Vapor-Liquid Equilibrium Relationships of Binary Systems

Propane–*n*-Alkane Systems, *n*-Hexane and *n*-Heptane

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The *P-V-T-x* relationships of the propane–*n*-hexane system and the *P-T-x* relationships of the propane–*n*-heptane system have been determined. The experimental results cover a range from about 200 psia and room temperature to the highest pressure and temperature at which liquid and vapor can coexist. The data are presented in tabular form. *P-T-x*, density-*T-x*, and *T-x* diagrams are given.

This investigation of the *P-V-T-x* relationships of binary systems composed of the *n*-alkanes with propane was undertaken to study the effect of the relative size of the molecules on the phase behavior of their mixtures. In a previous paper (*2*) these data were reported for the binary systems composed of *n*-butane and *n*-pentane with propane. In this paper, a summary of the *P-V-T-x* data for the propane-*n*-hexane and the *P-T-x* data for the propane-*n*-heptane systems are given.

EXPERIMENTAL

The *P-V-T-x* relationships were obtained by the experimental determination of the *P-T* border curves of a series of mixtures of each of the binary systems. The relationships between any set of variables were then derived by appropriate cross plots of the curves.

The static method of measuring vapor pressure and the orthobaric densities of the liquid and vapor phases was employed. An air-free sample of known composition was enclosed over mercury in the sealed end of a precision-bore glass capillary of 2-mm i.d. The tube was fastened in a mercury-filled compressor and heated by the vapors of pure boiling liquids confined in a jacket surrounding the tube. The liquids were vaporized in a side-arm flask attached to the jacket. By controlling the pressure over the boiling liquid, the temperature of the condensing vapors was held constant to 0.02° C, as measured with a copper-constantan thermocouple with the aid of a sensitive potentiometer. The couple was calibrated by comparing it with a platinum resistance thermometer, which had been certified by the National Bureau of Standards, at a series of temperatures covering the temperature range of the measurements. From these data, a deviation curve was constructed for correcting the thermocouple reading. The pressure was indicated by a precision spring gage, marked in 2 psi divisions and read to within 0.2 psi. It was checked at 20-lb intervals by means of a calibrated dead weight gage. A deviation curve was constructed which was used to correct the indicated pressure. The length of the tube occupied by the sample was measured with a cathetometer reading to 0.02 mm. The total volume of the tube was expressed analytically as a function of the distance from the sealed end. The coefficients of the equation were determined by a least-square procedure using experimental values of the mass of mercury required to fill the tube to various levels. Equilibrium between the liquid and vapor phases was attained by moving a small steel ball, enclosed in the tube, by means of a magnet around the outside of the jacket.

MATERIALS AND PREPARATION OF MIXTURES

The propane, *n*-hexane, and *n*-heptane had a purity of 99.5 mol % or better. They were used without further purification except that each was degassed by freezing with liquid nitrogen, pumping off the noncondensable gas until

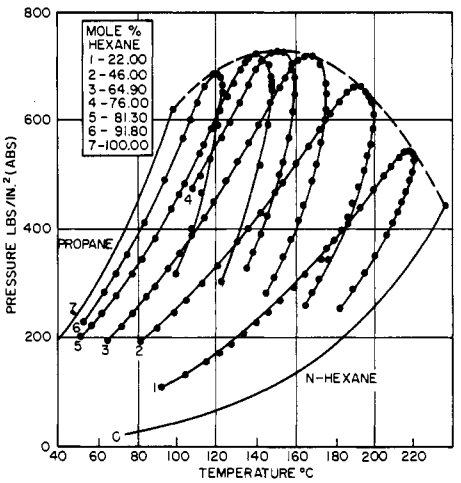

Figure 1. Pressure-temperature diagram of propane–*n*-hexane system

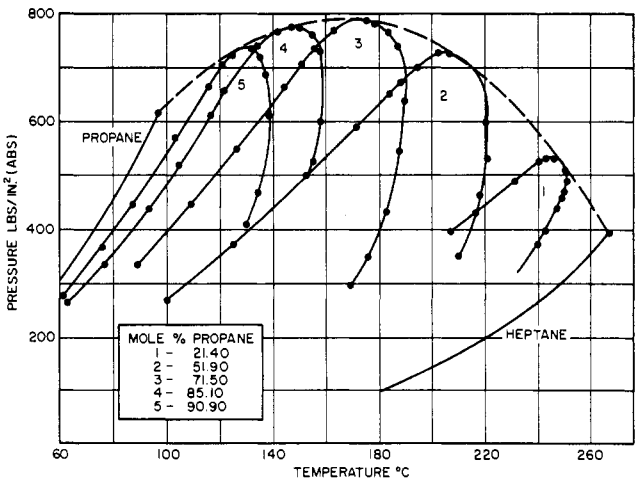

Figure 2. Pressure-temperature diagram of propane–*n*-heptane system

Table I. Summary of Temperature, Pressure and Density Relationships at Phase Boundaries

Propane–*n*-hexane system, data by Porthouse (*6*)

Press, lb/in.² abs	Liquid Temp, °C	Liquid Density, g/cc	Vapor Temp, °C	Vapor Density, g/cc
	Composition: 21.98 Mol % Propane			
150	110.3	0.509	158.3	...
200	129.5	0.486	171.4	...
250	145.7	0.478	182.0	...
300	159.5	0.441	191.2	...
350	171.8	0.419	199.4	...
400	183.0	0.395	207.0	0.093
450	193.8	0.367	213.5	0.115
500	204.2	0.333	217.5	0.1458
540	213.8	0.278	...	...
	Composition: 45.98 Mol % Propane			
200	82.5	0.515	150.5	...
250	98.0	0.495	160.2	...
300	111.1	0.478	168.5	...
350	123.2	0.459	175.7	...
400	134.8	0.441	182.1	...
450	145.3	0.421	187.8	...
500	155.6	0.399	192.4	0.1024
550	165.5	0.375	195.8	0.1265
600	174.8	0.348	197.4	0.156
650	185.5	0.300	193.8	0.225
655	187.5	0.287	192.5	0.241
	Composition: 64.87 Mol % Propane			
200	65.3	0.514	132.1	...
250	77.7	0.497	140.3	...
300	88.8	0.480	147.4	...
350	98.7	0.465	153.4	...
400	108.2	0.448	158.8	...
450	117.2	0.431	163.3	...
500	125.5	0.415	166.9	0.088
550	133.6	0.396	170.9	0.1063
600	141.1	0.376	172.8	0.1205
650	148.8	0.350	173.8	0.1450
700	158.5	0.303	170.8	0.1960
712	160.5	0.289	167.0	0.2350

Press, lb/in.² abs	Liquid Temp, °C	Liquid Density, g/cc	Vapor Temp, °C	Vapor Density, g/cc
	Composition: 75.99 Mol % Propane			
350	...	...	...	...
400	...	...	141.4	0.0614
450	...	...	146.3	0.0704
500	111.0	...	150.2	0.0802
550	118.5	...	153.2	0.0957
600	125.5	0.369	156.5	0.1265
650	132.7	0.342	156.7	0.1320
700	140.9	0.302	156.0	0.165
724	149.0	0.240	...	...
	Composition: 81.29 Mol % Propane			
200	51.8	0.502	106.7	...
250	63.2	0.486	114.3	...
300	73.0	0.470	120.7	...
350	81.8	0.455	126.2	...
400	89.8	0.439	131.3	...
450	97.6	0.422	135.7	...
500	104.7	0.404	139.5	...
550	111.6	0.384	142.2	0.2000
600	118.4	0.361	144.4	0.1730
650	124.8	0.335	145.7	0.1550
700	132.5	0.391	145.0	0.120
718	138.0	0.244	142.5	0.0945
	Composition: 91.76 Mol % Propane			
250	55.2	0.464	90.1	...
300	64.6	0.448	96.2	...
350	72.6	0.433	101.8	...
400	80.3	0.416	106.6	...
450	87.1	0.399	110.5	...
500	93.6	0.381	114.1	0.0800
550	99.6	0.360	117.0	0.0927
600	105.4	0.337	119.4	0.1112
650	111.4	0.299	121.1	0.150
680	117.0	0.239	120.4	0.180

the pressure was less than 10^{-6} torr, followed by melting and freezing. This cyclic process was repeated 8–10 times. The effectiveness of the deaerating process was checked by measuring the isothermal pressure change between the bubble and dew point of a sample of the pure liquid. The purity was considered satisfactory if the pressure change was no greater than 1.5 psi.

Mixtures of propane with either *n*-hexane or *n*-heptane were prepared by loading the experimental tube with a sample of pure *n*-hexane, calculating the weight from the measured volume and density, and then adding a measured volume of propane gas to make a mixture of known concentration. The apparatus and procedure have been described in previous publications (*1*, *3*).

EQUILIBRIUM DATA

Measurements of the pressure and temperature at the bubble and dew points were made for a series of mixtures of known composition of both propane–*n*-hexane and propane–*n*-heptane. The data were plotted and are shown in Figures 1 and 2. Figure 3 shows the density-temperature curves for the six mixtures of propane and *n*-hexane. Large-scale plots of these diagrams were constructed from which values of the temperature and density at the bubble and dew points were read at regular intervals of the pressure. These are listed in Tables I and II. T-x data were obtained from cross plots of Figures 1 and 2; Tables III and IV list the temperatures at the bubble and dew points at regular intervals of the composition. From the T-x diagrams, vapor-liquid equilibrium ratios, $K = y/x$, for each of the components in each of the systems were calculated and are given in Tables V and VI. The pressure and temperature at the critical point, maximum pressure point, and maximum temperature point on the P-T border curves of each of the mixtures are listed in Tables VII and VIII. Densities are given only for the propane–*n*-hexane system. The critical point was determined visually by the disappearance-of-the-meniscus method, whereas the pressure and temperature at the maximum pressure and maximum temperature points were obtained graphically from large plots of the P-T border curves in the critical region of the mixture. The

Table II. Summary of Temperature and Pressure Relationships at Phase Boundaries

Propane–*n*-heptane system, data by Ng (5)

Press, lb/in.² abs	Liquid temp, °C	Vapor temp, °C	Press, lb/in.² abs	Liquid temp, °C	Vapor temp, °C
Compn: 21.39 Mol % Propane			Compn: 71.54 Mol % Propane		
300	180.0	229.5	700	150.4	189.5
350	194.0	236.0	750	158.8	186.1
400	208.1	243.0			
450	221.4	248.3	Compn: 85.06 Mol % Propane		
500	234.0	250.3	300	69.6	...
			350	79.1	...
Compn: 51.87 Mol % Propane			400	87.0	...
350	120.2	209.2	450	94.7	...
400	131.2	214.3	500	101.8	...
450	142.0	217.7	550	108.5	156.0
500	152.2	219.9	600	114.8	157.9
550	163.5	220.6	650	120.7	159.2
600	172.6	220.8	700	126.7	159.2
650	183.6	219.9	750	136.8	156.6
700	214.0	193.8			
			Compn: 90.90 Mol % Propane		
Compn: 71.54 Mol % Propane			300	65.2	119.2
			350	73.6	125.2
350	91.8	175.4	400	81.4	130.4
400	100.8	180.3	450	88.4	134.3
450	109.4	183.6	500	94.9	136.7
500	117.6	186.4	550	101.1	138.0
550	127.6	188.1	600	107.2	138.2
600	133.8	188.9	650	113.7	138.0
650	142.3	189.8	700	120.7	136.5

Table III. Isobaric Temperature-Composition Relationships of Propane–*n*-Hexane System

Compn, mol % propane	Temperature, °C, Press lb/in.² abs: 300 Liquid	300 Vapor	400 Liquid	400 Vapor	500 Liquid	500 Vapor
0	209.0	209.0	228.2	228.2	...	...
10	186.0	200.9	206.6	218.7	...	...
20	164.0	192.8	185.7	209.0	208.4	219.6
30	142.7	184.2	165.6	199.1	187.9	210.0
40	122.4	174.7	146.5	188.8	167.6	199.6
50	106.8	164.5	129.6	177.7	148.1	187.8
60	94.2	153.2	114.6	165.5	132.2	174.7
70	83.4	139.8	102.0	151.2	118.5	160.0
80	74.0	123.2	91.1	133.8	106.4	142.6
90	65.8	101.4	81.7	111.4	95.5	119.1
100	59.0	59.0	73.2	73.2	85.1	85.1
	600		700		723.8	
40	187.8	203.2	...	...	...	...
50	166.5	192.8	...	...	...	...
60	149.0	180.0	169.4	175.8	...	...
70	133.7	164.9	149.6	164.5	...	...
76.0	...	...	...	...	148.9	148.9
80	120.2	146.8	134.6	148.2		
88.3	...	...	126.4	126.4		
90	107.6	124.2				
100	95.1	95.1				

Table IV. Isobaric Temperature-Composition Relationships of Propane–*n*-Heptane System

Compn, mol % propane	Temperature, °C, Press, lb/in.² abs: 300 Liquid	300 Vapor	400 Liquid	400 Vapor	500 Liquid	500 Vapor
0	246.0	246.0	266.0	266.0	...	...
10.0	214.2	238.8	239.5	258.7	...	...
16.8	...	...	...	...	252.0	252.0
20	184.0	231.0	211.8	249.0	238.5	253.8
30	150.6	223.0	185.0	239.0	209.7	244.0
40	131.3	214.5	159.2	228.1	182.4	233.5
50	110.5	205.2	135.4	216.2	157.0	222.0
60	95.9	193.0	117.2	202.0	137.0	207.4
70	83.0	174.4	103.0	183.6	119.8	190.2
80	74.0	151.2	91.9	160.0	107.5	168.6
90	67.0	118.5	81.8	127.0	96.7	137.0
100	58.5	58.5	73.8	73.8	84.8	84.8
	600		700			
33.0	235.0	235.0	...	...		
40	202.0	235.8	...	...		
49.2	...	...	214.0	214.0		
50	177.0	223.8	201.5	216.8		
60	155.5	209.0	172.7	206.0		
70	136.3	192.0	152.8	192.0		
80	121.2	171.2	135.0	173.0		
90	108.0	141.8	199.0	141.8		
100	95.2	95.2	117.0	117.0		

Table V. Vapor-Liquid Equilibrium Ratios for Propane–n-Hexane System

Temp, °C	Press, lb/in.² abs	K_{C_3}	K_{C_6}	Temp, °C	Press, lb/in.² abs	K_{C_3}	K_{C_6}
90	300	1.47	0.175	120	300	1.97	0.314
	400	1.19	0.186		400	1.54	0.308
	500	1.04	0.271		500	1.30	0.331
					600	1.15	0.417
100	300	1.64	0.212	150	300	2.36	0.509
	400	1.31	0.219		400	1.86	0.472
	500	1.12	0.280		500	1.55	0.482
	600	1.027	0.350		600	1.32	0.531
					700	1.14	0.689
110	300	1.81	0.257	180	300	2.52	0.75
	400	1.43	0.259		400	2.09	0.674
	500	1.21	0.299		500	1.69	0.664
	600	1.08	0.383		600	1.37	0.708

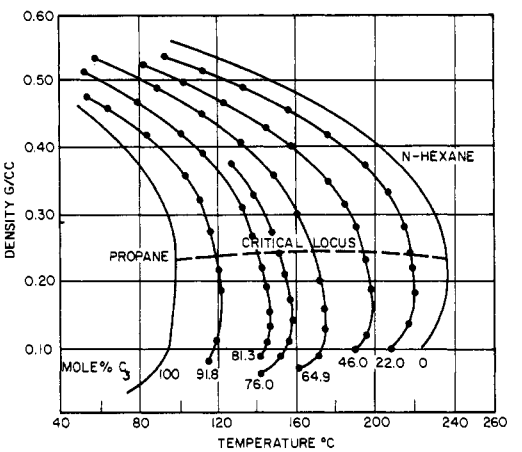

Figure 3. Density-temperature relationships of propane–*n*-hexane system

Table VI. Vapor-Liquid Equilibrium Ratios for Propane–*n*-Heptane System

Temp, °C	Press, lb/in.² abs	K_{c_3}	K_{c_7}	Temp, °C	Press, lb/in.² abs	K_{c_3}	K_{c_7}
90	300	1.49	0.141	150	300	2.46	0.301
	400	1.19	0.143		400	1.91	0.286
	500	1.04	0.167		500	1.63	0.289
					600	1.40	0.325
100	300	1.64	0.160		700	1.23	0.427
	400	1.32	0.156				
	500	1.13	0.167	180	300	3.15	0.415
	600	1.03	0.210		400	2.24	0.410
					500	1.84	0.420
110	300	1.81	0.181		600	1.56	0.464
	400	1.45	0.176		700	1.35	0.541
	500	1.23	0.183	200	300	3.74	0.530
	600	1.10	0.224		400	2.52	0.518
					500	1.93	0.535
120	300	1.96	0.211		600	1.58	0.588
	400	1.57	0.199		700	1.28	0.72
	500	1.34	0.199				
	600	1.18	0.242	250	400	3.07	0.864
	700	1.05	0.591		500	1.41	0.916

Table VIII. Critical Constants of Propane–*n*-Heptane System

Compn, mol %, propane	Critical point T_c, °C	Critical point P_c, lb/in.² abs	Point of maximum press. $T_{P_{max}}$, °C	Point of maximum press. $P_{P_{max}}$, lb/in.² abs	Point of maximum temp $T_{T_{max}}$, °C	Point of maximum temp $P_{T_{max}}$, lb/in.² abs
0	266.85[a]	396.9[a]	266.9	396.9	266.9	396.9
21.4	248.0	523.0	245	530	251.0	497.4
51.9	209.7	706.5	206	718	220.8	626
71.5	175.0	781.5	173	784	190.6	673
85.1	144.1	774.0	148	788	159.3	680
90.9	127.5	741.0	131	740	139.5	678
100	96.87[b]	617.9[b]	96.7	618	96.7	618

[a] Ref (*4*). [b] Ref (*1*).

Table VII. Critical Constants of Propane–*n*-Hexane System

Compn, mol % propane	Critical point T_c, °C	Critical point P_c, lb/in.² abs	Density, g/cc	Point of max press. $T_{P_{max}}$, °C	Point of max press. $P_{P_{max}}$, lb/in.² abs	Point of max press. Density, g/cc	Point of max temp $T_{T_{max}}$, °C	Point of max temp $P_{T_{max}}$, lb/in.² abs	Point of max temp Density, g/cc
0	234.7[a]	440.0[a]	0.233[a]						
22.0	217.5	537.5	0.226	215.1	542.3	...	219.5	526.1	0.179
46.0	193.1	652.1	0.230	190.1	659.0	0.264	197.6	610.4	0.211
64.9	167.0	712.2	0.235	164.6	714.4	0.254	173.8	648.7	0.145
76.0	149.0	723.8	0.236	149.9	723.8	0.236	156.8	666.6	0.141
81.3	138.3	718.2	0.237	140.9	719.8	0.211	145.9	665.6	0.139
91.8	116.9	680.2	0.238	118.6	683.3	0.212	121.1	656.0	0.205
100	96.87[a]	617.9[a]	0.226						

[a] Ref. 2. [b] Ref. 1.

experimental data have been deposited with ASIS. The coordinates of the maximum pressure point in the *P-T-x* space are as follows:

Propane–*n*-hexane: P = 724 ± 1.0 psia; T = 148.9 ± 0.5° C; mol % propane, 76 ± 1.0

Propane–*n*-heptane: P = 786 ± 1.0 psia; T = 163.5 ± 0.5° C mol % propane, 77 ± 1.0

The accuracy of the tabulated data is estimated to be as follows: Temperature, ±0.5° C; pressure, ±2.0 psi; density, ±0.001 g/cc for the liquid; and ±0.0001 g/cc for the vapor. However, in the critical region, the uncertainty in the values reported may be somewhat greater because of the difficulty in assessing the accuracy of the measurements in this region.

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