0.1049                     | 0.0207            | 0.3195            | 0.6598                     |
| 0.799             | 0.1767            | 0.7257            | 0.0976                     | 0.0155            | 0.3774            | 0.6071                     |
| 0.800             | 0.1372            | 0.7663            | 0.0965                     | 0.0118            | 0.4238            | 0.5644                     |
| 0.800             | 0.0000            | 0.9224            | 0.0776                     | 0.0000            | 0.6534            | 0.3466                     |

Table 12. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> at 230K and 4.0 MPa

| Pressure<br>(MPa) | Y <sub>CH<sub>4</sub></sub> | Y <sub>CO<sub>2</sub></sub> | Y <sub>C<sub>3</sub>H<sub>8</sub></sub> | X <sub>CH<sub>4</sub></sub> | X <sub>CO<sub>2</sub></sub> | X <sub>C<sub>3</sub>H<sub>8</sub></sub> |
|-------------------|-----------------------------|-----------------------------|---|-----------------------------|-----------------------------|---|
| 4.000             | 0.9558                      | 0.0000                      | 0.0442                                  | 0.4179                      | 0.0000                      | 0.5821                                  |
| 4.000             | 0.9260                      | 0.0317                      | 0.0423                                  | 0.4135                      | 0.0378                      | 0.5487                                  |
| 4.002             | 0.9126                      | 0.0451                      | 0.0423                                  | 0.4044                      | 0.0548                      | 0.5408                                  |
| 4.000             | 0.8935                      | 0.0651                      | 0.0414                                  | 0.3970                      | 0.0823                      | 0.5207                                  |
| 3.995             | 0.8221                      | 0.1417                      | 0.0362                                  | 0.3685                      | 0.2167                      | 0.4148                                  |
| 4.000             | 0.8053                      | 0.1600                      | 0.0347                                  | 0.3617                      | 0.2598                      | 0.3785                                  |
| 4.002             | -                           | -                           | -                                       | 0.3538                      | 0.3057                      | 0.3405                                  |
| 4.002             | 0.7852                      | 0.1828                      | 0.0320                                  | 0.3466                      | 0.3208                      | 0.3327                                  |
| 3.997             | 0.7828                      | 0.1852                      | 0.0320                                  | 0.3451                      | 0.3260                      | 0.3289                                  |
| 3.995             | 0.7772                      | 0.1918                      | 0.0310                                  | 0.3407                      | 0.3461                      | 0.3132                                  |
| 4.002             | 0.7603                      | 0.2116                      | 0.0281                                  | 0.3247                      | 0.4137                      | 0.2616                                  |
| 4.002             | 0.7482                      | 0.2256                      | 0.0262                                  | 0.3040                      | 0.4686                      | 0.2274                                  |
| 3.997             | 0.7335                      | 0.2541                      | 0.0214                                  | 0.2874                      | 0.5525                      | 0.1601                                  |
| 4.002             | 0.7277                      | 0.2519                      | 0.0204                                  | 0.2746                      | 0.5825                      | 0.1429                                  |
| 3.999             | 0.7186                      | 0.2647                      | 0.0167                                  | 0.2439                      | 0.6487                      | 0.1074                                  |
| 4.002             | 0.7123                      | 0.2750                      | 0.0127                                  | 0.2173                      | 0.7120                      | 0.0707                                  |
| 4.003             | 0.7012                      | 0.2988                      | 0.0000                                  | 0.1617                      | 0.8383                      | 0.0000                                  |

Table 13.  $\text{CH}_4\text{-CO}_2\text{-C}_3\text{H}_8$  at 230K and 7.0 MPa

| Pressure<br>(MPa) | $Y_{\text{CH}_4}$ | $Y_{\text{CO}_2}$ | $Y_{\text{C}_3\text{H}_8}$ | $X_{\text{CH}_4}$ | $X_{\text{CO}_2}$ | $X_{\text{C}_3\text{H}_8}$ |
|-------------------|-------------------|-------------------|----------------------------|-------------------|-------------------|----------------------------|
| 7.000             | 0.9415            | 0.0000            | 0.0585                     | 0.7298            | 0.0000            | 0.2702                     |
| 7.000             | 0.9384            | 0.0017            | 0.0599                     | 0.7273            | 0.0021            | 0.2706                     |
| 7.000             | 0.8220            | 0.1278            | 0.0502                     | 0.7002            | 0.1719            | 0.1279                     |
| 7.002             | 0.7975            | 0.1550            | 0.0475                     | 0.6858            | 0.2050            | 0.1092                     |
| 7.000             | 0.7762            | 0.1814            | 0.0424                     | 0.6794            | 0.2366            | 0.0840                     |
| 7.001             | 0.7334            | 0.2433            | 0.0233                     | 0.6369            | 0.3221            | 0.0410                     |
| 6.992             | 0.7220            | 0.2692            | 0.0088                     | 0.5894            | 0.3937            | 0.0169                     |
| 7.000             | 0.7217            | 0.2783            | 0.0000                     | 0.5480            | 0.4520            | 0.0000                     |

Table 14. CH<sub>4</sub>-CO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> at 270K and 2.8 MPa

| Pressure<br>(MPa) | Y <sub>CH<sub>4</sub></sub> | Y <sub>CO<sub>2</sub></sub> | Y <sub>C<sub>3</sub>H<sub>8</sub></sub> | X <sub>CH<sub>4</sub></sub> | X <sub>CO<sub>2</sub></sub> | X <sub>C<sub>3</sub>H<sub>8</sub></sub> |
|-------------------|-----------------------------|-----------------------------|---|-----------------------------|-----------------------------|---|
| 2.798             | 0.7969                      | 0.0000                      | 2.0310                                  | 0.1718                      | 0.0000                      | 0.8282                                  |
| 2.800             | 0.7365                      | 0.0642                      | 0.1993                                  | 0.1569                      | 0.0303                      | 0.8128                                  |
| 2.799             | 0.7138                      | 0.0878                      | 0.1984                                  | 0.1564                      | 0.0424                      | 0.8012                                  |
| 2.801             | 0.7004                      | 0.1027                      | 0.1969                                  | -                           | -                           | -                                       |
| 2.801             | 0.6755                      | 0.1292                      | 0.1953                                  | 0.1466                      | 0.0628                      | 0.7906                                  |
| 2.798             | 0.6515                      | 0.1539                      | 0.1946                                  | 0.1400                      | 0.0760                      | 0.7840                                  |
| 2.799             | 0.6029                      | 0.2066                      | 0.1905                                  | 0.1322                      | 0.1056                      | 0.7622                                  |
| 2.800             | 0.5629                      | 0.2502                      | 0.1869                                  | 0.1239                      | 0.1314                      | 0.7447                                  |
| 2.800             | 0.5154                      | 0.3006                      | 0.1840                                  | 0.1150                      | 0.1629                      | 0.7221                                  |
| 2.798             | 0.4356                      | 0.3878                      | 0.1766                                  | 0.0979                      | 0.2221                      | 0.6800                                  |
| 2.801             | 0.3682                      | 0.4621                      | 0.1697                                  | 0.0829                      | 0.2785                      | 0.6386                                  |
| 2.799             | 0.3265                      | 0.5082                      | 0.1653                                  | 0.0746                      | 0.3196                      | 0.6058                                  |
| 2.799             | 0.2860                      | 0.5536                      | 0.1604                                  | 0.0668                      | 0.3621                      | 0.5711                                  |
| 2.800             | 0.2402                      | 0.6059                      | 0.1539                                  | 0.0563                      | 0.4186                      | 0.5251                                  |
| 2.799             | 0.2084                      | 0.6429                      | 0.1487                                  | 0.0480                      | 0.4495                      | 0.5025                                  |
| 2.799             | 0.1755                      | 0.6816                      | 0.1429                                  | 0.0395                      | 0.4892                      | 0.4713                                  |
| 2.799             | 0.1441                      | 0.7191                      | 0.1368                                  | 0.0318                      | 0.5306                      | 0.4376                                  |
| 2.799             | 0.1008                      | 0.7723                      | 0.1269                                  | 0.0219                      | 0.5989                      | 0.3792                                  |
| 2.798             | 0.0689                      | 0.8134                      | 0.1177                                  | 0.0146                      | 0.6509                      | 0.3345                                  |
| 2.799             | 0.0470                      | 0.8419                      | 0.1111                                  | 0.0099                      | 0.6923                      | 0.2978                                  |
| 2.799             | 0.0000                      | 0.9066                      | 0.0934                                  | 0.0000                      | 0.7716                      | 0.2284                                  |

Table 15.  $\text{CH}_4\text{-CO}_2\text{-C}_3\text{H}_8$  at 270K and 5.5 MPa

| Pressure<br>(MPa) | $Y_{\text{CH}_4}$ | $Y_{\text{CO}_2}$ | $Y_{\text{C}_3\text{H}_8}$ | $X_{\text{CH}_4}$ | $X_{\text{CO}_2}$ | $X_{\text{C}_3\text{H}_8}$ |
|-------------------|-------------------|-------------------|----------------------------|-------------------|-------------------|----------------------------|
| 5.502             | 0.8543            | 0.0000            | 0.1457                     | 0.3601            | 0.0000            | 0.6399                     |
| 5.503             | 0.6494            | 0.2244            | 0.1262                     | 0.2877            | 0.2071            | 0.5052                     |
| 5.501             | 0.6300            | 0.2454            | 0.1256                     | 0.2815            | 0.2313            | 0.4872                     |
| 5.501             | 0.5493            | 0.3378            | 0.1128                     | 0.2477            | 0.3445            | 0.4078                     |
| 5.505             | 0.5074            | 0.3877            | 0.1049                     | 0.2296            | 0.4134            | 0.3570                     |
| 5.499             | 0.4388            | 0.4741            | 0.0871                     | 0.1913            | 0.5440            | 0.2647                     |
| 5.501             | 0.4180            | 0.5000            | 0.0820                     | 0.1803            | 0.5843            | 0.2354                     |
| 5.501             | 0.3689            | 0.5753            | 0.0558                     | 0.1463            | 0.7126            | 0.1411                     |
| 5.499             | 0.3653            | 0.5800            | 0.0547                     | 0.1440            | 0.7227            | 0.1333                     |
| 5.503             | 0.3128            | 0.6872            | 0.0000                     | 0.0948            | 0.9052            | 0.0000                     |

Table 16.  $\text{CH}_4\text{-CO}_2\text{-C}_3\text{H}_8$  at 270K and 8.0 MPa

| Pressure<br>(MPa) | $Y_{\text{CH}_4}$ | $Y_{\text{CO}_2}$ | $Y_{\text{C}_3\text{H}_8}$ | $X_{\text{CH}_4}$ | $X_{\text{CO}_2}$ | $X_{\text{C}_3\text{H}_8}$ |
|-------------------|-------------------|-------------------|----------------------------|-------------------|-------------------|----------------------------|
| 8.000             | 0.8426            | 0.0000            | 0.1574                     | 0.5345            | 0.0000            | 0.4655                     |
| 7.998             | 0.8307            | 0.0120            | 0.1573                     | 0.5297            | 0.0115            | 0.4588                     |
| 7.998             | 0.7832            | 0.0643            | 0.1525                     | -                 | -                 | -                          |
| 8.000             | 0.7561            | 0.0941            | 0.1498                     | 0.5013            | 0.0950            | 0.4037                     |
| 7.997             | 0.6093            | 0.2524            | 0.1383                     | 0.4412            | 0.2739            | 0.2849                     |
| 7.999             | 0.5701            | 0.2983            | 0.1316                     | 0.4245            | 0.3271            | 0.2484                     |
| 8.010             | 0.4224            | 0.5113            | 0.0663                     | -                 | -                 | -                          |
| 7.996             | 0.4004            | 0.5711            | 0.0285                     | 0.2880            | 0.6715            | 0.0405                     |
| 7.997             | 0.4004            | 0.5932            | 0.0064                     | 0.2528            | 0.7377            | 0.0095                     |
| 8.003             | 0.3974            | 0.6026            | 0.0000                     | 0.2490            | 0.7510            | 0.0000                     |

## APPENDIX C: HENRY'S CONSTANTS

This appendix contains a description of the procedure and the results of the calculated Henry's constants used in mutual consistency test for the VLE data. The Krichevsky-Kasarnovsky equation as described by Prausnitz et al. (1986) was used to calculate the Henry's constant without the simplifying assumption that the constant is not a function of pressure. The dependence of the Henry's constant on pressure is given by equation (3), where  $\bar{v}_i$  is the partial

$$\left( \frac{\partial \ln f_i^L}{\partial P} \right)_{T,x} = \frac{\bar{v}_i}{RT} \quad (3)$$

molar volume of  $i$  in the liquid phase. The thermodynamic definition of Henry's constant is given in equation (4).

$$H_{i,\text{solvent}} \equiv \lim_{x_i \rightarrow 0} \frac{f_i^L}{x_i} \quad (\text{at constant temperature}) \quad (4)$$

substitution of equation (4) into equation (3) gives

$$\left( \frac{\partial \ln H_{i,\text{solvent}}}{\partial P} \right)_T = \frac{\bar{v}_i^\infty}{RT} \quad (5)$$

where  $\overline{v}_i^\infty$  is the partial molar volume of solute  $i$  in the liquid phase at infinite dilution. Integrating equation (5) and assuming the fugacity of  $i$  at constant temperature and pressure is proportional to  $x_i$  gives equation (6), where

$$\ln \frac{f_i}{x_i} = \ln H_{i,\text{solvent}}^{(P^r)} + \frac{\int_{P^r}^P \overline{v}_i^\infty dP}{RT} \quad (6)$$

$H_{i,\text{solvent}}^{(P^r)}$  is the Henry's constant evaluated at an arbitrary reference pressure  $P^r$ . As  $x_i \rightarrow 0$  the total pressure is the vapor pressure of the solvent,  $P_1^s$ . It is convenient to use this as the reference pressure.

Assuming that  $\overline{v}_i^\infty$  is independent of pressure letting subscript 1 refer to the solvent and subscript 2 refer to the solute equation (6) becomes:

$$\ln \frac{f_2}{x_2} = \ln H_{2,1}^{(P^r)} + \frac{\overline{v}_2^\infty (P - P_1^s)}{RT} \quad (7)$$

Equation (7) is the Krichevsky-Kasarnovsky equation.

A program written by Dr. A. J. Kidnay was used to calculate Henry's constants using equation (7). In this

program the SRK equation with the interaction coefficient set to zero was used to calculate the fugacities. The calculated value of  $Y_1$  was used to determine the vapor phase fugacities; the experimental  $X_1$  value was used. Newton-Raphson method was used for the volume. The following critical constants were used:

| Component                     | Critical<br>Temp (K) | Critical<br>Press (Bar) | Acentric<br>Factor |
|-------------------------------|----------------------|-------------------------|--------------------|
| CH <sub>4</sub>               | 190.555              | 45.950                  | 0.008              |
| C <sub>3</sub> H <sub>8</sub> | 369.85               | 42.475                  | 0.153              |
| CO <sub>2</sub>               | 304.21               | 73.825                  | 0.220              |

The basis for the mutual consistency test was to generate a relative comparison of the data not to find the true Henry's constants. Table 17 lists the Henry's constants obtained by this approach.

Table 17. Henry's Constants

| $\text{CH}_4\text{-C}_3\text{H}_8$ |                    |                           |
|------------------------------------|--------------------|---------------------------|
| Data Set                           | Temperature<br>(K) | Henry's Constant<br>(Bar) |
| This Study                         | 230                | 89.7                      |
|                                    | 270                | 125.4                     |
| Akers et al. 1954                  | 273.15             | 159.3                     |
|                                    | 256.48             | 117.7                     |
|                                    | 241.48             | 100.1                     |
|                                    | 226.48             | 99.5                      |
| Wichterle and Kobayashi 1972       | 213.71             | 69.5                      |
|                                    | 195.2              | 51.7                      |
|                                    | 192.3              | 47.3                      |
|                                    | 172.04             | 30.3                      |
| Reamer et al. 1950                 | 277.59             | 142.1                     |
|                                    | 310.9              | 141.9                     |
|                                    | 327.59             | 127.7                     |
|                                    | 344.26             | 137.9                     |
|                                    | 294.3              | 153.1                     |
| Price and Kobayashi 1959           | 283.15             | 168.7                     |
|                                    | 255.37             | 114.7                     |
| $\text{CO}_2\text{-C}_3\text{H}_8$ |                    |                           |
| This Study                         | 230                | 45.6                      |
|                                    | 270                | 55.8                      |
| Nagahma et al. 1974                | 273.45             | 71.9                      |
|                                    | 252.95             | 37.5                      |

Table 17. Henry's Constants (continued)

|                    |        |      |
|--------------------|--------|------|
| Reamer et al. 1951 | 277.6  | 63.5 |
|                    | 294.26 | 47.2 |
|                    | 310.93 | 79.5 |
|                    | 327.6  | 88.3 |
|                    | 344.26 | 75.7 |
| Hamam and Lu 1976  | 266.5  | 58.1 |
|                    | 244.3  | 34   |

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## APPENDIX D: EQUIPMENT SUPPLIERS

|   |   |
|---|---|
| High Temperature Pump                                 | Precision Services-<br>Raymond J. Martin<br>5430 Patterson Rd.<br>Manvel, Texas 77578<br>Ph (713)527-8101 ext 3507<br>Fax (713)285-5478 |
| Copper Tubing-Refrigeration Grade                     | Myers Hardware<br>1103 Arapahoe<br>Golden, CO<br>Ph (303)279-3393   |
| Swagelok fittings, Whitey valves,<br>and Nupro valves | Denver Valve & Fitting Co<br>950 Simms St.<br>Lakewood, CO 80215<br>Ph(303)892-7003   |
| Ethylene Glycol-Technical Grade                       | Industrial Chemicals<br>4711 W. 58th Ave.<br>Arvada, CO<br>Ph(303)427-2727  |
| Gas Chromatograph Column                              | Alltech<br>2051 Waukegan Rd.<br>Deerfield, IL 60015-1899<br>Ph(708)948-8600   |
| Vacuum Hose   | Central States Hose<br>5199 East 48th Ave.<br>Ph(303)321-2661   |

|   |  |
|---|--|
| Standard Resistor Calibration                         | Leeds & Northrup Company<br>Sumney Town Pike<br>North Wales, PA 19454<br>Ph 1-800-533-3726       |
| Meriam Manometer 30"                                  | The Meter and Valve Co.<br>8100 South Park Way #A-3<br>Littleton, CO 80120                       |
| Solid Teflon Single Turn<br>Backup Ring (size 139)    | Aspen Seal and Packing<br>1880 W. Hamilton Pl.<br>Englewood, CO<br>Ph(303)761-9049               |
| SS rods, bolts, and nuts                              | A&I Bolt and Nut, Inc.<br>209 Kalamanth St.<br>Denver, CO 80223<br>Ph(303)893-5555               |
| 225 Watt tubular heaters with<br>single end terminals | Omega Engineering Inc.<br>One Omega Drive Box 4047<br>Stamford, CT 06907-0047<br>Ph(203)359-1660 |