# Vapor + Liquid Equilibria for the Ternary System Methane + Ethane + Carbon Dioxide at 230 K and Its Constituent Binaries at Temperatures from 207 to 270 K

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Vapor–liquid equilibrium data for the binary system methane + carbon dioxide were measured at 230, 250, and 270 K. The ethane + carbon dioxide system was studied at 207, 210, 213, 230, 250, and 270 K, and the methane + ethane system was studied at 210, 230, 250, and 270 K. Ternary vapor–liquid equilibria for the methane + ethane + carbon dioxide system were measured at 230 K over the pressure range from 1.15 to 6.59 MPa. The Peng–Robinson equation of state was used to model the systems, and binary interaction coefficients are reported.

## Introduction

In addition to their academic interest, systems of carbon dioxide in multicomponent mixtures with light paraffins are important to the natural gas industry, since it has become common practice in recent years to process gas streams with moderate to high carbon dioxide levels. There are, however, surprisingly little data available on the phase behavior of carbon dioxide in multicomponent systems, and the main purpose of this study is to provide a package of reliable data for equation of state modeling.

Since all equations of state used for phase equilibrium predictions require at least one binary interaction parameter obtained from experimental data, the necessity for measuring binary vapor–liquid equilibrium (VLE) is obvious. The need for ternary data, however, is not quite so apparent, and thus it is worthwhile to discuss the place of ternary measurements in thermodynamic modeling. Van Ness and Abbott (1982) given an excellent and succinct statement of the situation: "All predictive methods presume the availability of a large and accurate VLE data base for binary systems; the emphasis put on binary systems is therefore not misplaced. However, such data are insufficient. Predictions must approximate reality; accurate data are required against which to compare the results of prediction. Ternary mixtures are by far the easiest to treat experimentally, and clearly represent the most appropriate testing ground for predictive models."

Prausnitz (1985) makes much the same point when he says "At present, our experience is limited to binary mixtures. We do not as yet know how successful these calculations will be for ternary and higher mixtures. Extension of the mixing rules to ternaries (and higher) is straight forward but the crucial question is: will binary parameters, obtained from binary data, be sufficient to predict multicomponent equilibria?".

## Review of Previous Work

The literature through 1976 for the binary systems was summarized by Davalos et al. (1976), and Hiza et al. (1979) reviewed and evaluated all previous studies on methane + ethane. The only additional references are Mraw et al. (1978) on methane + carbon dioxide and Brown et al. (1988) on ethane + carbon dioxide. The study of Davalos et al. (1976) is the only available work on the ternary system.

## Equipment

The vapor-circulation apparatus used in this study was a modified version of that first used by Somait (1976), and a complete description of the equipment is given in this reference.

The temperature was measured to 0.02 K using a calibrated (IPTS-68) platinum resistance thermometer coupled with a Mueller bridge and a null detector. Pressures were measured with a series of bourdon tube gauges (0–7, 0–35, 0–100, 0–170 MPa) calibrated against dead weight testers. All gauges had accuracies of 0.1% of the full scale reading.

Liquid and vapor samples were analyzed in a gas chromatograph equipped with a thermal conductivity detector. Two or three analyses were made on each sample, and an electronic integrator was used to measure the peak areas of the components. These areas were then related to composition through the calibration curves which were established by measuring the areas of the pure gases as well as six ternary samples gravimetrically prepared in this laboratory. All three of the components exhibited linear relationships between the partial pressure and the peak area. The calibrations were checked periodically during the course of the measurements to eliminate the possibility of electronic drift in the instrumentation. The mole fractions, as a result of all instrumental and calibration uncertainties, are believed to be accurate to 0.002, but the results are reported to four significant figures since the

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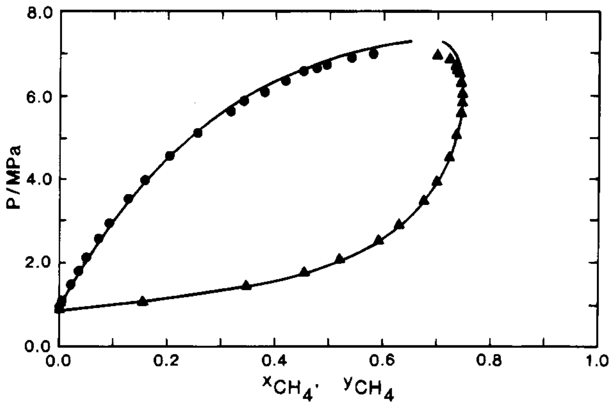

**Figure 1.** Vapor−liquid equilibria for methane + carbon dioxide at 230.00 K: ●, liquid; ▲, vapor; —, Peng−Robinson equation.

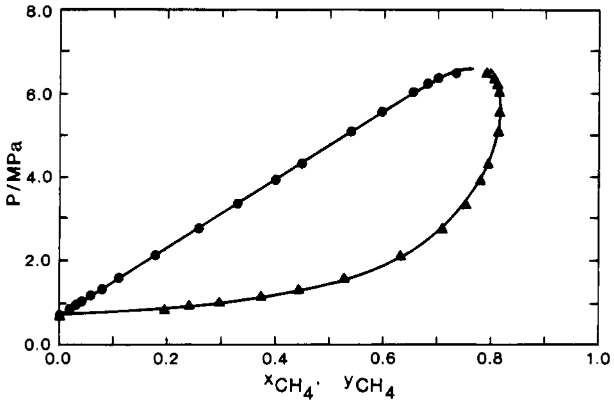

**Figure 2.** Vapor−liquid equilibra for methane + ethane at 230.00 K: ●, liquid; ▼, vapor; —, Peng−Robinson equation.

precision of the chromatograph is considerably greater than the accuracy. All of the experimental mole fractions have been normalized. Random errors due primarily to gas or liquid sampling cause some of the data points to exhibit more scatter than is attributable to the temperature, pressure, or composition calibrations.

The accuracy of temperature and pressure measurements was checked regularly during the course of the experiments by measuring the vapor pressures of carbon dioxide and ethane and comparing with the accepted literature values of Angus et al. (1976) and Goodwin et al. (1976). The maximum deviation of these measurements from Angus and Goodwin was 0.2%. The performance of the apparatus was also checked by making measurements on the carbon dioxide + ethane, the methane + ethane, and the ternary system at 250 K and comparing with the data of Davalos (1976). The agreement between the data sets is excellent.

The gases used in this study were purchased commercially and were used without further purification. The minimum purities were (methane) 99.97%, (carbon dioxide) 99.99%, and (ethane) 99%. All gases were determined to be chromatographically pure; that is, no extraneous peaks were observed.

## Results and Discussion

Binary vapor−liquid equilibria were measured for the systems methane + carbon dioxide at 230, 250, and 270 K, carbon dioxide + ethane at 207, 210, 213, 230, 250, and 270 K and for methane + ethane at 210, 230, 250, and 270 K. The ternary system was studied extensively at 230 K over the pressure range 1.15−6.59 MPa. All of the experimental data are reported in Tables 1 and 2.

In recent years numerous equations of state and mixing rules have been proposed for phase equilibrium calculations, but from an industrial perspective only a few are of any importance. The most generally accepted relations are simple cubic expressions that are modifications of the van der Waals equation, generally used with the original van der Waals mixing rules with the introduction of a single binary interaction parameter, $k_{ij}$. In gas processing the equation proposed by Peng and Robinson (1976) is widely used, and this is the relation selected in this study. Their equation is

$$P = RT/(v - b) - a(T)/[v(v + b) + b(v - b)] \quad (1)$$

The constants $a$ and $b$ are obtained from the relations

$$a(T) = a(T_c)\alpha(T_R,\omega) \quad (2)$$

$$b = b(T_c) \quad (3)$$

where

$$a(T_c) = 0.45724(R^2T_c^{\,2}/P_c) \quad (4)$$

$$b(T_c) = 0.07780(RT_c/P_c) \quad (5)$$

and

$$\alpha^{1/2} = 1 + \kappa(1 - T_R^{\,1/2}) \quad (6)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (7)$$

The mixing rules are

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (8)$$

$$b = \sum_i x_i b_i \quad (9)$$

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

In the above equations, $T_c$ and $P_c$ are the critical temperature and pressure, the subscript R indicates a reduced property, $\omega$ is the acentric factor, and $k_{ij}$ is the binary interaction coefficient. The original paper should be consulted for details of the equation and its application to phase equilibrium calculations.

The interaction coefficients for the measurements reported here were obtained by selecting the $k_{ij}$ which minimized the absolute differences between calculated and experimental vapor and liquid mole fractions for the binary isotherms. The values obtained using this method differ insignificantly from those obtained using the maximum likelihood technique. The critical constants (Angus et al., 1976, 1979; Goodwin et al., 1976) and acentric factors used in all calculations are shown in Table 3. The binary interaction coefficients are summarized in Table 4.

Figure 1 shows the methane + carbon dioxide system at 230 K, including calculations with the Peng−Robinson equation of state. The equation matches the experimental results very well at lower pressures but deviates substantially near the critical region. It is a common feature of simple cubic equations such as Peng−Robinson equation to inaccurately represent critical behavior.

The methane + ethane system was studied at 210, 230, 250, and 270 K. The 250 K isotherm was measured to compare with the earlier work of Davalos (1976). Figure 2 shows the excellent agreement found between calculations and experiment to near the critical point. The

**Table 1. Vapor–Liquid Equilibria for the Systems Methane (1) + Ethane (2), Methane (1) + Carbon Dioxide (3), and Ethane (2) + Carbon Dioxide (3) at Temperature *T* and Pressure *P* Where *x* and *y* are the Mole Fractions of Liquid and Vapor, Respectively**

| *P*/MPa | $x_1$ | $y_1$ | *P*/MPa | $x_1$ | $y_1$ | *P*/MPa | $x_1$ | $y_1$ | *P*/MPa | $x_1$ | $y_1$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_4$ (1) + $C_2H_6$ (2) | | | | | | | | | | | |
| *T* = 210.00 K | | | | | | | | | | | |
| 0.334 | 0.0000 | 0.0000 | 2.055 | 0.2947 | 0.8244 | 4.656 | 0.7137 | 0.9134 | 5.378 | 0.8218 | 0.9179 |
| 0.966 | 0.1100 | 0.6411 | 2.651 | 0.3938 | 0.8574 | 4.841 | 0.7477 | 0.9162 | 5.582 | 0.8552 | 0.9151 |
| 1.091 | 0.1304 | 0.6807 | 3.826 | 0.5885 | 0.8990 | 5.182 | 0.7944 | 0.9170 | | | |
| 1.610 | 0.2263 | 0.7782 | 4.382 | 0.6700 | 0.9101 | 5.330 | 0.8149 | 0.9177 | | | |
| *T* = 230.00 K | | | | | | | | | | | |
| 0.701 | 0.0000 | 0.0000 | 1.320 | 0.0787 | 0.4445 | 3.916 | 0.4002 | 0.7806 | 6.222 | 0.6813 | 0.8113 |
| 0.845 | 0.0186 | 0.1957 | 1.580 | 0.1110 | 0.5276 | 4.309 | 0.4480 | 0.7948 | 6.361 | 0.7017 | 0.8056 |
| 0.938 | 0.0315 | 0.2420 | 2.118 | 0.1785 | 0.6319 | 5.093 | 0.5392 | 0.8133 | 6.487 | 0.7341 | 0.7915 |
| 1.027 | 0.0417 | 0.2968 | 2.756 | 0.2573 | 0.7100 | 5.558 | 0.5962 | 0.8163 | | | |
| 1.158 | 0.0585 | 0.3737 | 3.339 | 0.3294 | 0.7538 | 6.033 | 0.6543 | 0.8146 | | | |
| *T* = 250.00 K | | | | | | | | | | | |
| 1.302 | 0.0000 | 0.0000 | 1.881 | 0.0561 | 0.2734 | 4.083 | 0.2733 | 0.6125 | 5.951 | 0.4638 | 0.6795 |
| 1.563 | 0.0247 | 0.1489 | 2.849 | 0.1497 | 0.4911 | 4.898 | 0.3521 | 0.6550 | | | |
| *T* = 270.00 K | | | | | | | | | | | |
| 2.210 | 0.0000 | 0.0000 | 2.819 | 0.0498 | 0.1728 | 4.882 | 0.2256 | 0.4430 | 6.282 | 0.3684 | 0.4869 |
| 2.307 | 0.0080 | 0.0347 | 3.030 | 0.0682 | 0.2211 | 5.463 | 0.2763 | 0.4722 | 6.340 | 0.3751 | 0.4855 |
| 2.486 | 0.0235 | 0.0926 | 3.440 | 0.1031 | 0.2852 | 5.809 | 0.3088 | 0.4831 | 6.474 | 0.3922 | 0.4811 |
| 2.606 | 0.0330 | 0.1247 | 3.916 | 0.1443 | 0.3591 | 6.139 | 0.3516 | 0.4874 | | | |
| $CH_4$ (1) + $CO_2$ (3) | | | | | | | | | | | |
| *T* = 230.00 K | | | | | | | | | | | |
| 0.892 | 0.0000 | 0.0000 | 2.551 | 0.0730 | 0.5929 | 5.116 | 0.2560 | 0.7368 | 6.586 | 0.4523 | 0.7411 |
| 1.078 | 0.0070 | 0.1553 | 2.916 | 0.0920 | 0.6320 | 5.640 | 0.3171 | 0.7449 | 6.663 | 0.4762 | 0.7369 |
| 1.453 | 0.0221 | 0.3480 | 3.503 | 0.1269 | 0.6770 | 5.885 | 0.3416 | 0.7466 | 6.736 | 0.4952 | 0.7338 |
| 1.786 | 0.0365 | 0.4550 | 3.968 | 0.1577 | 0.7005 | 6.086 | 0.3805 | 0.7461 | 6.901 | 0.5407 | 0.7247 |
| 2.092 | 0.0503 | 0.5218 | 4.565 | 0.2042 | 0.7237 | 6.353 | 0.4187 | 0.7448 | 6.991 | 0.5814 | 0.7004 |
| *T* = 250.00 K | | | | | | | | | | | |
| 1.783 | 0.0000 | 0.0000 | 2.759 | 0.0379 | 0.3001 | 4.200 | 0.1041 | 0.4855 | 7.399 | 0.3366 | 0.5856 |
| 1.967 | 0.0065 | 0.0782 | 2.964 | 0.0465 | 0.3381 | 4.792 | 0.1368 | 0.5262 | 7.684 | 0.3718 | 0.5761 |
| 2.071 | 0.0106 | 0.1174 | 3.131 | 0.0536 | 0.3655 | 5.378 | 0.1715 | 0.5559 | 7.983 | 0.4163 | 0.5523 |
| 2.315 | 0.0201 | 0.1952 | 3.446 | 0.0676 | 0.4090 | 6.150 | 0.2246 | 0.5812 | 8.053 | 0.4252 | 0.5408 |
| 2.488 | 0.0269 | 0.2408 | 3.836 | 0.0863 | 0.4533 | 6.715 | 0.2711 | 0.5914 | | | |
| *T* = 270.00 K | | | | | | | | | | | |
| 3.209 | 0.0000 | 0.0000 | 4.146 | 0.0377 | 0.1778 | 7.093 | 0.1834 | 0.3942 | 8.381 | 0.2995 | 0.3782 |
| 3.558 | 0.0151 | 0.0766 | 4.506 | 0.0504 | 0.2203 | 7.868 | 0.2407 | 0.4061 | | | |
| 3.673 | 0.0198 | 0.1047 | 4.915 | 0.0724 | 0.2661 | 8.197 | 0.2696 | 0.3952 | | | |
| 3.883 | 0.0305 | 0.1461 | 5.851 | 0.1154 | 0.3372 | 8.282 | 0.2803 | 0.3887 | | | |

| *P*/MPa | $x_3$ | $y_3$ | *P*/MPa | $x_3$ | $y_3$ | *P*/MPa | $x_3$ | $y_3$ | *P*/MPa | $x_3$ | $y_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_6$ (2) + $CO_2$ (3) | | | | | | | | | | | |
| *T* = 207.00 K | | | | | | | | | | | |
| 0.292 | 0.0000 | 0.0000 | 0.444 | 0.2285 | 0.4292 | 0.461 | 0.3028 | 0.4759 | 0.471[a] | 0.3738 | 0.5104 |
| 0.372 | 0.0778 | 0.2624 | 0.456 | 0.2744 | 0.4592 | 0.462 | 0.3111 | 0.4786 | | | |
| 0.419 | 0.1638 | 0.3714 | 0.459 | 0.2923 | 0.4699 | 0.465 | 0.3364 | 0.4937 | | | |
| *T* = 210.00 K | | | | | | | | | | | |
| 0.335 | 0.0000 | 0.0000 | 0.522 | 0.2961 | 0.4737 | 0.547 | 0.5572 | 0.5698 | 0.540 | 0.6963 | 0.6172 |
| 0.380 | 0.0358 | 0.1322 | 0.537 | 0.3842 | 0.5129 | 0.546 | 0.6150 | 0.5924 | 0.538[a] | 0.7093 | 0.6213 |
| 0.426 | 0.0877 | 0.2571 | 0.539 | 0.4093 | 0.5203 | 0.545 | 0.6566 | 0.6053 | | | |
| 0.454 | 0.1254 | 0.3194 | 0.541 | 0.4316 | 0.5288 | 0.543 | 0.6651 | 0.6097 | | | |
| 0.498 | 0.2153 | 0.4185 | 0.545 | 0.4965 | 0.5506 | 0.541 | 0.6844 | 0.6149 | | | |
| *T* = 213.00 K | | | | | | | | | | | |
| 0.376 | 0.0000 | 0.0000 | 0.532 | 0.1706 | 0.3725 | 0.616 | 0.5557 | 0.5800 | 0.594 | 0.7601 | 0.6588 |
| 0.432 | 0.0442 | 0.1458 | 0.583 | 0.3075 | 0.4770 | 0.613 | 0.6089 | 0.5911 | 0.576 | 0.8317 | 0.7055 |
| 0.471 | 0.0837 | 0.2401 | 0.607 | 0.4282 | 0.5302 | 0.610 | 0.6503 | 0.6022 | 0.564[a] | 0.8678 | 0.7327 |
| 0.508 | 0.1306 | 0.3185 | 0.613 | 0.4789 | 0.5531 | 0.604 | 0.6982 | 0.6319 | | | |
| *T* = 230.00 K | | | | | | | | | | | |
| 0.701 | 0.0000 | 0.0000 | 0.883 | 0.1035 | 0.2452 | 1.112 | 0.4092 | 0.5227 | 1.100 | 0.8438 | 0.7403 |
| 0.727 | 0.0096 | 0.0345 | 0.921 | 0.1280 | 0.2820 | 1.122 | 0.4422 | 0.5402 | 1.023 | 0.9326 | 0.8389 |
| 0.799 | 0.0485 | 0.1513 | 0.948 | 0.1548 | 0.3225 | 1.138 | 0.5195 | 0.5750 | 0.936 | 0.9828 | 0.9451 |
| 0.841 | 0.0745 | 0.1982 | 1.080 | 0.3300 | 0.4782 | 1.145 | 0.6844 | 0.6484 | 0.891 | 1.0000 | 1.0000 |
| *T* = 250.00 K | | | | | | | | | | | |
| 1.303 | 0.0000 | 0.0000 | 1.649 | 0.1280 | 0.2576 | 2.100 | 0.5170 | 0.5807 | 2.082 | 0.8279 | 0.7685 |
| 1.348 | 0.0113 | 0.0322 | 1.750 | 0.1783 | 0.3216 | 2.116 | 0.5525 | 0.6001 | 1.991 | 0.9048 | 0.8497 |
| 1.418 | 0.0337 | 0.0869 | 1.837 | 0.2326 | 0.4280 | 2.120 | 0.5720 | 0.6107 | 1.905 | 0.9589 | 0.9170 |
| 1.482 | 0.0571 | 0.1442 | 2.022 | 0.3884 | 0.5023 | 2.128 | 0.6046 | 0.6287 | 1.821 | 0.9891 | 0.9790 |
| 1.576 | 0.0974 | 0.2109 | 2.081 | 0.4754 | 0.5561 | 2.134 | 0.6601 | 0.6589 | 1.787 | 1.0000 | 1.0000 |
| *T* = 270.00 K | | | | | | | | | | | |
| 2.208 | 0.0000 | 0.0000 | 2.797 | 0.1568 | 0.2689 | 3.567 | 0.8418 | 0.8095 | 3.344 | 0.9642 | 0.9337 |
| 2.543 | 0.0801 | 0.1633 | 3.151 | 0.2907 | 0.4116 | | | | | | |

[a] Solidification of $CO_2$ occurs.

**Table 2. Vapor–Liquid Equilibria for the System $CH_4$ (1) + $C_2H_6$ (2) + $CO_2$ (3) at Temperature $T$ and Pressure $P$, Where $x$ and $y$ are the Mole Fractions of Liquid and Vapor, Respectively**

| $x_1$ | $x_3$ | $x_2$ | $y_1$ | $y_3$ | $y_2$ | $x_1$ | $x_3$ | $x_2$ | $y_1$ | $y_3$ | $y_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$ = 230.00 K, $P$ = 1.15 MPa | | | | | | | | | | | |
| 0.0571[a] | | 0.9429 | 0.3679 | | 0.6321 | 0.0017 | 0.5114 | 0.4869 | 0.0127 | 0.5678 | 0.4195 |
| 0.0427 | 0.0582 | 0.8991 | 0.2744 | 0.1221 | 0.6035 | 0.0005 | 0.6860 | 0.3135 | 0.0052 | 0.6473 | 0.3475 |
| 0.0345 | 0.1015 | 0.8640 | 0.2189 | 0.1975 | 0.5836 | 0.0014 | 0.7521 | 0.2465 | 0.0151 | 0.6743 | 0.3105 |
| 0.0249 | 0.1618 | 0.8133 | 0.1608 | 0.2847 | 0.5544 | 0.0025 | 0.8093 | 0.1882 | 0.0323 | 0.6956 | 0.2721 |
| 0.0155 | 0.2398 | 0.7447 | 0.1004 | 0.3770 | 0.5226 | 0.0039 | 0.8605 | 0.1356 | 0.0510 | 0.7232 | 0.2258 |
| 0.0093 | 0.3167 | 0.6740 | 0.0633 | 0.4457 | 0.4909 | 0.0066 | 0.9403 | 0.0531 | 0.0957 | 0.7867 | 0.1177 |
| 0.0040 | 0.4222 | 0.5738 | 0.0275 | 0.5194 | 0.4531 | 0.0209[a] | 0.9791 | | 0.1941 | 0.8059 | |
| $T$ = 230.00 K, $P$ = 1.52 MPa | | | | | | | | | | | |
| 0.1045[a] | | 0.8955 | 0.5113 | | 0.4887 | 0.0476 | 0.3825 | 0.5698 | 0.2479 | 0.3934 | 0.3587 |
| 0.0897 | 0.0588 | 0.8515 | 0.4373 | 0.0932 | 0.4665 | 0.0444 | 0.4356 | 0.5200 | 0.2380 | 0.4212 | 0.3408 |
| 0.0824 | 0.0958 | 0.8218 | 0.3997 | 0.1474 | 0.4528 | 0.0398 | 0.5130 | 0.4472 | 0.2270 | 0.4558 | 0.3171 |
| 0.0759 | 0.1323 | 0.7917 | 0.3688 | 0.1922 | 0.4389 | 0.0356 | 0.6001 | 0.3643 | 0.2199 | 0.4912 | 0.2889 |
| 0.0693 | 0.1747 | 0.7561 | 0.3375 | 0.2381 | 0.4245 | 0.0332 | 0.6478 | 0.3190 | 0.2204 | 0.5078 | 0.2718 |
| 0.0614 | 0.2380 | 0.7005 | 0.3001 | 0.2974 | 0.4025 | 0.0281 | 0.7675 | 0.2044 | 0.2225 | 0.5546 | 0.2229 |
| 0.0542 | 0.3041 | 0.6417 | 0.2707 | 0.3455 | 0.3837 | 0.0249 | 0.8650 | 0.1101 | 0.2499 | 0.5963 | 0.1538 |
| 0.0538 | 0.3117 | 0.6345 | 0.2715 | 0.3479 | 0.3806 | 0.0229 | 0.9217 | 0.0555 | 0.2999 | 0.6026 | 0.0975 |
| 0.0504 | 0.3543 | 0.5953 | 0.2581 | 0.3742 | 0.3677 | 0.0282[a] | 0.9718 | | 0.3766 | 0.6234 | |
| $T$ = 230.00 K, $P$ = 2.53 MPa | | | | | | | | | | | |
| 0.2324[a] | | 0.7676 | 0.6831 | | 0.3169 | 0.1448 | 0.4997 | 0.3555 | 0.5097 | 0.3030 | 0.1866 |
| 0.2168 | 0.0615 | 0.7217 | 0.6384 | 0.0666 | 0.2951 | 0.1263 | 0.6145 | 0.2592 | 0.5079 | 0.3353 | 0.1568 |
| 0.1996 | 0.1461 | 0.6542 | 0.5890 | 0.1366 | 0.2744 | 0.1167 | 0.6678 | 0.2155 | 0.5100 | 0.3483 | 0.1416 |
| 0.1931 | 0.1801 | 0.6269 | 0.5725 | 0.1639 | 0.2635 | 0.0878 | 0.8346 | 0.0775 | 0.5393 | 0.3866 | 0.0741 |
| 0.1781 | 0.2738 | 0.5481 | 0.5398 | 0.2183 | 0.2418 | 0.0737 | 0.9171 | 0.0092 | 0.5785 | 0.4097 | 0.0118 |
| 0.1662 | 0.3556 | 0.4781 | 0.5232 | 0.2555 | 0.2212 | 0.0719[a] | 0.9281 | | 0.5851 | 0.4149 | |
| 0.1551 | 0.4248 | 0.4201 | 0.5129 | 0.2816 | 0.2055 | | | | | | |
| $T$ = 230.00 K, $P$ = 3.55 MPa | | | | | | | | | | | |
| 0.3574[a] | | 0.6426 | 0.7637 | | 0.2363 | 0.2687 | 0.3867 | 0.3445 | 0.6310 | 0.2207 | 0.1484 |
| 0.3466 | 0.0451 | 0.6083 | 0.7343 | 0.0410 | 0.2247 | 0.2545 | 0.4446 | 0.3009 | 0.6155 | 0.2445 | 0.1400 |
| 0.3396 | 0.0650 | 0.5954 | 0.7221 | 0.0567 | 0.2211 | 0.2381 | 0.5173 | 0.2447 | 0.6254 | 0.2562 | 0.1184 |
| 0.3247 | 0.1277 | 0.5476 | 0.6923 | 0.1010 | 0.2068 | 0.2211 | 0.5795 | 0.1994 | 0.6243 | 0.2708 | 0.1048 |
| 0.3165 | 0.1681 | 0.5153 | 0.6773 | 0.1257 | 0.1970 | 0.1968 | 0.6577 | 0.1455 | 0.6306 | 0.2845 | 0.0849 |
| 0.3091 | 0.2046 | 0.4863 | 0.6660 | 0.1456 | 0.1884 | 0.1642 | 0.7640 | 0.0718 | 0.6475 | 0.3020 | 0.0505 |
| 0.3002 | 0.2438 | 0.4560 | 0.6553 | 0.1650 | 0.1797 | 0.1505 | 0.8059 | 0.0437 | 0.6553 | 0.3108 | 0.0339 |
| 0.2914 | 0.2855 | 0.4231 | 0.6457 | 0.1838 | 0.1705 | 0.1302[a] | 0.8698 | | 0.6792 | 0.3208 | |
| 0.2794 | 0.3520 | 0.3686 | 0.6374 | 0.2082 | 0.1545 | | | | | | |
| $T$ = 230.00 K, $P$ = 4.56 MPa | | | | | | | | | | | |
| 0.4790[a] | | 0.5210 | 0.8003 | | 0.1997 | 0.3532 | 0.4391 | 0.2077 | 0.6865 | 0.2184 | 0.0950 |
| 0.4660 | 0.0475 | 0.4865 | 0.7743 | 0.0373 | 0.1884 | 0.3327 | 0.4950 | 0.1723 | 0.6865 | 0.2307 | 0.0828 |
| 0.4498 | 0.1104 | 0.4398 | 0.7462 | 0.0806 | 0.1732 | 0.3121 | 0.5484 | 0.1396 | 0.6867 | 0.2425 | 0.0708 |
| 0.4278 | 0.1924 | 0.3798 | 0.7199 | 0.1273 | 0.1528 | 0.2434 | 0.7081 | 0.0486 | 0.6949 | 0.2745 | 0.0306 |
| 0.4009 | 0.2904 | 0.3087 | 0.6992 | 0.1715 | 0.1292 | 0.2214 | 0.7566 | 0.0220 | 0.7110 | 0.2743 | 0.0147 |
| 0.3801 | 0.3684 | 0.2515 | 0.6889 | 0.1985 | 0.1126 | 0.2037[a] | 0.7963 | | 0.7200 | 0.2800 | |
| $T$ = 230.00 K, $P$ = 5.57 MPa | | | | | | | | | | | |
| 0.5994[a] | | 0.4006 | 0.8158 | | 0.1842 | 0.4408 | 0.4443 | 0.1149 | 0.7175 | 0.2232 | 0.0593 |
| 0.5812 | 0.0617 | 0.3571 | 0.7849 | 0.0459 | 0.1692 | 0.3510 | 0.6143 | 0.0347 | 0.7304 | 0.2496 | 0.0200 |
| 0.5579 | 0.1315 | 0.3106 | 0.7554 | 0.0948 | 0.1498 | 0.3254 | 0.6602 | 0.0144 | 0.7347 | 0.2567 | 0.0086 |
| 0.5028 | 0.2986 | 0.1986 | 0.7193 | 0.1816 | 0.0991 | 0.3018[a] | 0.6982 | | 0.7393 | 0.2607 | |
| 0.4831 | 0.3489 | 0.1680 | 0.7168 | 0.1984 | 0.0848 | | | | | | |
| $T$ = 230.00 K, $P$ = 6.49 MPa | | | | | | | | | | | |
| 0.7231[a] | | 0.2769 | 0.8037 | | 0.1963 | 0.6372 | 0.2204 | 0.1424 | 0.7013 | 0.1911 | 0.1076 |
| 0.7178 | 0.0291 | 0.2531 | 0.7854 | 0.0262 | 0.1885 | 0.6154 | 0.2673 | 0.1173 | 0.6882 | 0.2251 | 0.0867 |
| 0.7017 | 0.0672 | 0.2311 | 0.7688 | 0.0597 | 0.1715 | 0.5828 | 0.3254 | 0.0918 | 0.6918 | 0.2443 | 0.0639 |
| 0.6824 | 0.1171 | 0.2005 | 0.7441 | 0.0988 | 0.1571 | 0.5316 | 0.4128 | 0.0556 | 0.7117 | 0.2556 | 0.0327 |
| 0.6678 | 0.1493 | 0.1829 | 0.7302 | 0.1277 | 0.1421 | 0.4808 | 0.4984 | 0.0208 | 0.7253 | 0.2607 | 0.0141 |
| 0.6481 | 0.1987 | 0.1531 | 0.7107 | 0.1722 | 0.1171 | 0.4362[a] | 0.5638 | | 0.7381 | 0.2619 | |
| $T$ = 230.00 K, $P$ = 6.59 MPa | | | | | | | | | | | |
| 0.4511[a] | 0.5489 | | 0.7423 | 0.2577 | | 0.5343 | 0.4199 | 0.0458 | 0.7232 | 0.2472 | 0.0297 |
| 0.4866 | 0.4966 | 0.0168 | 0.7345 | 0.2556 | 0.0100 | 0.5927 | 0.3268 | 0.0805 | 0.7104 | 0.2331 | 0.0565 |

[a] Binary system.

**Table 3. Critical Constants and Acentric Factors**

| component | $T_c$/K | $P_c$/MPa | acentric factor |
|---|---|---|---|
| $CH_4$ | 190.555 | 4.5950 | 0.008 |
| $CO_2$ | 304.21 | 7.3825 | 0.220 |
| $C_2H_6$ | 305.33 | 4.8714 | 0.099 |

superior modeling results compared to methane + carbon dioxide are due to the fact that methane and ethane are similar, nonpolar molecules and consequently a relatively simple equation with a single adjustable parameter is satisfactory. In the case of methane and carbon dioxide, however, the molecules are dissimilar chemically, and in addition carbon dioxide has a significant quadrupole moment. Consequently simple cubic equations such as the Peng–Robinson equation are far less satisfactory.

The carbon dioxide + ethane system, which exhibits a maximum-pressure azeotrope, was measured at six temperatures between 207 and 270 K. The 230 K isotherm and Peng–Robinson calculations are shown in Figure 3. The azeotropic pressures measured in this study are

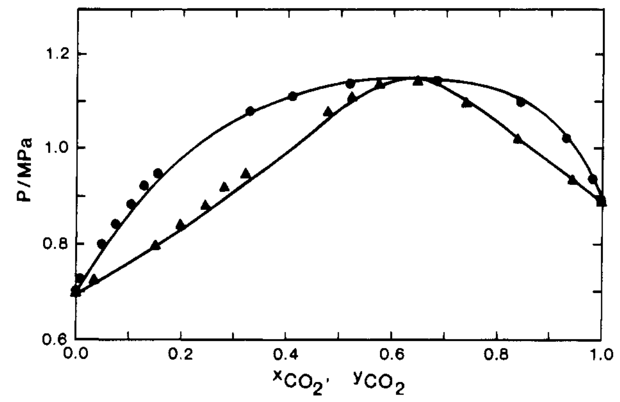

**Figure 3.** Vapor–liquid equilibria for carbon dioxide + ethane at 230.00 K: ●, liquid; ▲, vapor; —, Peng–Robinson equation.

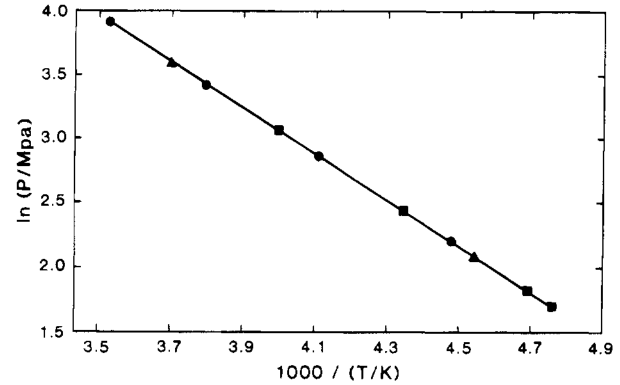

**Figure 4.** Pressures at the azeotrope for carbon dioxide + ethane: ●, Fredenslund and Mollerup (1974); ▲, Brown et al. (1988); ■, this investigation.

**Table 4. Binary Interaction Coefficients**

| system | T/K | $k_{ij}$ |
|---|---|---|
| $CH_4 + CO_2$ | 230.00 | 0.095 |
| | 250.00 | 0.096 |
| | 270.00 | 0.096 |
| $CH_4 + C_2H_6$ | 210.00 | 0.003 |
| | 230.00 | 0.005 |
| | 250.00 | 0.015 |
| | 270.00 | 0.013 |
| $CO_2 + C_2H_6$ | 207.00 | 0.133 |
| | 210.00 | 0.130 |
| | 213.00 | 0.130 |
| | 230.00 | 0.130 |
| | 250.00 | 0.128 |
| | 270.00 | 0.123 |

compared with the results of Fredenslund and Mollerup (1974) and Brown et al. (1988) in Figure 4. A linear regression, $\ln P = -1793.5/T + 7.9339$, fits all the data with a maximium error in pressure of 0.90% and an average error of 0.24%.

The ternary isobaric vapor–liquid equilibria were measured at 230 K. The measurements covered eight pressures from 1.15 MPa (the azeotropic pressure of carbon dioxide + ethane at 230 K) to 6.59 MPa. The pressure of 6.49 MPa was selected since it is just below the critical point of the methane + ethane system, and 6.59 MPa was chosen since it is at or slightly above the methane + ethane critical point and just below the critical point of the methane + carbon dioxide system. Unfortunately measurements in the critical region are very difficult, and it was not possible to complete the 6.59 MPa isobar. Five of the isobars along with calculations made using the Peng–Robinson equation are shown in Figures 5–7.

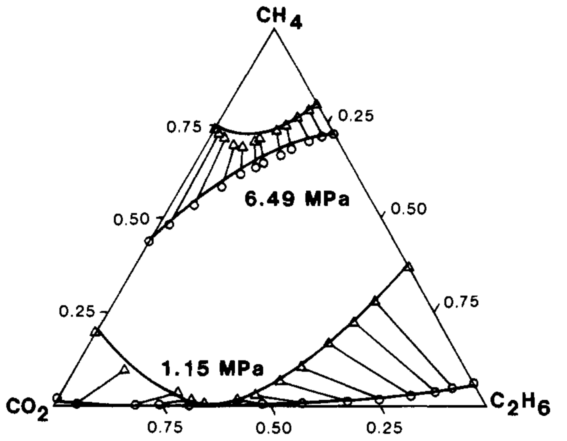

**Figure 5.** Vapor–liquid equilibria for methane + ethane + carbon dioxide at 230.00 K and pressures of 1.15 and 6.49 MPa: ●, liquid; ▲, vapor; —, Peng–Robinson equation.

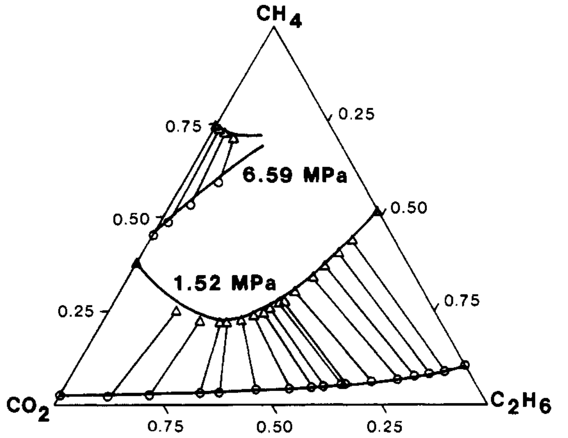

**Figure 6.** Vapor–liquid equilibria for methane + ethane + carbon dioxide at 230.00 K and pressures of 1.52 and 6.59 MPa: ●, liquid; ▲, vapor; —, Peng–Robinson equation..

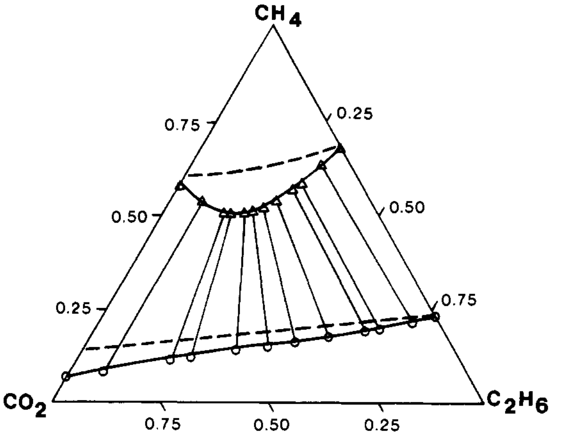

**Figure 7.** Vapor–liquid equilibria for methane + ethane + carbon dioxide at 230.00 K and 2.53 MPa: ●, liquid; ▲, vapor; —, Peng–Robinson equation; - - -, Peng–Robinson equation with $k_{ij} = 0$.

Several interesting trends are evident in the results. The bubble-point curves are concave at low pressures, become straight lines at intermediate pressures, and then become convex at higher pressures. Another feature shown in the sequence of graphs is that the bubble-point and dew-point curves coincide at the carbon dioxide + ethane azeotrope at 1.15 MPa. As the pressure increases, the distance between the curves increases to a maximum and then decreases. However, the system did not form a ternary azeotrope. The Peng–Robinson calculations, also shown in Figures 5–7, were made using only the $k_{ij}$ values obtained from the binary data. The results are generally satisfactory, with the maximum discrepancies occurring in regions of high carbon dioxide concentrations and at elevated pressures. Near the critical region of the binary system methane + carbon dioxide (6.5 MPa and above) the Peng–Robinson equation fails to accurately represent the binary data (Figure 1), and this is reflected in the ternary data in the same pressure region.

The conclusion reached here is that binary interaction coefficients ($k_{ij}$) are generally satisfactory for modeling ternary data provided that the binary isotherms themselves are well represented by the equation of state. This conclusion has been verified in this laboratory for a number of other natural gas systems. The importance of the interaction coefficients is clearly shown in Figure 7, where Peng–Robinson calculations using $k_{ij}$ values of zero are shown.

## Literature Cited

Angus, S.; Armstrong, B; de Reuck, K. M. *International Thermodynamic Tables of the Fluid State-3: Carbon Dioxide*; Pergamon Press: New York, 1976.

Angus, S.; de Reuck, K. M.; Armstrong, B.; Jacobsen, R. T.; Stewart, R. B. *International Thermodynamic Tables of the Fluid State-6: Nitrogen*; Pergamon Press: New York, 1979.

Brown, T. S.; Kidnay, A. J.; Sloan, E. D. Vapor-Liquid Equilibria in the Carbon Dioxide + Ethane System. *Fluid Phase Equilib.* **1988**, *40*, 169–84.

Davalos, J.; Anderson, W. R.; Phelps, R. E.; Kidnay, A. J. *Liquid*-Vapor Equilibria at 250.00 K for Systems Containing Methane, Ethane and Carbon Dioxide. *J. Chem. Eng. Data* **1976**, *21*, 81–84.

Fredenslund, A.; Mollerup, J. Measurement and Prediction of Equilibrium Ratios for the $C_2H_6$ + $CO_2$ System. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 1653–60.

Goodwin, R. D.; Roder, H. M.; Straty, G. C. Thermodynamic Properties of Ethane, From 90 to 600 K at Pressures to 700 Bar. National Bureau of Standards Technical Note 684; National Bureau of Standares: Washington, DC, 1976.

Hiza, M. J.; Miller, R. C.; Kidnay, A. J. A Review, Evaluation and Correlation of the Phase Equilibria, Heat of Mixing and Change of Volume on Mixing for Liquid Mixtures of Methane + Ethane. *J. Phys. Chem. Ref. Data* **1979**, *8*, 799–816.

Mraw, S. C.; Hwang, S.-C.; Kobayashi, R. Vapor-Liquid Equilibrium of the $CH_4$–$CO_2$ System at Low Temperatures. *J. Chem. Eng. Data* **1978**, *23*, 135–139.

Peng, D.-Y.; Robinson, D. B.; 1976, A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

Prausnitz, J. M. Equations of State from van der Waals Theory: The Legacy of Otto Redlich. *Fluid Phase Equilib.* **1985**, *24*, 63–76.

Somait, F. A.; Kidnay, A. J. Liquid-Vapor Equilibria at 270.00 K for Systems Containing Nitrogen, Methane, and Carbon Dioxide. *J. Chem. Eng. Data* **1978**, *23*, 301–305.

Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions, With Applications to Phase Equilibria*; McGraw-Hill: New York, 1982; pp 342–3.

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