

A review, evaluation, and correlation of the phase equilibria, heat of mixing, and change in volume on mixing for liquid mixtures of methane + propane

Cite as: Journal of Physical and Chemical Reference Data **9**, 721 (1980); <https://doi.org/10.1063/1.555626>
Published Online: 15 October 2009

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A Review, Evaluation, and Correlation of the Phase Equilibria, Heat of Mixing, and Change in Volume on Mixing for Liquid Mixtures of Methane + Propane

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The available experimental data for liquid-vapor equilibria, heat of mixing, and change in volume on mixing for the methane + propane system have been reviewed and where possible evaluated for consistency. The derived properties chosen for analysis and correlation were liquid mixture excess Gibbs free energies, Henry's constants, and K values. Data sets, selected on the basis of the consistency tests applied, were correlated as a function of temperature and composition to provide internally consistent sets of property values suitable for engineering design calculations.

Key words: Binary mixtures; data correlation; excess volumes, heat of mixing; liquid-vapor equilibria; methane + propane.

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1. Introduction

This is a continuation of previous work [1]¹ on the review, evaluation, and correlation of phase equilibria and related data on industrially important binary systems. The first system considered was methane + ethane [1], and the present work is concerned with the methane + propane system. These are two of the most important systems related to the natural gas industry.

Many of the methods used to evaluate and correlate data were described in detail in the previous paper [1]. Where possible, discussion of these techniques has been kept to a minimum in the present manuscript.

Units for physical quantities have been consistently taken from the SI system, although the literature data appear in many diverse systems. The conversions used in this work are as follows:

$$P(\text{MPa}) = 0.1 P(\text{bar}) = 0.101325 P(\text{atm}) = 0.0068948 P(\text{psia}), \quad (1)$$

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15 = T(^{\circ}\text{R})/1.8 = [T(^{\circ}\text{F}) + 459.67]/1.8. \quad (2)$$

A number of surveys were used to locate the pertinent methane + propane literature [2,3,4]. Published liquid-vapor equilibria references are listed in table I. Papers in which phase equilibrium variables (P - T - y - x) were reported in connection with measurements of other physical properties were not included unless there were indications that the liquid and vapor were in fact brought to equilibrium. Experimental methods, approximate temperatures and pressures, and comments concerning the type of data presented are listed in table I for each reference.

2. Evaluation of Phase Equilibria Data

A preliminary evaluation of the methane + propane data has been published [24]. Equimolar excess Gibbs energies and infinite dilution Henry's constants for methane

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¹ Figures in brackets indicate literature references at the end of this paper.

TABLE I. Survey of liquid-vapor equilibria data for methane + propane

Reference	Experimental method	Approximate temperatures and pressures	Comments
Frolich, Tauch, Hogan and Peer (1931) [5]	Static gas solubility system	298 K (3 to 9 MPa)	Data are given in graphical form only.
Sage, Lacey and Schaafsma (1934) [6]	Dew points plus bubble points from breaks in volumetric curves from isochoric system	293 K (1 to 10 MPa) 313 K (2 to 9 MPa) 328 K (2 to 8 MPa) 343 K (3 to 7 MPa) 353 K (4 to 6 MPa) 363 K (4 to 5 MPa)	Smoothed isothermal P - x - y data are given in tabular form (including critical data). All data from this source were later repeated in the same lab with more accurate methods.
Reamer, Sage and Lacey (1950) [7]	Dew and bubble points from breaks in volumetric curves from isochoric system	278 K (1 to 10 MPa) 294 K (1 to 10 MPa) 311 K (1 to 9 MPa) 328 K (2 to 8 MPa) 344 K (3 to 7 MPa) 361 K (4 to 5 MPa)	Smoothed isothermal P - x - y data are given in tabular form (including critical data).
Akers, Burns and Fairchild (1954) [8]	Single pass separator	158 K (0.3 to 1 MPa) 174 K (1 to 3 MPa) 195 K (1 to 5 MPa) 213 K (1 to 7 MPa) 226 K (1 to 8 MPa) 241 K (1 to 9 MPa) 256 K (1 to 10 MPa) 273 K (1 to 10 MPa)	Smoothed isothermal P - x - y data are given in tabular form (including critical data). Vapor compositions are not given for the 158 K isotherm.
Price and Kobayashi (1959) [9]	Vapor recirculation cell	144 K (0.7 MPa) 172 K (0.7 to 1.4 MPa) 200 K (1 to 4 MPa) 228 K (1 to 7 MPa) 255 K (1 to 9 MPa) 283 K (1 to 8 MPa)	Direct isothermal P - x - y data are tabulated for the methane + ethane + propane system, including 31 points for the methane + propane binary system.
Rutherford (1962) [10]	Dew-point, bubble-point cell	316 K (6 to 9 MPa)	Data are given in graphical form only.
Cheung and Wang (1964) [11]	Static equilibrium cell	92 K (0.001 to 0.009 MPa) 113 K (0.005 to 0.06 MPa) 128 K (0.01 to 0.2 MPa)	Isothermal P - x data are given in tabular form at low CH_4 concentrations.
Cutler and Morrison (1965) [12]	Static equilibrium cell	90 K (0.001 to 0.01 MPa) 95 K (0.002 to 0.02 MPa) 100 K (0.003 to 0.03 MPa) 105 K (0.005 to 0.05 MPa) 110 K (0.007 to 0.08 MPa)	Isothermal P - x data are given in tabular form.
Ahland (1966) [13]	Dew point cell	271 to 274 K (0.6 to 7 MPa)	T - P - y data are tabulated. Gases were used which were contaminated with butanes.
Roof and Baron (1967) [14]	Dew-point, bubble-point cell	305 to 356 K (6 to 9 MPa)	Tabulated T - P - x data are given along the critical locus.
Yesavage, Katz and Powers (1969) [15]	Dew and bubble points from breaks in enthalpy curves from flow calorimeter	210 to 350 K (2 to 5 MPa)	Tabulated T - P data are given for a 77 mole percent C_3H_8 mixture.
Skipka et al. (1970) [16]	Vapor recirculation cell	123 K (0.02 to 0.2 MPa) 133 K (0.04 to 0.5 MPa) 143 K (0.05 to 0.8 MPa) 153 K (0.09 to 1 MPa)	Smoothed isothermal P - x data are given in tabular form.

TABLE I. Survey of vapor-liquid equilibria data for methane + propane — Continued

Reference	Experimental method	Approximate temperatures and pressures	Comments
Stoekli and Staveley (1970) [17]	Static equilibrium cell	91 K (0.005 to 0.01 MPa)	Isothermal P - x data are given in tabular form.
Yesavage, Katz and Powers (1970) [18]	Dew and bubble points from breaks in enthalpy curves from flow calorimeter	180 to 329 K (2 to 7 MPa)	Tabulated T - P data are given for a 51 mole percent C_4H_{10} mixture.
Wichterle and Kobayashi (1972) [19]	Vapor recirculation cell	130 K (0.2 to 0.3 MPa) 144 K (0.2 to 0.7 MPa) 158 K (0.2 to 1 MPa) 172 K (0.2 to 2 MPa) 187 K (0.3 to 4 MPa) 190 K (4 to 5 MPa) 191 K (2 to 5 MPa) 192 K (0.2 to 5 MPa) 195 K (0.2 to 5 MPa) 200 K (0.2 to 5 MPa) 214 K (0.2 to 6 MPa)	Direct isothermal P - x - y data are tabulated (including the critical region). Data are also given for the methane + ethane + propane ternary system.
Calado, Garcia and Staveley (1974) [20]	Static equilibrium cell	116 K (0.02 to 0.1 MPa) 135 K (0.1 to 0.5 MPa)	Isothermal P - x data are given in tabular form.
Poon and Lu (1974) [21]	Vapor recirculation cell	114 K (0.04 to 0.1 MPa) 118 K (0.05 to 0.2 MPa) 122 K (0.05 to 0.2 MPa)	Isothermal P - x - y values are tabulated. Vapor compositions are not reported for some points.
Kalra and Robinson (1975) [22]	Static equilibrium cell	214 K (0.8 to 4.7 MPa)	Isothermal P - x - y data are given in tabular form.
Wilson (1975) [23] ^a	Static equilibrium cell	111 K (0 to 0.1 MPa)	Isothermal P - x data are given in tabular form.

^a This isotherm was inadvertently omitted in the evaluation and correlation work reported in this paper.

were obtained and intercompared from the reported isothermal P - x data using the orthogonal collocation method [25]. The available critical locus data were also compared. The conclusion was that there are inconsistencies in the data throughout the available temperature range (90 to 360 K), including some modest disparities in the reported critical conditions.

The first step in the current data evaluation was to compare reported component vapor pressures with the recent compilations of Goodwin [26, 27]. Comparisons in table 2 indicate that the methane and higher temperature propane values agree with the best available compilations within the accuracy of the pressure gauges used for measurement. The lower temperature propane vapor pressures reported by Wichterle and Kobayashi [19] were taken from measurements in a separate apparatus by Carruth [28]. They probably lie within the uncertainties in the compilation. No excessive temperature measurement, pressure measurement, or sample impurity problems are indicated by the table 2 comparisons.

If reported, the experimental vapor pressures were used in all evaluation work. If not reported, they were taken from the Goodwin compilations [26, 27].

For evaluation purposes, the methane + propane liquid-vapor data were divided into low-temperature and high-tem-

perature regions. A temperature of approximately 172 K, or $0.9 T_c$ for methane, was chosen as the dividing line.

2.1. Low-Temperature Phase Equilibria Data

Initial screening of the data below 172 K was done by intercomparison of excess Gibbs energies (G^E). Barker—method [29] calculations were used to determine coefficients in the three-term Redlich-Kister expansion for G^E at zero reference pressure. The Peng-Robinson equation of state [30] was used to calculate gas phase fugacity coefficients. Component parameters were calculated from the generalized relations of [30], and the mixing rules were as per Appendix C of [1]. The binary parameters were taken to be $j_{12} = 0.015$ and $k_{12} = 0.080$, as optimized to liquid-vapor equilibria calculations (discussed below). Actually, gas-phase fugacity coefficients are not very sensitive to the values of these binary parameters for methane + propane phase equilibria conditions below 172 K. Barker-method G^E results changed by less than 0.1 J/mol when the parameters were changed to $j_{12} = 0$ and $k_{12} = 0.050$ or to $j_{12} = 0$ and $k_{12} = 0.080$.

Except for the equation of state, all other details of the Barker-method calculations were given in Appendix A of [1]. The Goodwin compilations [26, 27] were used as a

TABLE 2. Comparison of experimental (EXPR) vapor pressures (in MPa) with those listed in compilations (COMP)

T, K	Methane			Propane			Reference
	EXPR	COMP ^a	Δ , %	EXPR	COMP ^b	Δ , %	
90.68	0.011688	0.01174	0.4				Stoekli and Staveley [17]
95.00	0.019845	0.01991	0.3				Cutler and Morrison [12]
100.00	0.034508	0.03451	0.0				Cutler and Morrison [12]
105.00	0.056509	0.05657	0.1				Cutler and Morrison [12]
110.00	0.088243	0.08840	0.2				Cutler and Morrison [12]
114.10	0.123	0.12359	0.5				Poon and Lu [21]
115.77	0.14033	0.14065	0.2				Calado et al. [20]
118.30	0.170	0.16985	0.1				Poon and Lu [21]
122.20	0.223	0.22356	0.3				Poon and Lu [21]
123.15	0.238	0.23839	0.2				Skripka et al. [16]
130.37	0.372	0.37630	1.1	1.78×10^{-5}	1.858×10^{-5}	4.2	Wichterle and Kobayashi [19]
133.15	0.442	0.44260	0.1				Skripka et al. [16]
134.83	0.48668	0.48662	0.0				Calado et al. [20]
143.15	0.752	0.75318	0.2				Skripka et al. [16]
144.26	0.786	0.79538	1.2	1.287×10^{-4}	1.353×10^{-4}	4.9	Wichterle and Kobayashi [19]
153.15	1.194	1.1975	0.3				Skripka et al. [16]
157.59	1.482	1.4451	2.6				Akers et al. [8]
158.15	1.469	1.4788	0.7	6.674×10^{-4}	6.786×10^{-4}	1.7	Wichterle and Kobayashi [19]
172.04	2.493	2.5069	0.6	2.655×10^{-3}	2.560×10^{-3}	3.7	Wichterle and Kobayashi [19]
174.26	2.689	2.7093	0.7				Akers et al. [8]
187.54	4.178	4.1867	0.2	8.853×10^{-3}	8.705×10^{-3}	1.7	Wichterle and Kobayashi [19]
190.58	4.599						Wichterle and Kobayashi [19]
190.95				0.01122	0.01106	1.4	Wichterle and Kobayashi [19]
192.30				0.01224	0.01212	1.0	Wichterle and Kobayashi [19]
195.20				0.01483	0.01470	0.9	Wichterle and Kobayashi [19]
213.71				0.04379	0.04368	0.3	Wichterle and Kobayashi [19]
277.59				0.545	0.5431	0.3	Reamer et al. [7]
294.26				0.862	0.8629	0.1	Reamer et al. [7]
310.93				1.303	1.3034	0.0	Reamer et al. [7]
327.59				1.889	1.8893	0.0	Reamer et al. [7]
344.26				2.648	2.6484	0.0	Reamer et al. [7]
360.93				3.620	3.6155	0.1	Reamer et al. [7]

^a Reference 26.^b Reference 27.^c Above the critical temperature.

source of liquid molar volumes and isothermal compressibilities. Liquid mixture excess volumes were estimated from [31], with extrapolations to higher temperatures by an extended corresponding states approach [32].

Resulting least-square Redlich-Kister coefficients, with their standard deviation, and average deviations in pressure are given in table 3. Also shown are the average absolute deviations between calculated and experimental γ values for isotherms where they were measured.

Equimolar G^E values were compared on a plot of G^E/T against $1/T$ (figure 1). Although the G^E values shown are at zero pressure, the maximum difference from saturated liquid G^E values was only 7 J/mol (at 172 K). Also shown on the plot is a dashed curve with slopes at 91.5 and 112.0 K equal to equimolar H^E values from [33]. On the basis of this comparison, five isotherms (data points circled on figure 1) stand out as being in serious disagreement with the remaining data.

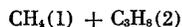
The differences between calculated and experimental γ values shown in table 4 also serve as a form of thermodynamic consistency test. For the isotherms at lower temperatures [21], the measured propane γ 's are more than

an order of magnitude larger than the calculated values, indicating a severe inconsistency. The propane γ values are larger at the higher temperatures [19], and there is agreement between calculation and experiment within reasonable experimental uncertainties.

The equal areas test was also applied to the isotherms where γ values were measured. Activity coefficients were calculated directly from the isothermal P - x - γ data using equations A1, A2, A12, and A14 of [1].

The Peng-Robinson equation of state was used for gas-phase fugacity coefficients. The test was applied by plotting $\ln(\gamma_1/\gamma_2)$ against x_1 and comparing areas above and below the $\ln(\gamma_1/\gamma_2) = 0$ line. For the higher temperature isotherms [19], the difference divided by the sum of the absolute values of the positive and negative areas ranged from 0.15 to 0.3. These values are not excessive for light-hydrocarbon mixtures exhibiting only moderate nonideality, and they compare favorably with results for the methane + ethane system [1]. Data for the lower three isotherms [21] were well below the $\ln(\gamma_1/\gamma_2) = 0$ line at all compositions, again indicating severe inconsistency.

TABLE 3. Results of Barker—method analyses of the individual isotherms



$$G^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2]$$

T, K	A	B	C	$(\Delta P /P_1^s) \times 100$	$ \Delta y_2 $	Reference
90.00	755.5 ± 8 ^a	277.1 ± 12 ^a	19.5 ± 20 ^a	0.29		Cutler and Morrison [12]
90.68	753.0 ± 13	299.6 ± 18	75.0 ± 21	0.21		Stoekli and Staveley [17]
95.00	753.1 ± 5	286.6 ± 7	39.0 ± 11	0.17		Cutler and Morrison [12]
100.00	756.9 ± 5	297.1 ± 7	44.6 ± 12	0.17		Cutler and Morrison [12]
105.00	763.5 ± 6	308.2 ± 8	42.1 ± 13	0.19		Cutler and Morrison [12]
110.00	772.5 ± 7	321.2 ± 10	44.2 ± 16	0.19		Cutler and Morrison [12]
114.10 ^b	1010.7 ± 25	289.9 ± 37	74.7 ± 67	0.59	0.00048	Poon and Lu [21]
115.77	836.8 ± 9	275.3 ± 12	151.5 ± 19	0.21		Calado, Garcia and Staveley [20]
118.30 ^b	1003.9 ± 28	218.5 ± 46	250.3 ± 71	0.62	0.00064	Poon and Lu [21]
122.20 ^b	1142.7 ± 37	346.5 ± 66	259.4 ± 116	1.19	0.00065	Poon and Lu [21]
123.15 ^b	635.8 ± 25	344.7 ± 35	210.7 ± 54	0.38		Skripka et al. [16]
133.15	870.7 ± 31	182.5 ± 44	182.3 ± 70	0.53		Skripka et al. [16]
134.83	902.9 ± 6	287.2 ± 8	130.1 ± 13	0.10		Calado, Garcia and Staveley [20]
143.15 ^b	738.6 ± 47	310.5 ± 65	262.1 ± 100	0.64		Skripka et al. [16]
144.26	897.7 ± 81	575.8 ± 137	58.4 ± 189	0.94	0.00003	Wichterle and Kobayashi [19]
153.15	938.6 ± 55	334.0 ± 76	347.1 ± 118	0.71		Skripka et al. [16]
158.15	1151.6 ± 22	532.7 ± 32	112.4 ± 51	0.36	0.00009	Wichterle and Kobayashi [19]
172.04	1227.1 ± 19	516.1 ± 26	225.2 ± 41	0.25	0.00046	Wichterle and Kobayashi [19]
172.04	1249.8 ± 37	535.2 ± 54	284.3 ± 101	0.39	0.00045	Wichterle and Kobayashi [19]

^a Standard deviations in the coefficients.

^b Isotherms not used in correlational work.

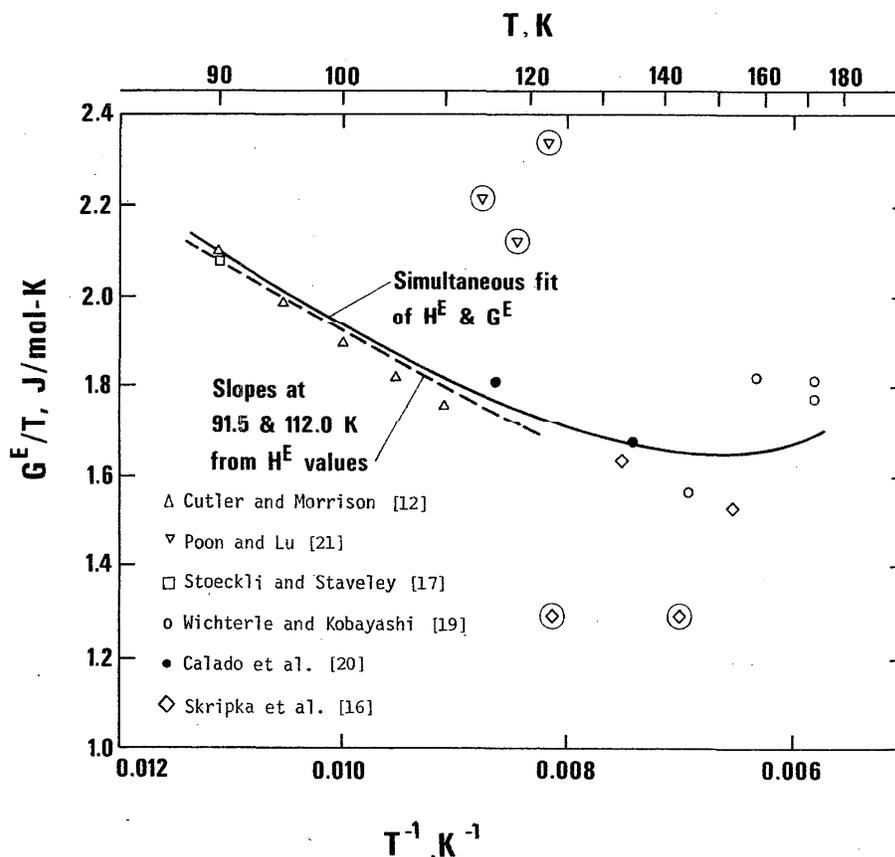


FIGURE 1. Excess Gibbs energies at zero pressure (G^E) as a function of temperature for equimolar liquid mixtures of methane + propane.

On the basis of the above evaluations the five isotherms at 114.10, 118.30, 122.20, 123.15, and 143.15 K (data points circled on figure 1, cf., table 3) were dropped from consideration in the correlational work.

2.2. High-Temperature Phase Equilibria Data

The orthogonal collocation method (unsymmetric convention) of Christiansen and Fredenslund [25] was used to test the phase equilibria data above 172 K for thermodynamic consistency. Documentation for this method is given in [24, 25] and in Appendix B of [1]. P - x data along isotherms were processed to calculate consistent y values. Comparisons are made in table 4 with the experimental vapor mole fractions. The number of collocation points was chosen to minimize the average absolute Δy values, although changing this number within reasonable ranges has little effect. The method failed to give results for the highest temperature isotherms using larger numbers of collocation points. Results could not be obtained for an isotherm at 361 K [7] using any reasonable number of collocation points.

As proposed [25], thermodynamic consistency is indicated if the average absolute Δy is within the combined uncertainty in measured x and y values. By current standards combined errors in the determination of phase compositions (x and y) should not greatly exceed 0.006 in mole fraction. At very low concentrations of propane in the gas phase, the accuracies must be even better to yield meaningful phase equilibria data. For most of the isotherms, average $|\Delta y|$ values do not greatly exceed the above criteria. According to this test, somewhat better

consistency is indicated for the reference [19] data at lower temperatures and reference [7] data at higher temperatures than for the other data sets available. The newer Reamer, Sage, and Lacey data [7] should definitely be used instead of the older Sage, Lacey, and Schaafsma data [6], as suggested by these workers themselves.

Henry's constants from the orthogonal collocation work are also listed in table 4. There is considerable scatter in these results which is in some part due to the emphasis placed on the data at lowest methane concentrations in the liquid. There are generally greater uncertainties in the P - x curve under these conditions. The collocation program [25] uses a Lagrangian extrapolation scheme to obtain infinite dilution Henry's constants. It is not possible to reach definite conclusions concerning data set discrepancies by intercomparison of these Henry's constants.

2.3. Critical Locus

The available critical locus data are shown in figure 2. There are significant discrepancies between the newer data of Roof and Baron [14] and the older data of Reamer et al. [7]. The more recent data were obtained by dew and bubble point measurements in a visual cell, with observation of critical opalescence. Dew points are difficult to observe accurately. The older data were obtained in a blind cell from discontinuities in volumetric curves, which are also hard to pinpoint accurately on the dew point curve. With only two sets of data available from 280 to 360 K, definite conclusions cannot be reached concerning which set is more accurate.

TABLE 4. Results of the orthogonal collocation calculations

T , K	Number of collocation points	Avg $ \Delta y_2 $	H_{12} , MPa	Reference
187.54	10	0.002	4.20 ^a	Wichterle and Kobayashi [19]
190.95	11	0.001	5.02	Wichterle and Kobayashi [19]
192.30	14	0.002	4.63	Wichterle and Kobayashi [19]
194.82	14	0.005	4.74	Akers et al. [8]
195.20	14	0.002	5.11	Wichterle and Kobayashi [19]
199.82	14	0.005	4.21	Price and Kobayashi [9]
213.15	13	0.009	6.10	Akers et al. [8]
213.71	14	0.004	7.27	Wichterle and Kobayashi [19]
226.48	14	0.005	10.23	Akers et al. [8]
227.59	12	0.007	6.38	Price and Kobayashi [9]
241.48	11	0.006	10.18	Akers et al. [8]
255.37	12	0.014	11.12	Price and Kobayashi [9]
256.48	11	0.012	11.66	Akers et al. [8]
273.15	10	0.014	18.16	Akers et al. [8]
277.59	10	0.006	13.35	Reamer et al. [7]
283.15	12	0.010	17.64	Price and Kobayashi [9]
293.15	14	0.014	20.58	Sage et al. [6]
294.26	9	0.007	15.20	Reamer et al. [7]
310.93	13	0.005	13.66	Reamer et al. [7]
327.59	9	0.007	14.49	Reamer et al. [7]
328.15	10	0.013	20.30	Sage et al. [6]
343.15	8	0.020	17.90	Sage et al. [6]
344.26	8	0.005	14.21	Reamer et al. [7]
353.15	8	0.020	16.66	Sage et al. [6]

^a Evaluated at the propane vapor pressure.

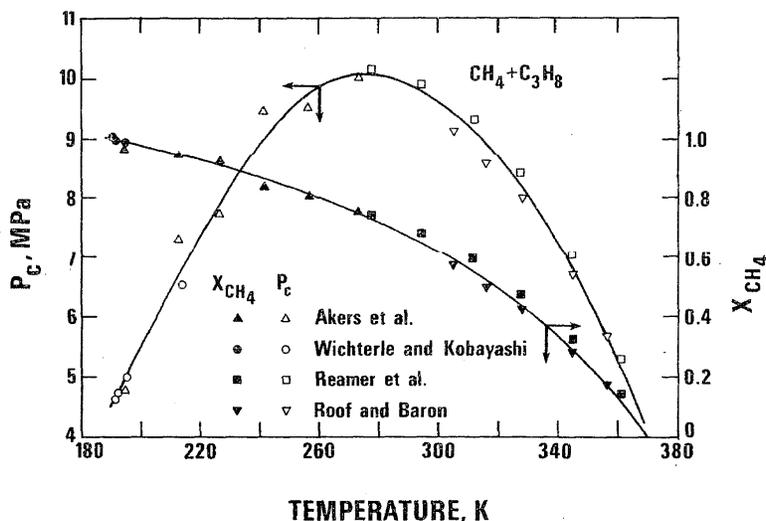


FIGURE 2. Critical pressure and critical mole fraction of methane versus temperature for methane + propane. Solid curves are estimated best fits of the data.

3. Correlation of Phase-Equilibria Data

3.1. Correlation of Barker-Method G^E Values

The methane + propane phase equilibria data below 172 K have been correlated by use of a liquid-phase activity-coefficient model combined with a gas-phase equation of state. A three-term Redlich-Kister expansion with coefficients quadratic in temperature was used to represent the zero pressure $G^E(T, x)$ data. Values of G^E at each reported liquid composition from the Barker-method analysis of the 14 selected isotherms (table 3) were fitted simultaneously with the available H^E data [33] at 91.5 and 112.0 K. Details of the least squares procedure were reported in [1]. The correlating G^E equation and the least-squares coefficients with standard deviations for the simultaneous G^E and H^E fit are given in table 5.

TABLE 5. Temperature—dependent Redlich—Kister equation determined by simultaneous fit of selected G^E and H^E data

$$G^E = x_1 x_2 (A_0 + A_1 T + A_2 T^2) + (B_0 + B_1 T + B_2 T^2) (x_1 - x_2) + (C_0 + C_1 T + C_2 T^2) (x_1 - x_2)^2$$

Coefficient	Value ^a	Standard deviation ^a
A_0	1032.54	58
A_1	- 7.2816	1.1
A_2	0.046710	0.0048
B_0	468.04	139
B_1	- 4.6099	2.5
B_2	0.028344	0.011
C_0	966.96	416
C_1	-17.1126	7.1
C_2	0.079304	0.029

Standard deviation in G^E and H^E fit = 9.48 J/mol.

^a Units are such that T is in kelvins and G^E is in J/mol.

Standard deviation for the 117 experimental G^E and H^E values was 9.5 J/mol, which is only slightly larger than 8.4 J/mol value for a similar methane + ethane data fit [1]. Root-mean-square deviation for the H^E data alone was 13.9 J/mol, which is considerably larger than the estimated uncertainty in these data. Weighting the H^E data produced an inferior G^E correlation at the higher temperatures. This is because the H^E data are all at the low end of the temperature range.

Comparisons were made between the experimental isotherms and calculations based on the table 5 equation. The Peng-Robinson equation of state was again used for gas-phase fugacity coefficients, and all data and relations were the same as used in the original Barker-method calculations (Section 2.1). Bubble-point pressures were calculated for comparison with the experimental isotherms for which γ values were not measured. For comparison with isothermal P - x - y measurements, x - y values (and K values) were calculated at the experimental T - P values. The comparisons are given in table 6. Most of the calculated bubble point pressures agree with experiment within 0.5% of the methane vapor pressures for the isotherms used to develop the correlation. There is considerable scatter in the two Skripka et al. [16] isotherms at 133.15 K and 153.15 K. For the four Wichterle and Kobayashi [19] isotherms, average absolute deviations in K values are about 2% for methane and 13% for propane. For the most part, calculated propane K values are larger than the experimental values. Average deviations in all properties are excessively large for the isotherms not used in the correlation (bottom portion of table 6).

Representation of the G^E values is given by table 5. For mixtures in the mid range of compositions, the absolute uncertainty in G^E values from the equation is estimated to be about 3 J/mol at 90 K, increasing to about 20 J/mol at 172 K. Larger uncertainties at the higher tem-

TABLE 6. Comparison of deviations between correlation and experiment for low temperature bubble point pressures or y - x values

T, K	Average deviations ^a						Reference
	$(\Delta P /P_1^s) \times 100$	$\Delta P/P_1^s \times 100$	$ \Delta x_1 $	Δx_1	$ \Delta y_2 $	Δy_2	
90.00	0.45	-0.22					Cutler and Morrison [12]
90.68	0.31	0.23					Stoekli and Staveley [17]
95.00	0.25	-0.20					Cutler and Morrison [12]
100.00	0.26	-0.15					Cutler and Morrison [12]
105.00	0.30	-0.18					Cutler and Morrison [12]
110.00	0.30	-0.15					Cutler and Morrison [12]
115.77	0.53	0.36					Calado et al. [20]
133.15	1.26	-0.52					Skripka et al. [16]
134.83	0.51	-0.41					Calado et al. [20]
153.15	1.25	-0.37					Skripka et al. [16]
144.26			0.015	-0.010	0.0000	0.0000	Wichterle and Kobayashi [19]
158.15			0.009	-0.009	0.0001	0.0001	Wichterle and Kobayashi [19]
172.04			0.005	-0.001	0.0005	0.0005	Wichterle and Kobayashi [19]
172.04 ^b			0.009	-0.007	0.0005	0.0005	Wichterle and Kobayashi [19]
123.15 ^c	2.19	-1.51					Skripka et al. [16]
143.15 ^c	2.13	-1.52					Skripka et al. [16]
114.10 ^c			0.034	-0.034	0.0005	0.0005	Poon and Lu [21]
118.30 ^c			0.024	-0.024	0.0006	0.0006	Poon and Lu [21]
122.20 ^c			0.049	-0.049	0.0007	0.0007	Poon and Lu [21]

^aAll deviations are "experimental" minus "calculated". Subscript 1 refers to methane.

^bBinary data taken as part of the ternary CH₄ + C₂H₆ + C₃H₈ study.

^cThese isotherms were not used in the development of the correlation.

peratures are due to restricting the temperature dependence of G^E to a quadratic form, greater scatter in the phase equilibria P - x data, and the absence of any H^E data above 112 K. Curves are shown in Figure 3 of G^E (at zero pressure) versus composition at 90, 130, and 170 K as calculated from table 5.

3.2. Correlation using an Equation of State

The methane + propane liquid-vapor equilibria data from 90 K to 280 K were correlated using the Peng-Robinson equation of state [30] (described above in section 2.1). Two binary mixing rule deviation parameters were determined to optimize the fit of y and x values for selected experimental isotherms. The values so determined are $j_{12} = 0.015$ and $k_{12} = 0.080$. Table 7 presents deviations between calculated and experimental x and y values and K values for each component. On the basis of these results, combined with the data evaluations discussed above, the isotherms are divided into two categories. Those in the top portion of the table are selected as being the data of highest quality and in best internal agreement. For the selected isotherms below 280 K average deviations in K values were 5% for methane and 10% for propane. Above 280 K, deviations in K values increase for methane.

3.3. Henry's Constants

The selected high-temperature isotherms (cf., table 7), for which data were reported at reasonably low concen-

trations of methane in the liquid, were treated by the method of Gunn et al. [34] to determine infinite dilution Henry's Law constants at the propane vapor pressures. This method was discussed in Appendix B of [1]. Resulting Henry's constants are plotted against temperature in figure 4. A least-squares procedure was used to fit these data with the following results:

$$T < 270 \text{ K } (H_{12}/\text{MPa}) = -17.97 + 0.11798 (T/\text{K}) \quad (3)$$

$$T > 270 \text{ K } (H_{12}/\text{MPa}) = -70.29 + 0.54030 (T/\text{K}) \\ - 0.00084327 (T/\text{K})^2 \quad (4)$$

Standard deviations from equations (3) and (4) were both 0.17 MPa.

3.4. K-Value Chart

The K -value versus pressure chart for the methane + propane system, shown as figure 5, was produced by combining information from a number of sources. Vapor pressures were taken from the compilations of Goodwin [26, 27], and critical points were estimated from figure 2. Isotherms below 172 K were calculated by the method of section 3.1. This correlation was based on a Redlich-Kister equation for the liquid-phase activity coefficients, combined with the Peng-Robinson equation of state for gas-phase nonidealities. Above 172 K, isothermal K -values were evaluated by the method of section 3.2. This method used the Peng-Robinson equation of state for both phases.

The K -value chart covers temperatures from 90 K to 280 K, with pressures from 0.001 MPa to 10 MPa. It is

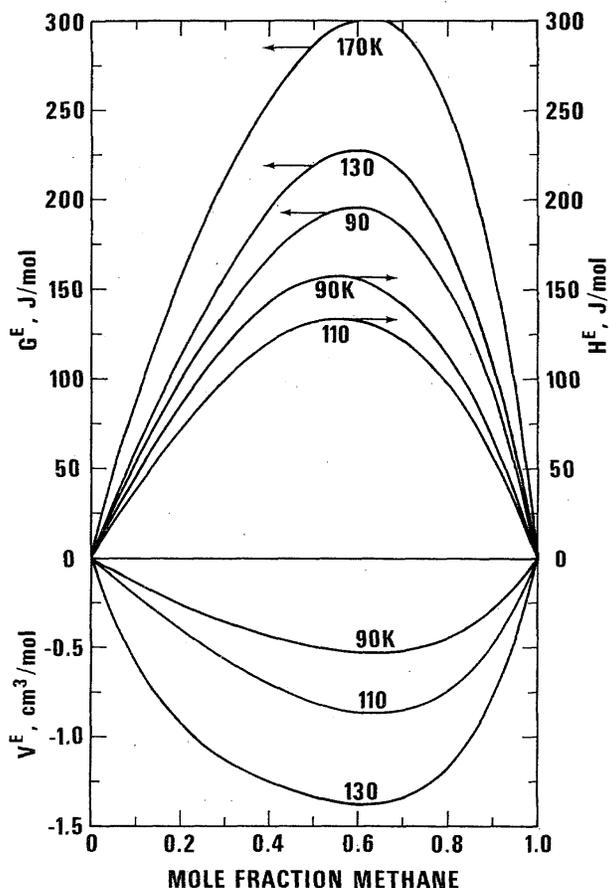


FIGURE 3. Excess Gibbs energies at zero pressure (G^E) from table 5, excess enthalpies at zero pressure (H^E) from table 8 and excess volumes (V^E) from table 9 versus liquid mole fraction methane for methane + propane along various isotherms.

believed that the methane K -values are as accurate as they can be read from the chart ($\pm 5\%$). The propane K -values should be accurate to about $\pm 10\%$ at most conditions. At the lowest temperatures there is insufficient experimental information to confirm the absolute uncertainty in the propane K -values. The line for $K_{C_3H_8}^\infty$ of figure 5 is not in good agreement at all temperatures with the values listed by Wichterle and Kobayashi [19]. This is not surprising considering the difficulties associated with the measurement of the extremely small vapor phase concentrations of propane in this region and the inaccuracies involved in extrapolation to infinite dilution.

3.5. Excess Enthalpies and Volumes

As mentioned in section 3.1, the table 5 simultaneous fit of G^E and H^E data does not represent the H^E data at 91.5 K and 112.0 K [33] within the estimated experimental uncertainty of 3 J/mol. A two-term Redlich-Kister expansion with coefficients linear in temperature was used to closely fit the H^E data from reference [33]. The resulting least-squares coefficients with their standard deviations are shown in table 8. Standard deviation in H^E for the fit was 1.1 J/mol, with a maximum deviation of 1.7 J/mol. The data do not justify use of a third coefficient in the general Redlich-Kister expansion. Curves of H^E against mole fraction methane from table 8 are shown in figure 3 at 90 K and 110 K. These H^E values may be considered to be at either zero pressure or at the mixture saturation pressures, since differences are less than 0.1 J/mol in all cases.

Saturated liquid excess volume data were reported in references [17, 31, 35, 36, 37] between 90 K and 130 K, and the data were fit by a three-term Redlich-Kister expansion with coefficients quadratic in temperature. The result-

TABLE 7. Comparison of Peng-Robinson calculations with experimental phase equilibria data

T, K	P_{max}, MPa	Average absolute deviations ^a				Reference
		Δx_1	Δy_2	$\Delta K_1, \%$	$\Delta K_2, \%$	
90.00 ^b	°	0.013	°	2.9	°	Cutler and Morrison [12]
90.68	°	0.007	°	1.5	°	Stoekli and Staveley [17]
95.00 ^b	°	0.010	°	2.1	°	Cutler and Morrison [12]
100.00 ^b	°	0.011	°	2.5	°	Cutler and Morrison [12]
105.00 ^b	°	0.011	°	2.6	°	Cutler and Morrison [12]
110.00 ^b	°	0.012	°	2.6	°	Cutler and Morrison [12]
115.77	°	0.014	°	3.6	°	Calado et al. [20]
128.40	°	0.005	°	2.3	°	Cheung and Wang [11]
130.37	°	0.010	0.0000	2.2	10.9	Wichterle and Kobayashi [19]
133.15	°	0.009	°	3.8	°	Skripka et al. [16]
134.83	°	0.008	°	2.3	°	Calado et al. [20]
144.26	°	0.014	0.0000	3.3	17.9	Wichterle and Kobayashi [19]
153.15	°	0.009	°	2.2	°	Skripka et al. [16]
158.15	°	0.014	0.0000	3.2	6.1	Wichterle and Kobayashi [19]
158.15	°	0.008	0.0002	2.6	7.2	Wichterle and Kobayashi [19]
172.04	°	0.010	0.0003	1.8	15.7	Wichterle and Kobayashi [19]
172.04 ^f	°	0.007	0.0003	2.1	11.6	Wichterle and Kobayashi [19]
185.93	1.4	0.005	0.001	2.7	7.2	Wichterle and Kobayashi [19]
187.54	4.0	0.006	0.001	1.3	10.6	Wichterle and Kobayashi [19]
190.58	4.5	0.003	0.000	0.3	29.8	Wichterle and Kobayashi [19]

TABLE 7. Comparison of Peng-Robinson calculations with experimental phase equilibria data — Continued

T, K	Approximate Temperatures					Reference
	P_{max} , MPa	Δx_1	Δy_2	ΔK_1 , %	ΔK_2 , %	
190.95	4.5	0.008	0.001	1.2	15.5	Wichterle and Kobayashi [19]
192.30	4.6	0.005	0.001	1.4	11.9	Wichterle and Kobayashi [19]
195.20	4.7	0.007	0.001	1.3	8.2	Wichterle and Kobayashi [19]
199.82	5.0	0.010	0.001	2.7	10.5	Wichterle and Kobayashi [19]
213.71	6.5	0.013	0.002	2.5	8.4	Wichterle and Kobayashi [19]
213.71	5.5	0.014	0.001	3.2	5.3	Wichterle and Kobayashi [19]
227.59 ^b	6.9	0.009	0.001	2.1	3.8	Price and Kobayashi [9]
241.48	8.3	0.007	0.003	1.7	3.3	Akers et al. [8]
255.37	9.0	0.009	0.007	2.6	5.6	Price and Kobayashi [9]
256.48	8.3	0.006	0.004	1.8	3.8	Akers et al. [8]
273.15	9.0	0.012	0.016	3.5	6.9	Akers et al. [8]
277.59	9.7	0.004	0.009	2.8	4.2	Reamer et al. [7]
283.15	8.3	0.007	0.010	4.6	2.2	Price and Kobayashi [9]
294.26	9.7	0.004	0.016	4.4	4.8	Reamer et al. [7]
310.93	9.0	0.006	0.021	5.9	6.6	Reamer et al. [7]
327.59	7.6	0.010	0.014	8.0	4.4	Reamer et al. [7]
344.26	6.2	0.009	0.009	10.1	2.5	Reamer et al. [7]
360.93	5.0	0.003	0.020	21.0	2.6	Reamer et al. [7]
91.70 ^c	^e	0.041	^d	19.2	^d	Cheung and Wang [11]
112.50	^e	0.012	^d	6.8	^d	Cheung and Wang [11]
114.10	^e	0.042	0.0005	10.5	95.2	Poon and Lu [21]
118.30	^e	0.039	0.0006	8.8	92.1	Poon and Lu [21]
122.20	^e	0.060	0.0006	15.9	80.5	Poon and Lu [21]
123.15	^e	0.013	^d	5.7	^d	Skripka et al. [16]
143.15	^e	0.015	^d	5.2	^d	Skripka et al. [16]
144.26	^e	0.043	0.0006	5.0	78.9	Price and Kobayashi [9]
157.59	^e	0.036	^d	8.3	^d	Akers et al. [8]
172.04	^e	0.005	0.0021	1.7	41.8	Price and Kobayashi [9]
174.26	^e	0.023	0.0012	5.2	68.9	Akers et al. [8]
194.82	4.1	0.017	0.004	5.0	30.4	Akers et al. [8]
199.82	4.1	0.010	0.004	4.2	17.6	Price and Kobayashi [9]
213.15	6.2	0.015	0.006	5.0	16.0	Akers et al. [8]
226.48	7.6	0.024	0.007	4.9	12.6	Akers et al. [8]
293.15	9.1	0.020	0.016	9.1	1.9	Sage et al. [6]
328.15	7.6	0.018	0.012	13.2	4.7	Sage et al. [6]
343.15	6.1	0.014	0.018	19.1	4.4	Sage et al. [6]
353.15	5.6	0.017	0.025	29.4	5.2	Sage et al. [6]

^aThe deviations in the K values are expressed as percentages of the experimental K values.

^bThe data point with lowest methane concentration was omitted for these isotherms as being inconsistent with the Peng-Robinson calculations.

^cAt the lower temperatures, the maximum pressure was simply the highest pressure point reported. At higher temperatures convergence could not be obtained for points at pressures above those indicated in this table.

^dNo y values were measured.

^eIsotherms in the lower part of the table (91.70 K to 353.15 K isotherms) involve greater scatter in the data, are not highly consistent with the isotherms in the upper part of the table, and/or are thermodynamically inconsistent.

^fBinary data taken as part of the ternary $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_3\text{H}_8$ study.

ing least-squares coefficients with their standard deviations are shown in table 9. Standard deviation in V^E for the fit was $0.020 \text{ cm}^3/\text{mol}$, with a maximum deviation of $0.037 \text{ cm}^3/\text{mol}$. This maximum value is less than 0.1% of the smallest mixture molar volume and certainly within the estimated absolute uncertainties in the V^E data. A two-term Redlich-Kister expansion, again with coefficients quadratic in temperature, gave a standard deviation of $0.030 \text{ cm}^3/\text{mol}$. This fit was considered satisfactory; however, the plots of V^E against mole fraction methane along isotherms were of peculiar shape at low methane concen-

tration. Since there are no data in this region, it can not be stated with certainty that the three-term form extrapolates more accurately to low methane concentrations than the two-term form. It does appear that the three-term form is somewhat more reasonable, based on the V^E behavior for other systems.

In figure 3, curves are shown of V^E versus mole fraction methane at 90 K, 110 K, and 130 K from the equation in table 9. These V^E values may be considered to be at zero pressure, though evaluated at the mixture saturation pressures, since differences are less than $0.01 \text{ cm}^3/\text{mol}$.

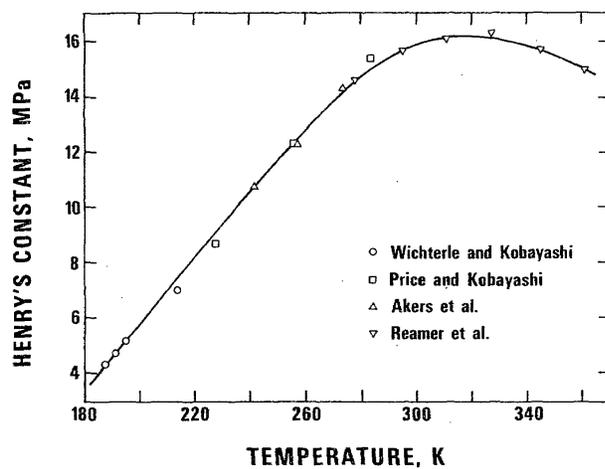


FIGURE 4. Henry's constants (H_{12}) at the pure propane vapor pressure as a function of temperature for methane + propane.

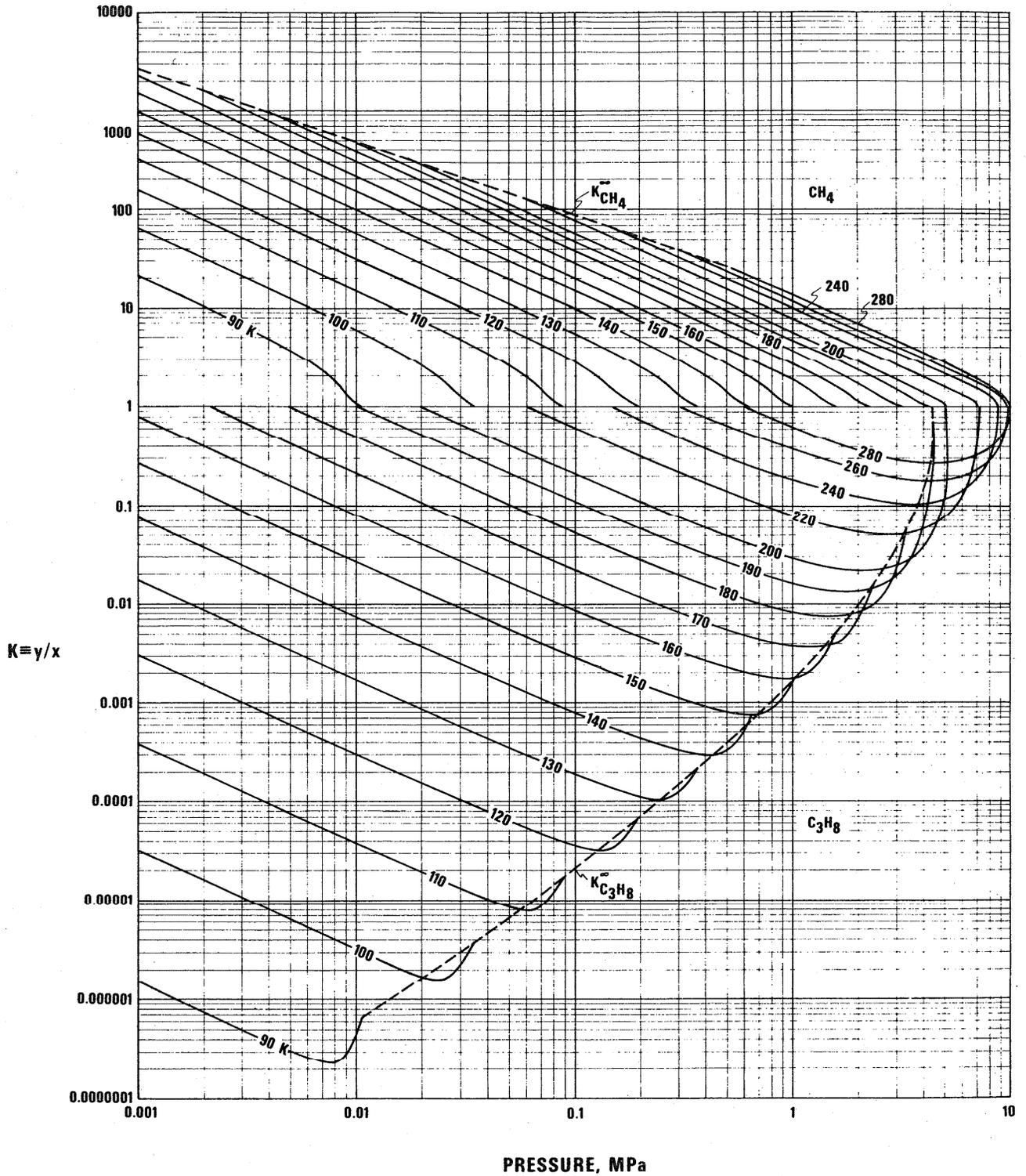


FIGURE 5. K values (y/x) versus pressure along isotherms for methane + propane.

TABLE 8. Coefficients for temperature-dependent Redlich-Kister equation determined by fit of H^E data at 91.5 K and 112.0 K



$$H^E = x_1 x_2 [(A_0 + A_1 T) + (B_0 + B_1 T) (x_1 - x_2)]$$

Coefficient	Value ^a	Standard deviation ^a
A_0	1062.81	15.2
A_1	-4.8754	0.15
B_0	203.94	54.5
B_1	-0.6514	0.52

^aUnits are such that H^E is in J/mol when T is in kelvins.

TABLE 9. Coefficients for temperature-dependent Redlich-Kister equation determined by fit of V^E data at 91 K to 130 K



$$V^E = x_1 x_2 [(A_0 + A_1 T + A_2 T^2) + (B_0 + B_1 T + B_2 T^2) (x_1 - x_2) + (C_0 + C_1 T + C_2 T^2) (x_1 - x_2)^2]$$

Coefficient	Value ^a	Standard deviation ^a
A_0	-6.182	1.8
A_1	0.13852	0.034
A_2	-0.0010142	0.00016
B_0	17.875	14.7
B_1	-0.34944	0.30
B_2	0.0015535	0.0015
C_0	-27.096	30.8
C_1	0.54203	0.62
C_2	-0.0027772	0.0031

^a Units are such that V^E is in cm^3/mol when T is in kelvins.

Acknowledgments

The orthogonal collocation computer program and some of the calculated results therefrom were supplied by W. R. Parrish. Financial support for this work was provided by the Office of Standard Reference Data, National Bureau of Standards.

Notation

Symbols

- $A_0, A_1, A_2,$
 $B_0, B_1, B_2,$ = Redlich-Kister coefficients
 $C_0, C_1, C_2,$
 G^E = excess Gibbs energy
 H_{12} = Henry's constant
 H^E = excess enthalpy or heat of mixing
 j_{12}, k_{12} = equation-of-state interaction constants, dimensionless

Symbols (cont.)

- K = y/x
 P = pressure
 R = gas constant
 T = absolute temperature
 V^E = excess volume
 x = liquid mole fraction
 y = vapor mole fraction
 γ = liquid activity coefficient, dimensionless

Subscripts

- 1 = methane
 2 = propane
 c = critical

Superscripts

- S = saturation conditions
 ∞ = value at infinite dilution

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