Vapor-Liquid Equilibrium of Methane–*n*-Pentane System at Low Temperatures and High Pressures

Teh-Cheng Chu,[1] Roger J. J. Chen,[2] Patsy S. Chappelear,[3] and Riki Kobayashi[3]
Department of Chemical Engineering, William Marsh Rice University, P.O. Box 1892, Houston, Tex. 77001

Measurements of the bubble-point compositions are reported and combined with earlier dew-point data from this laboratory to give *K*-values for the methane–*n*-pentane system at seven temperatures: 0°, −25°, −50°, −75°, −80.95°, and −100°C from the vapor pressure of *n*-pentane up to the critical pressure or vapor pressure of methane. The data may also be evaluated isobarically without interpolation being necessary.

The existing data on the methane–*n*-pentane system are above the ice point, with the single exception of a Russian investigation (*10*) at 0°C only, as reported in the recent bibliography (*6*) on vapor-liquid equilibria from Berlin. The investigations at higher temperatures include three isotherms by Boomer et al. (*3*) and extensive investigations by Sage and coworkers (*2, 8, 9*). These data reported here cover the low-temperature range 0° down to −100°C, a region of present day application in gas processing. The publication by Berry and Sage (*2*) is an excellent compilation and evaluation of previous works, but it does not present any new experimental data. The work of Boomer et al. (*3*) was actually a ternary; their methane had 5.6% nitrogen.

Experimental Details

The purpose of this study was to measure the bubble-point compositions of the methane–*n*-pentane system at the same conditions as an earlier dew-point investigation (*5*) which used an elution technique. This study used the same recycle equilibrium apparatus (Figure 1) as used by Elliot et al. (*7*) in the methane–*n*-butane investigation. Only details specific to this investigation are presented here.

The problem of nonhomogeneous evaporation of the liquid phase in the sample line encountered by Elliot was more pronounced in this work. The temperature of the sampling line was kept at more than 75°C to keep the sample in the vapor phase. A stirred pot with a volume of approximately 150 ml was used to homogenize the sample of the liquid phase (as a vapor) by mixing.

The chromatographic column was a 4-ft length of ⅛-in. o.d. stainless-steel tubing packed with 80–100 mesh Duropak (OPN/PORASIL C). The same (*7*) flame ionization detector, chromatograph, and digital integrator were used. In addition to the two Heise gages (0–300, 0–2000 psia) used by Elliot, another Heise gage (0–4000 psia) was used in this study.

The experimental procedure was the same as used by Elliot. The isotherms were run in order of decreasing temperature. An average of 4 hr was required to attain steady state, after which at least six analyses were made.

Material Used

Ultrahigh purity methane was purchased from Matheson Gas Products Co. The gas was reported to analyze at least 99.97% methane, with the total amount of major impurities as 105 ppm. Research grade *n*-pentane (99.93%) was provided by Phillips Petroleum Co., with the most probable impurity as isopentane. Note that the method of analysis used in the dew-point measurements (*5*) essentially negates the impurities in the methane, since the difference between the methane from the supply cylinder and the methane vapor saturated with *n*-pentane caused the signal on the thermal conductivity cell used as a detector in the elution experiment.

Error Analysis

The error analysis is the same as for Elliot's work. The factors contributing are: temperature, controlled to ±0.02°C; pressure, controlled to ±1 psi; pressure, measured by Heise gages calibrated to 0.1% of full scale; concentration, determined by calibration and peak area ratios. The errors in the

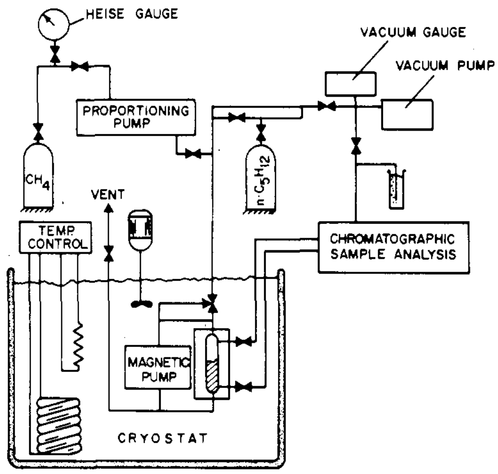

Figure 1. Recycle V-L-E apparatus

Table I. Bubble-Point Data for Methane–*n*-Pentane System
No corresponding dew point

Press, psia	Mole fraction of methane	Press, psia	Mole fraction of methane
T = 0.01°C = 32.02°F		T = −24.81°C = −12.66°F	
2100.	0.661	1850.	0.759
2150.	0.695	1880.	0.811
2190	0.767	1890.	0.859
T = −49.23°C = −56.61°F		T = −73.29°C = −99.92°F	
1300.	0.750	700.	0.6552
1330.	0.785	750.	0.7333
1370.	0.841	780.	0.799
1400.	0.9437	790.	0.863
T = −80.52°C = −112.94°F		T = −96.94°C = −142.49°F	
640.	0.835	250.	0.403
651.	0.9057	350.2	0.6262
660.	0.9538	370.	0.759
T = −78.98°C = −110.16°F			
650.	0.7386		
670.	0.8438		
680.	0.90431		

---

[1] Present address, Exxon Research Division, Baytown, Tex.
[2] Present address, Hudson Engineering Corp., Houston, Tex.
[3] To whom correspondence should be addressed.

Table II. Vapor-Liquid Equilibrium Data of Methane—*n*-Pentane System

x Methane	*y* Methane[a]	Psia	Atm	*K* Methane	*K* *n*-Pentane
		T = 0.01°C = 273.16K = 32.02°F = 491.69°R			
0.0000	0.0000	4.78[b]	0.0325[b]	147.[c]	1.000
0.09091	0.9758	200.2	13.622	10.73	0.02662
0.1653	0.9839	400.2	27.230	5.953	0.01929
0.2320	0.9855	600.	40.826	4.249	0.01888
0.2920	0.9856	800.	54.435	3.375	0.02034
0.3481	0.9839	1000.	68.044	2.854	0.02457
0.4005	0.9818	1200.	81.652	2.452	0.03036
0.4480	0.9782	1400.	95.261	2.183	0.03949
0.4980	0.9722	1600.	108.870	1.952	0.05538
0.5501	0.9623	1800.	122.478	1.750	0.08378
0.6117	0.9450	2000.	136.088	1.545	0.1416
0.9089[a]	0.9089[a]	2200.[d]	149.696[d]	1.000	1.000
		T = −24.81°C = 248.34K = −12.66°F = 447.01°R			
0.0000	0.0000	1.15[b]	0.0785[b]	1550.[c]	1.000
0.04943	0.9876	100.2	6.818	19.98	0.01304
0.1119	0.99281	200.2	13.622	8.872	0.008096
0.2089	0.99475	400.2	27.230	4.763	0.006636
0.2958	0.99478	600.	40.826	3.363	0.007412
0.3695	0.99400	800.	54.435	2.690	0.009516
0.4309	0.99223	1000.	68.044	2.303	0.01365
0.4965	0.9900	1200.	81.652	1.994	0.01986
0.5708	0.9845	1400.	95.261	1.725	0.03612
0.6491	0.9753	1600.	108.870	1.503	0.07039
0.7279	0.9587	1800.	122.478	1.317	0.1518
...	...	1904.[d]	129.559[d]	1.000	1.000
		T = −49.23°C = 223.92K = −56.61°F = 403.06°R			
0.0000	0.0000	0.210[b]	0.0143[b]	6700.[c]	1.000
0.08592	0.99738	100.2	6.818	11.61	0.002861
0.1667	0.99842	200.2	13.622	5.990	0.001898
0.2878	0.99848	400.2	27.230	3.469	0.002140
0.3888	0.99815	600.	40.826	2.567	0.003026
0.4737	0.99738	800.	54.435	2.106	0.004975
0.5652	0.99522	1000.	68.044	1.761	0.01099
0.6850	0.99071	1200.	81.652	1.446	0.02949
...	...	1417.[d]	96.421[d]	1.000	1.000
		T = −73.29°C = 199.86K = −99.92°F = 359.75°R			
0.0000	0.0000	0.0260[b]	0.00177[b]	40000.[c]	1.000
0.0566	0.99933	50.2	3.416	17.66	0.0007068
0.1166	0.999576	100.2	6.818	8.573	0.0004796
0.2212	0.999667	200.2	13.622	4.519	0.0004281
0.3758	0.999581	400.2	27.230	2.660	0.0006709
0.5265	0.999324	600.	40.826	1.898	0.001428
...	...	831.[d]	56.546[d]	1.000	1.000
		T = −78.98°C = 194.17K = −110.16°F = 349.51°R			
0.0000	0.0000	0.0147[b]	0.00100[b]	67000.[c]	1.000
0.1251	0.999735	100.1	6.811	7.991	0.0003027
0.2378	0.999781	200.1	13.616	4.204	0.0002870
0.4041	0.999732	400.1	27.225	2.474	0.0004496
0.6226	0.999404	600.	40.826	1.605	0.001578
...	...	722[d]	49.129[d]	1.000	1.000
		T = −80.52°C = 192.62K = −112.94°F = 346.73°R			
0.0000	0.0000	0.0125[b]	0.00085[b]	78000.[c]	1.000
0.1297	0.999767	100.2	6.818	7.708	0.0002675
0.2320	0.999811	200.2	13.622	4.310	0.0002464
0.4083	0.999775	400.2	27.230	2.448	0.0003810
0.6667	0.999425	600.	40.826	1.499	0.001726
...	...	695[d]	47.292[d]	1.000	1.000
		T = −96.94°C = 176.21K = −142.49°F = 317.18°R			
0.0000	0.0000	0.0019[b]	0.00013[b]	415000[c]	1.000
0.03195	0.999844	20.1	1.368	31.29	0.0001611
0.08509	0.999915	50.2	3.416	11.75	0.0000924
0.1681	0.999939	100.2	6.818	5.948	0.0000730
0.2504	0.999946	150.2	10.221	3.993	0.0000725
0.3316	0.999949	200.2	13.622	3.015	0.0000757
0.4819	0.999951	300.2	20.427	2.075	0.0000946
1.0000	1.0000	420.0[e]	28.579[e]	1.0000	0.0001[f]

[a] Interpolated from elution data (*5*). [b] Saturated vapor pressure of *n*-pentane (*4*). [c] $K_{CH_4}^{\infty}$. [d] Critical pressure. [e] Vapor pressure of methane (*1*). [f] $K_{nC_5H_{12}}^{\infty}$. Note: The instruments used were calibrated in °F and psia.

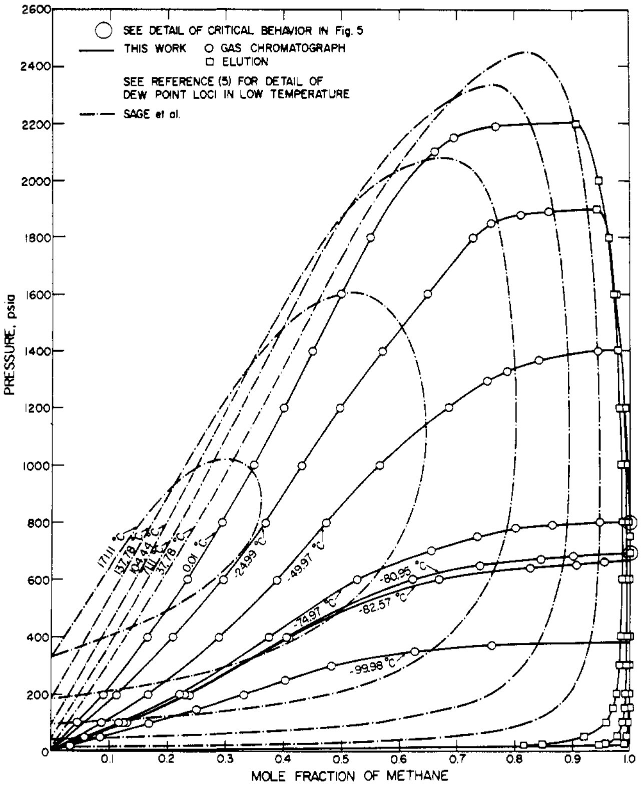

Figure 2. Pressure-composition diagram for methane–*n*-pentane system

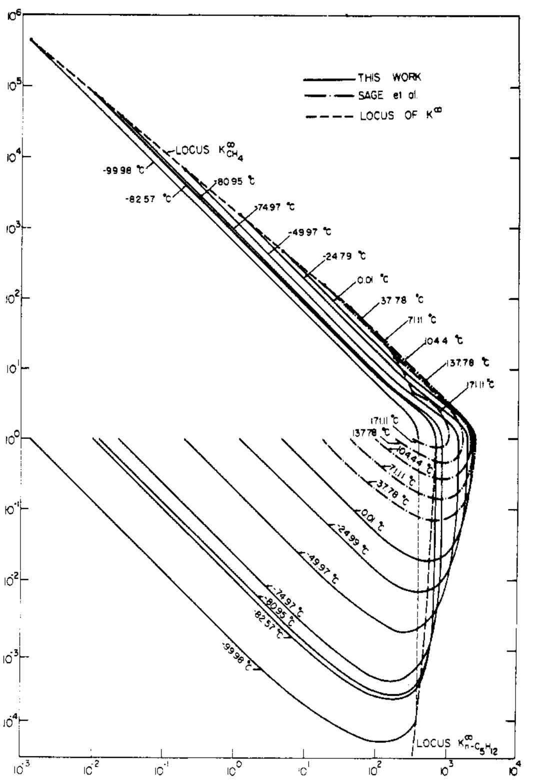

Figure 3. *K*-value vs. pressure along isotherms for methane–*n*-pentane system

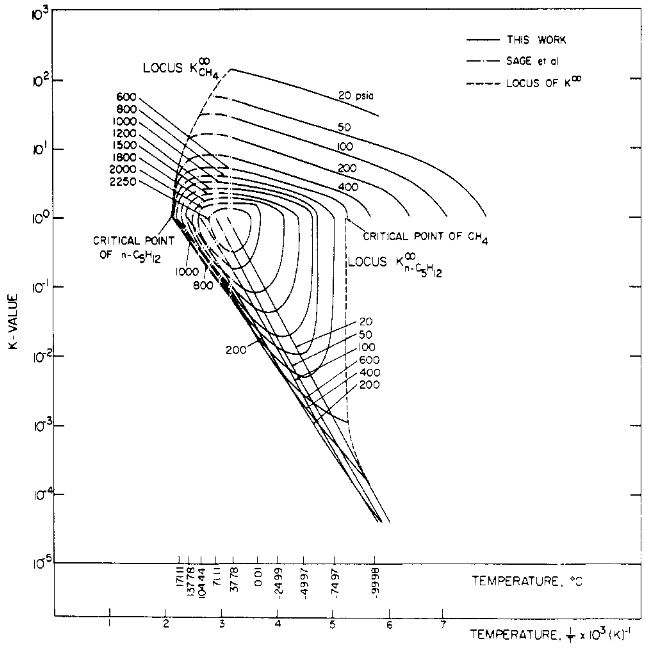

Figure 4. Temperature-*K*-value diagram for methane–*n*-pentane system

concentration measurement are at a maximum 2% or 0.005 in mole fraction; however, the vast majority of the data are good to four significant figures.

The dew-point measurements (*5*) reported the error in concentration either less than 2% or ±0.00001 in mole fraction of *n*-pentane. The total error in the resulting *K*-values will be a maximum of 2%.

Results

The experimental bubble-point data are tabulated in both Tables I and II and presented graphically in Figures 2 and 5. The data in Table I were taken at conditions *not* corresponding to pressure conditions for the dew-point data (*5*). Interpolated dew-point data are included in Table II along with limiting conditions. After galleys were prepared, an error in calculating the resistance for the temperature set point was found. This necessitated a small isobaric interpolation of the elution data to the conditions of this experiment. The corrected values are listed in the tables. The figures have not been corrected, since the error is not significant on the scale of Journal figures.

The original scale of the figures was over one meter on the side. In addition to the plots shown here, crossplots of isobaric concentration vs. reciprocal absolute temperature were prepared and used in evaluating the data. Figures 2–4 also indicate the higher temperature data of Sage and coworkers, which are consistent with these data.

Figure 5 shows the interesting behavior of the more volatile component as its critical temperature is approached.

Nomenclature

K = ratio of vapor concentration to liquid concentration
x = liquid concentration, mole fraction methane
y = vapor concentration, mole fraction methane
∞ = superscript denoting limiting value for the subscripted component at the limiting other pure component vapor pressure

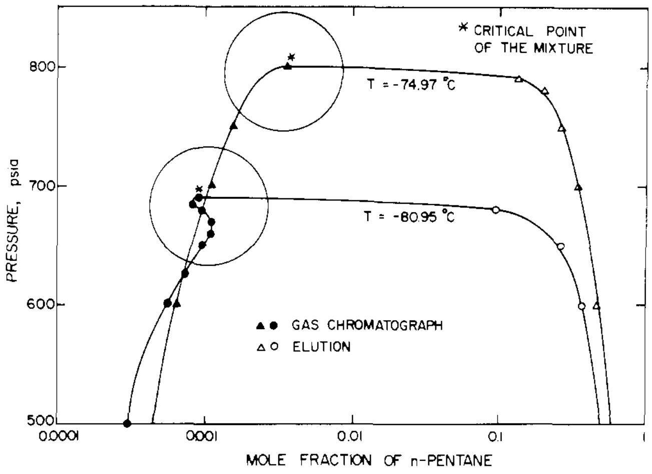

Figure 5. Detail of isotherms near critical point of methane (methane–*n*-pentane system)

Literature Cited

(1) API Research Project 44: "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", F. D. Rossini, Ed., Carnegie Press, Pittsburgh, Pa., 1953.

(2) Berry, V. M., Sage, B. H., *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **32,** 66 pp (1970).

(3) Boomer, E. H., Johnson, C. A., Piercey, A.G.A., *Can. J. Res.*, **B16,** 319 (1938).

(4) Carruth, G. F., Kobayashi, R., *J. Chem. Eng. Data,* **18,** 115 (1973).

(5) Chen, R.J.J., Chappelear, P. S., Kobayashi, R., *ibid.*, **19,** 58 (1974).

(6) Dellrich, L. R., Plöcker, U. J., Knapp, H., "Vapor-Liquid Equilibria", Institute of Thermodynamics at the Technical University of Berlin, Berlin, Germany, September 1973. (H. Knapp will supply single copies on request.)

(7) Elliot, D. G., Chen, R.J.J., Chappelear, P. S., Kobayashi, R., *J. Chem. Eng. Data,* **19,** 71 (1974).

(8) Sage, B. H., Reamer, H. H., Olds, R. H., Lacey, W. N., *Ind. Eng. Chem.*, **34,** 1108 (1942).

(9) Taylor, H. S., Wald, G. W., Sage, B. H., Lacey, W. N., *Oil Gas J.*, **38** (13), 46 (1939).

(10) Velikovskii, A. S., Stepanova, G. S., Vybornova, Ya. I., *Gazowaja Prom.*, **9** (2), 1 (1964).

Received for review December 20, 1974. Accepted July 24, 1975. Financial support provided by the American Gas Association, Columbia Gas Systems Service Corp., Gas Processors Association, and the National Science Foundation.

Isobaric Binary Vapor-Liquid Equilibria in Cyclohexane–*tert*-Butyl Alcohol and 2,4-Dimethylpentane–*tert*-Butyl Alcohol Systems

Raghunath P. Tripathi, Shri Krishna,[1] and Indar B. Gulati
Indian Institute of Petroleum, Dehra Dun, U.P., India

Measurements of binary vapor-liquid equilibria at 760 mm Hg pressure are reported for cyclohexane and 2,4-dimethylpentane separately with *tert*-butyl alcohol. The thermodynamic consistency of the experimental data under isobaric conditions is checked by Herington's area test, and the data are satisfactorily correlated by the two-parameter Wilson equation for both binary systems.

Cyclohexane and 2,4-dimethylpentane (2,4-DMP) are close boiling hydrocarbons forming a minimum boiling azeotrope (*6*) at 80.2°C. Their separation poses a problem and is facilitated by the use of polar solvents. Such situations are encountered in practical applications (*14*) during the purification of cyclohexane from commercial naphtha streams. Since most distillation processes are carried out at constant pressure rather than at constant temperature, temperature-composition (*t-x-y*) curves are more desirable for engineering calculations than pressure-composition curves, although from theoretical considerations the latter are preferred.

As part of our study of the vapor-liquid equilibrium (VLE) data of close boiling hydrocarbons in the presence of polar solvents, the VLE measurements of cyclohexane and 2,4-DMP have been studied with *tert*-butyl alcohol (TBA) at 760 mm Hg pressure. The generation of such binary equilibrium data on hydrocarbon-solvent systems helps in the development of correlations for testing the capability of predictive methods for multicomponent systems from binary data alone and also in better understanding the molecular processes in nonideal solutions. To the authors' knowledge, the VLE data of these two binary systems have not been reported previously.

Experimental

Materials. Cyclohexane and 2,4-DMP (manufactured by Phillips Petroleum Co.) were of 99.0 mol + % purity and were used as such without further purification. Tertiary butyl alcohol (obtained from M/S British Drug Houses, India) was dried over anhydrous calcium chloride and further purified by fractional distillation at a high reflux ratio in an Oldershaw column by collecting a heart cut and discarding the first 10% distillate and the last 15% residue. The important physical properties of the three components reported in Table I compare well with the literature values (*1, 10*).

Apparatus. The VLE data for the two binaries were studied in a modified Fowler-Norris (*2*) still with provision for vapor and liquid circulation. The reboiler, Cottrell pump, and equilibrium chamber were thoroughly lagged to avoid slugs of liquids rising up with vapors and for proper separation of vapor and liquid samples in the equilibrium chamber. The temperature in the equilibrium chamber was measured with the aid of mercury-in-glass thermometers within ±0.05°C after applying the following correction for the exposed stem (*3*):

$$t_c = t_o + 0.000158 \times l\ (to - tm)$$

where t_c is the corrected temperature, t_o and t_m are the observed and mean temperatures of the exposed stem, respectively, and l is the length in °C of the exposed stem. The pressure in the system was maintained at 760 ± 0.5 mm Hg with the help of a suitable pressure-regulating device. To establish the equilibrium time, a number of trial runs on each system

---

[1] To whom correspondence should be addressed.