

Dew-point loci for methane-n-pentane binary system

Roger J. J. Chen, Patsy S. Chapplelear, and Riki Kobayashi

J. Chem. Eng. Data, **1974**, 19 (1), 58-61 • DOI: 10.1021/je60060a010

Downloaded from <http://pubs.acs.org> on December 20, 2008

More About This Article

The permalink <http://dx.doi.org/10.1021/je60060a010> provides access to:

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article



ACS Publications
High quality. High impact.

temperature gets lower. Their smoothed data at -140°F are about four times higher than ours. This is the region where the vapor phase is so dilute in *n*-butane (0.005 in mole fraction) that the ordinary chromatographic method approaches its limit.

Acknowledgment

The late W. E. A. Ruska designed the equilibrium cell and metering pumps used in this experimental work. Phillips Petroleum Co. provided the research grade hydrocarbons.

Literature Cited

- (1) Chen, R. J. J., Ruska, W. E. A., Chappellear, P. S., Kobayashi, R., *Advan. Cryog. Eng.*, **18**, G-1 (1972).

- (2) Comité International des Poids et Mesures, *Int. J. Sci. Metrol.*, **5**, 35 (1969).
(3) Jansson, V., Gielen, H., DeBoelpaep, J., Verbeke, O. B., *Physica*, **46**, 213 (1970).
(4) Roberts, L. R., Wang, R. H., Azarnoosh, A., McKetta, J. J., *J. Chem. Eng. Data*, **7**, 484 (1962).
(5) Ruska, W. E. A., Carruth, G. F., Kobayashi, R., *Rev. Sci. Instrum.*, **43**, 1331 (1972).
(6) Sage, B. H., Hicks, B. L., Lacey, W. N., *Ind. Eng. Chem.*, **32**, 1085 (1940).
(7) Vennix, A. J., PhD thesis, Rice University, Houston, Tex., April 1966.
(8) Wang, R. H., McKetta, J. J., *J. Chem. Eng. Data*, **9**, 30 (1964).

Received for review April 19, 1973. Accepted October 9, 1973. Financial support for Roger J. J. Chen was provided by the Natural Gas Processors Association. The remainder of the cost of the investigation was supported by the National Science Foundation, the American Gas Association, and the Columbia Gas System Service Corp.

Dew-Point Loci for Methane-*n*-Pentane Binary System

Roger J. J. Chen, Patsy S. Chappellear,¹ and Riki Kobayashi

Department of Chemical Engineering, William Marsh Rice University, Houston, Tex. 77001

Dew-point loci for the binary system of methane and normal pentane were determined at nine temperatures from 0° to -100°C from 20 up to 2200 psia. A constant flow gas saturation technique was used for this experimental study. Quadruple-valued dew points in a narrow concentration range were observed for isotherms immediately above the critical temperature of pure methane.

No equilibrium-phase composition data for the methane-*n*-pentane binary system exist for temperatures below 0°C owing to the difficulty in the determination for the dew-point data. As shown in the previous paper on methane-*n*-butane (2), the errors which are inherent in pulsed chromatography become significant in the determination of the trace amount of the heavier component in the vapor phase. As the molecular size of the heavier component gets larger, its concentration becomes more dilute in the vapor phase; thus, the determination of the dew-point values for the methane-*n*-pentane system is more difficult than the methane-*n*-butane system.

The objective of this study is to determine the dew-point data for the methane-*n*-pentane system by the constant flow gas saturation technique which was used in the previous study. These data can then be combined with liquid-phase concentration data determined by ordinary chromatographic methods [as has been done by Elliot et al. (3) for the methane-*n*-butane system] to form a complete set of equilibrium data for this binary system.

Experimental Method

The experimental equipment and procedure are essentially the same as discussed in the previous paper. However, it was necessary to install a magnetic circulation pump to recycle the vapor from the top of the equilibrium cell to the inlet of the presaturator. This will accelerate the time to achieve equilibrium, particularly for high system pressures. Another Heise gage with a range of 0-4000 psia was added to the pressure measuring system for high-pressure measurements.

¹ To whom correspondence should be addressed.

The data were taken in two periods; in the first period, the dew-point values were determined up to 1000 psia for all isotherms. Since the equilibrium condition could be reached in a short time, the recycle pump was not needed in this period. In the second period, a high-pressure methane cylinder was used to determine the dew-point data above 1000 psi for temperatures at 0° , -25° , and -50°C . The recycle magnetic pump was installed and used in this period of investigation to shorten the time for reaching equilibrium. The points at 1000 psia were redetermined; they were in good agreement with the values determined in the first period.

Minor modifications were also necessary in the equipment for calibration. Because *n*-pentane is in the liquid state at room temperature and atmospheric pressure, it has to be gasified to insure good mixing with methane. In the previous work, the micropump and mixing valve were kept in the same temperature-controlled air bath at 32°C . The insulation material for the air bath cannot withstand higher temperature; therefore, for this study the mixing valve was placed into a separate insulated box above 70°C , which is well above the boiling point of *n*-pentane (36.07°C). This insures that the *n*-pentane becomes gasified at the valve seat. To avoid condensation, both the inlet and outlet lines of the mixing valve were insulated and heated above 70°C . The thermoconductivity detector was kept in a constant temperature air bath controlled at 74°C .

The calibration curve of the detector for this system is shown as curve B in Figure 2 of the previous paper (2). The response of the detector was linear from 4×10^{-5} to 0.05 mole fraction of normal pentane; mole fractions greater than 0.05 gave a curved response. The response curve was fit by a linear equation and a third-order polynomial for the respective regions by the least-squares method.

Materials

The *n*-pentane used in this investigation was donated by Phillips Petroleum Co. It was research grade with purity of 99.98 mol %. The ultra high-purity methane used in the first period was bought from Matheson Gas Products Co. The high-pressure (3500 psi) cylinder of pure meth-

ane used in the second period was bought from IWECO. It was a product of Union Carbide Chemicals Corp. The purity of methane in both cylinders was 99.97 mol % minimum. No further purification was made.

Experimental Results

The experimental dew-point data for the methane-*n*-pentane system are shown in Table I at temperatures

Table I. Dew-Point Data for Methane-*n*-Pentane System

$T = 0.01^{\circ}\text{C} = 32.02^{\circ}\text{F}$		$T = -24.99^{\circ}\text{C} = -12.98^{\circ}\text{F}$		$T = -49.97^{\circ}\text{C} = -57.95^{\circ}\text{F}$	
Press, psia	Mole fraction of <i>n</i> -pentane	Press, psia	Mole fraction of <i>n</i> -pentane	Press, psia	Mole fraction of <i>n</i> -pentane
20.8	0.183	20.2	0.0532	20.2	0.0106
25.6	0.151	25.2	0.0427	25.2	0.00874
49.9	0.0790	50.2	0.0220	50.2	0.00448
100.0	0.0419	100.2	0.0124	100.2	0.00252
150.0	0.0298	150.2	0.00901	150.2	0.00187
200.2	0.0242	200.2	0.00719	200.2	0.00151
300.2	0.0186	300.2	0.00579	300.2	0.00144
400.2	0.0161	400.2	0.00525	400.2	0.00146
600.	0.0145	600.	0.00522	600.	0.00178
800.	0.0144	800.	0.00600	800.	0.00264
1000.	0.0161	1000.	0.00777	1000.	0.00478
1200.	0.0182	1200.	0.0100	1200.	0.00942
1400.	0.0218	1400.	0.0155	1405.	0.0212
1600.	0.0278	1600.	0.0247		
1800.	0.0377	1800.	0.0413		
2000.	0.0550	1903.	0.0560		
2195.	0.0891				
2200.	0.0911				

$T = -74.97^{\circ}\text{C} = -102.95^{\circ}\text{F}$		$T = -80.57^{\circ}\text{C} = -113.03^{\circ}\text{F}$		$T = -80.95^{\circ}\text{C} = -113.71^{\circ}\text{F}$	
20.2	0.00137	500.2	0.000307	20.1	0.000792
25.2	0.00108	600.	0.000589	25.0	0.000628
50.2	0.000580	625.	0.000712	50.1	0.000329
100.2	0.000364	650.	0.000977	100.1	0.000224
150.2	0.000300	660.	0.00109	150.1	0.000193
200.2	0.000298	670.	0.00123	200.1	0.000179
300.2	0.000312	680.	0.00131	300.1	0.000176
400.2	0.000370	690.	0.00106	400.1	0.000213
600.	0.000647	695.	0.00121	500.1	0.000300
700.	0.00112			600.	0.000573
750.	0.00155			625.	0.000729
800.	0.00351			650.	0.000947
				660.	0.00107
				670.	0.00110
				680.	0.000946
				685.	0.000808
				690.	0.000894

$T = -82.07^{\circ}\text{C} = -115.73^{\circ}\text{F}$		$T = -82.57^{\circ}\text{C} = -116.63^{\circ}\text{F}$		$T = -99.98^{\circ}\text{C} = -147.96^{\circ}\text{F}$	
20.3	0.000705	20.2	0.000668	20.1	0.000102
100.3	0.000203	25.2	0.000540	25.2	0.000084
300.3	0.000158	50.2	0.000291	50.2	0.000060
500.3	0.000270	100.2	0.000195	100.2	0.000042
600.	0.000558	150.2	0.000168	150.2	0.000039
625.	0.000759	200.2	0.000154	200.2	0.000037
650.	0.000875	300.2	0.000150	300.2	0.000036
660.	0.000832	400.2	0.000174	350.2	0.000032
670.	0.000624	500.2	0.000257		
675.	0.000422	600.	0.000540		
677.	0.000274	625.	0.000697		
678.	0.000300	651.	0.000653		
		660.	0.000459		

from 0° down to -100°C . The pressure range of the data goes from 20 psia up either to the critical pressure of the mixture (for isotherms above the critical temperature of methane) or to the vapor pressure of pure methane (for isotherms below the critical temperature of methane).

Figure 1 is the pressure-concentration plot for isotherms from 0° to -50°C . An expanded concentration scale was used in Figure 2 to show the details of the

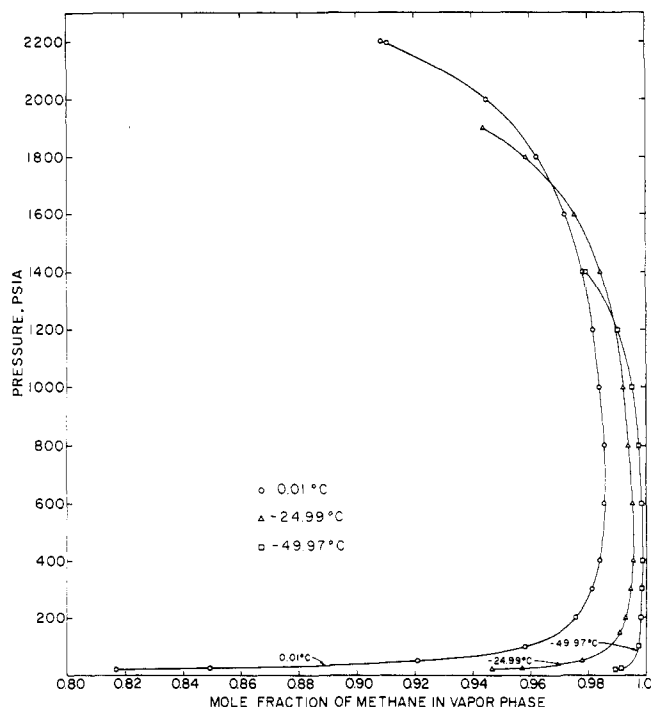


Figure 1. Isothermal dew-point data for methane-*n*-pentane at 0° , -25° , and -50°C

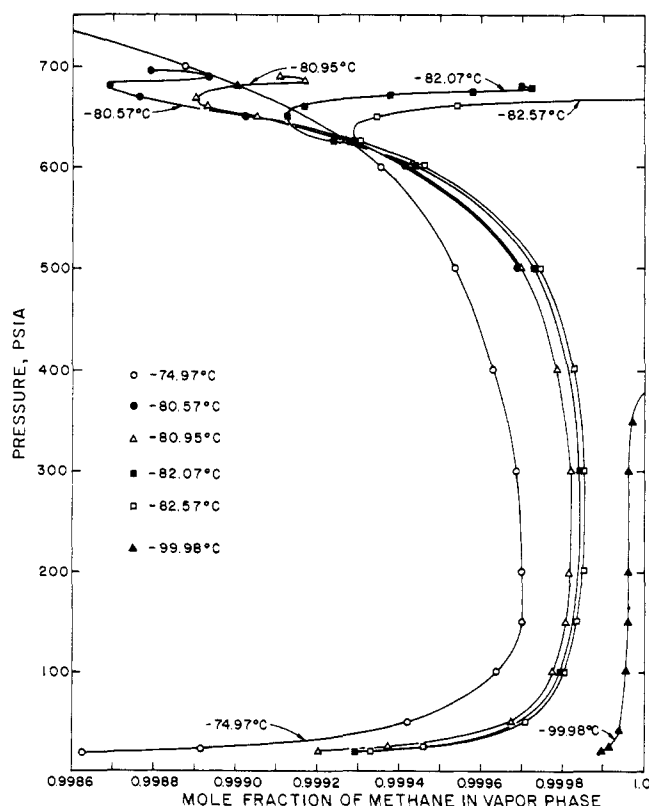


Figure 2. Isothermal dew-point data for methane-*n*-pentane at -75° to -100°C . Note magnitude of mole fraction scale

dew-point data in the low-temperature range (-75° to -100°C).

The isobaric behavior of the data is shown in Figure 3; the logarithm of the mole fraction of *n*-pentane was plotted against the reciprocal of the absolute temperature of the system. The temperatures of the system are reported on the IPTS (1968) temperature scale.

Accuracy

The sources of errors include the fluctuations in system temperature, the error in pressure measurement, the

error in calibration of the detector, and the error in the readout system. They were about the same magnitude as reported in the previous paper, since the same experimental method and equipment were used. The overall error in the dew-point data is either less than 2% or 0.00001 in mole fraction of *n*-pentane depending on which is larger.

Discussion of Results

Since we have found an unusual S-type bend in the upper part of the pressure-concentration curves at and immediately below the critical temperature of methane in the previous study of methane-*n*-butane (2), we decided to make some measurements at temperatures immediately above the critical temperature of methane in this study. Three temperatures were chosen at 0.5° , 1.62° , and 2°C above the critical temperature of methane. Double bends were found in the upper parts of these isotherms. Because of the continuity of the phase boundary surface, they still preserve the S-type bend which is evident at the critical temperature of methane (-80.95°C).

When the system pressure is increased approaching the critical point of the mixture, the thermodynamic constraint at critical $(\partial P/\partial y)_T = 0$ forces it to bend back to the critical points. Because of the double bending *P*-*y* curves, for a certain narrow range of concentration at a temperature immediately above the critical temperature of methane, quadruple-valued dew points exist for a given concentration of the system. As the system temperature becomes more removed from the critical, the bends will disappear; thus, no quadruple-valued behavior was observed for the isotherm at -75°C . The temperature region over which this behavior exists may be expected to increase as the molecular-weight difference of the components increases.

With the addition of the recycle magnetic pump, the high-pressure data are believed to be more accurate than those previously reported (2). Critical opalescence was noticed when the system reached the critical point; this phenomenon was not observed in the previous work. We believe the critical-point measurements are more accurate for this system.

Comparison of Data

No phase-equilibrium composition data were found for the methane-*n*-pentane system in the low-temperature

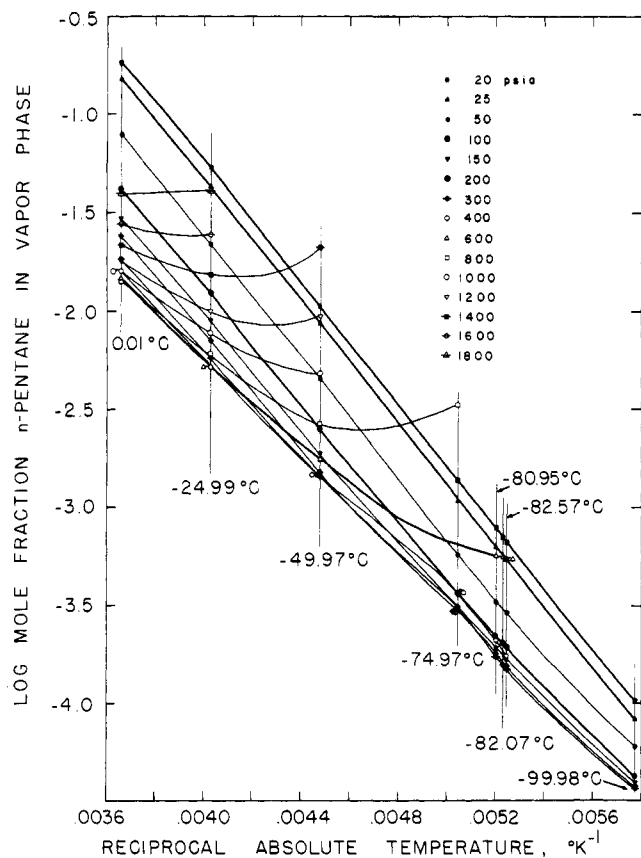


Figure 3. Isobaric dew-point data for methane-*n*-pentane from 20 to 1800 psia

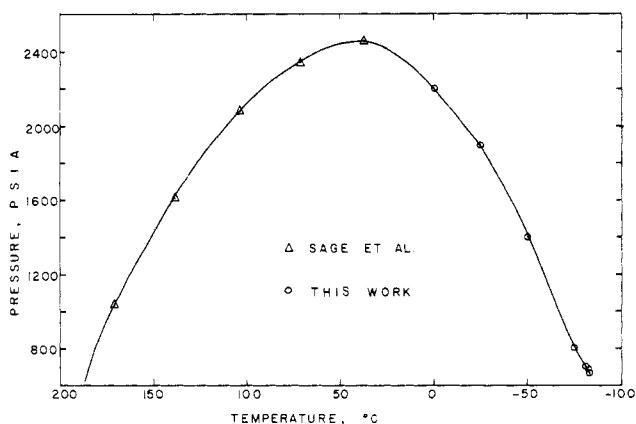


Figure 4. Critical pressure-temperature locus for methane-*n*-pentane system

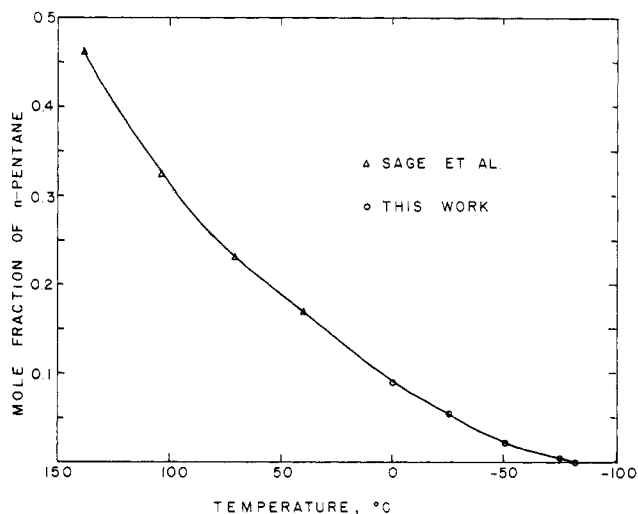


Figure 5. Critical composition locus for methane-*n*-pentane system

range. Sage et al. (4) reported equilibrium composition data for this system for temperatures from 100° up to 340°F.

Figure 4 shows their critical pressures for the methane-*n*-pentane system at high temperature match quite well with our critical pressures at low temperatures.

The critical composition loci of this system are shown in Figure 5. The critical compositions of Sage et al. have been converted from weight fraction to mole fraction to make this plot on the same basis. Our data also join smoothly with theirs in this plot.

Generalization

The triple-valued dew points observed in the methane-*n*-butane system (2) and the quadruple-valued dew points observed here are a general phenomena not specifically limited to these systems. Similar behavior will be observed for other binary systems of widely different rela-

tive volatilities. The pressure for such systems at the critical point at temperatures immediately above the critical temperature of the more volatile component falls below the critical pressure of that component. The authors have named this phenomenon "double retrograde vaporization" (7).

Literature Cited

- (1) Carnahan, N. F., Chen, R. J. J., Elliot, D. G., Chappellear, P. S., Kobayashi, R., presented at Van der Waals Centennial Conference, Amsterdam, The Netherlands, August 1973.
- (2) Chen, R. J., Chappellear, P. S., Kobayashi, R., *J. Chem. Eng. Data*, **19** (1), 53 (1974).
- (3) Elliot, D. G., Chen, R. J. J., Chappellear, P. S., Kobayashi, R., *J. Chem. Eng. Data*, *ibid.*, p 71.
- (4) Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., *Ind. Eng. Chem.*, **34**, 1108 (1942).

Received for review April 19, 1973. Accepted October 9, 1973. Financial support for Roger J. J. Chen was provided by the Natural Gas Processors Association. The remainder of the cost of the investigation was supported by the National Science Foundation, the American Gas Association, and the Columbia Gas Systems Service Corp.

Vapor-Liquid Equilibria in Three Binary and Ternary Systems Composed of *n*-Butane, Butene-1, and Butadiene-1,3

Dale R. Laurance and George W. Swift¹

Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, Kan. 66044

Total pressure and PVT data are reported on *n*-butane, butene-1, and butadiene-1,3 and their mixtures over the temperature range 100–150°F and the pressure range 20–500 psia. The data have an estimated precision of 0.1%. The experimental data are correlated, and the vapor-liquid equilibrium behavior of the binary systems is computed by integration of the general coexistence equation by the method of Manley and Swift. Wilson parameters for the binary systems are computed from the experimental data and used to predict the ternary system bubble-point pressures. The predicted pressures are compared with experimental results to test the validity of the predictions, and satisfactory agreement is achieved. No ternary azeotrope is observed over the range of conditions investigated. The precision of the computed results of this work is 0.003, 0.001, 0.007, and 0.005 relative volatility units for the systems butene-1-*n*-butane, butene-1-butadiene-1,3, *n*-butane-butadiene-1,3, and *n*-butane-butene-1-butadiene-1,3, respectively.

The accurate design of distillation units for systems made up of close boiling components requires precise vapor-liquid equilibrium-phase data. The C₄ hydrocarbon systems composed of mixtures of *n*-butane, butene-1, and butadiene-1,3 (butane, butene, and butadiene for brevity) are close boiling systems for which a paucity of vapor-liquid equilibrium data are available.

As shown by Manley and Swift (11) and Laurance and Swift (8), the direct sampling procedure for obtaining vapor-liquid equilibrium data by measuring the compositions of coexisting vapor and liquid phases at equilibrium is in general an unsatisfactory method for close boiling systems, and the total pressure method is far superior in precision. Since the relative volatility is close to 1 in

close boiling systems, errors in measured phase compositions lead to large errors in the computed relative volatilities, and in the subsequent design calculations, the level of imprecision is roughly 10 times the expected error in the measured phase compositions.

Manley (10) developed a method for computing vapor-phase compositions from experimental total pressure data by integrating the isothermal general coexistence equation. The method is described by Manley and Swift (11) and is completely rigorous and can be applied to a binary system if the following experimental data are available: the pure component and binary mixture bubble-point pressure as a function of liquid composition and temperature, and the vapor and liquid-phase specific volumes as a function of pressure, temperature, and composition.

Correlations of the experimental data are used to numerically integrate the isothermal general coexistence equation, and thermodynamically consistent vapor-phase compositions are computed. The significant advantage of the total pressure method is that the bubble point and PVT data may be used to calculate phase compositions with considerably greater precision than they can be measured in close boiling systems.

Experimental

The experimental apparatus used in this work has been described most recently by Laurance (7) and is discussed in earlier articles by Laurance and Swift (8), Manley (10), and Manley and Swift (11).

The materials used in this work are Phillips research-grade chemicals and have a stated purity of not less than 99.97, 99.85, and 99.89 mol % for butane, butene, and butadiene, respectively. The most probable impurities are isobutane in the butane, isobutylene and butadiene in the butene, and butene and tertiary butyl catechol (TBC) in the butadiene.

¹ To whom correspondence should be addressed.