

that the density change per unit concentration is constant. One might assume the linear relationship for all temperatures if the data for the 0.1M solution were not available. However, at higher temperatures the density change per unit concentration is greatest over the 0.0 to 0.1M region (Table I), and the linear relationship between the density and the concentration of KCl solutions applied only to the 0.1 to 1.0M region (Figure 2).

The densities of 1.27M  $\text{UO}_2\text{SO}_4$  at temperatures to 374° C. are also shown in Figure 1, together with the data of Krohn and Wymer for 1.38M  $\text{UO}_2\text{SO}_4$  (5). The general effect of temperature on the density of the uranyl sulfate solution is similar to that on the density of the KCl solutions. However, the density of the  $\text{UO}_2\text{SO}_4$  solution decreases much faster than the density of the KCl solutions, especially at temperatures above 250° C. The divergence of the two sets of density data for the  $\text{UO}_2\text{SO}_4$  solution (Figure 1) is the result of different solution concentrations at the higher temperatures. Different initial volumes of 1.27M  $\text{UO}_2\text{SO}_4$  induced different vapor volumes above the solution. Therefore, the mass transfer of solvent to the vapor phase was greater for the lower initial volume, and the concentration of that solution was greater at the higher temperatures.

The densities of 0.1, 0.5, and 1.0M KCl and of 1.27M and 1.344 molal  $\text{UO}_2\text{SO}_4$  at various temperatures (Table II) have been determined by linear interpolation of the density vs. concentration plots at the various temperatures. These data for the KCl solutions were interpolated from the data in this report only. These data for  $\text{UO}_2\text{SO}_4$  were interpolated from the data in this report and the data of Krohn and Wymer (5), obtained in numerical form from those authors.

The density change of the  $\text{UO}_2\text{SO}_4$  solution from 25° to 350° C. is 0.464 gram per ml., whereas the corresponding change for the 1.0M KCl solution is only 0.320 gram per ml. This difference in the change of the densities might be due to differences in the concentrations or the molecular weights of the two salts. However, the linear relationship between the density and concentration of the KCl solutions indicates that the densities of 1.27M KCl solution at all temperatures would be higher than the densities of the 1.0M KCl; but the rate of

Table II. Interpolated Densities of Solutions Having Constant Concentrations at Temperatures to 370° C.

Temp., ° C.	Density, Grams per Ml.				
	0.1 M KCl	0.5 M KCl	1.0 M KCl	1.27 M $\text{UO}_2\text{SO}_4$	1.344 m $\text{UO}_2\text{SO}_4$
25	1.003	1.018	1.039	1.411	1.411
100	0.971	0.985	1.004	1.370	1.363
150	0.933	0.947	0.964	1.319	1.314
200	0.882	0.900	0.922	1.278	1.253
225	0.858	0.876	0.899	1.258	1.223
250	0.823	0.848	0.878	1.233	1.189
275	0.788	0.867	0.856	1.207	1.144
285	0.773	0.804	0.846	1.186	1.124
300	0.743	0.780	0.816	1.149	1.088
350	0.618	0.674	0.744		
370	0.525	0.586	0.659		

density change would not approach that observed for  $\text{UO}_2\text{SO}_4$ . Also, normalizing the concentrations in terms of molality and normality and plotting the densities against these terms does not change the trends of, and the differences in, the densities of the KCl and  $\text{UO}_2\text{SO}_4$  solutions.

#### LITERATURE CITED

- (1) Bain, R. W., "Steam Tables 1964," Department of Scientific and Industrial Research, National Engineering Laboratory, Great Britain.
- (2) Bell, J. T., Biggers, R. E., Rogers, T. G., Rom, A. M., *Rev. Sci. Instr.* **40**, 985 (1969).
- (3) Copeland, C. S., Silverman, J., Benson, S. W., *J. Chem. Phys.* **21**, 12 (1952).
- (4) Ellis, A. J., Golding, R. M., *Am. J. Sci.* **261**, 47 (1963).
- (5) Krohn, N. A., Wymer, R. G., *Anal. Chem.* **34**, 121 (1962).
- (6) Secoy, C. H., Oak Ridge National Laboratory, Chem. Div. Quart. Rept. ORNL-336, pp. 24, 26-7 (Dec. 1948).
- (7) Sourirajan, S., Kennedy, G. C., U. S. Atomic Energy Commission Rept. No. UCRL-6175 (1960).

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## Vapor-Liquid Equilibrium Relations of Binary Systems. The Propane-*n*-Alkane Systems. *n*-Butane and *n*-Pentane

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IN THE COURSE of a long-range study of the critical properties of hydrocarbon mixtures, *P-V-T-x* data have been obtained for a series of binary systems of the normal and branched-chain hydrocarbons. In the selection of the systems of study, members of the homologous series of the paraffin hydrocarbons have been paired with a member of the same series, but of lower molecular weight. By this method, the effect of such variables as

molecular weight and molecular structure on the phase behavior can be investigated as parameters for the correlation of the *P-V-T* data. This first paper summarizes the data obtained for the two binary systems composed of *n*-butane and *n*-pentane, with propane as the common component. The work has been carried out by graduate students, each binary system serving as the thesis problem for the M.S. degree in chemical engineering.

The  $P$ - $V$ - $T$ - $x$  relations of the binary systems of  $n$ -butane and  $n$ -pentane, with propane as a common component, have been determined. The experimental results cover a range from about 200 p.s.i.a. 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 isobaric  $T$ - $x$  diagrams are given.

## EXPERIMENTAL

To determine the  $P$ - $V$ - $T$ - $x$  relations for the binary propane- $n$ -alkane systems, the  $P$ - $T$  border curves and density-temperature curves were obtained for a series of mixtures of known composition for each system. The relationships between any set of variables were then derived by appropriate cross plots of the curves.

The apparatus and experimental procedures were the

same as those employed in earlier studies (5, 6). A fluid mixture, prepared by combining measured amounts of the pure air-free components, was confined over mercury in the sealed end of a thick-walled glass tube. The tube was heated to a constant temperature by the vapors of a series of pure organic compounds which were confined in a jacket surrounding the tube. The temperature was measured to within  $0.02^\circ\text{C}$ . by a thermocouple projecting into the jacket. The tube was held in one leg of a mercury-in-steel U-tube, the other leg of which was connected to a source of high-pressure nitrogen gas for pressurizing the sample. The pressure on the system was measured to within 0.5 p.s.i. by a precision spring gage. Both the thermocouple and pressure gage were calibrated, the former by comparison with a platinum re-

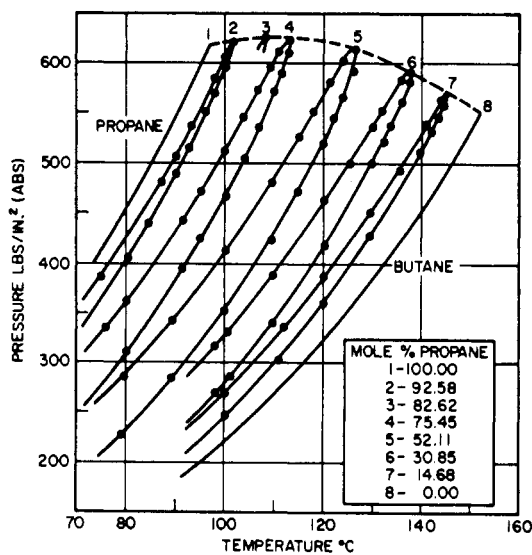


Figure 1. Pressure-temperature-composition diagram for propane- $n$ -butane system

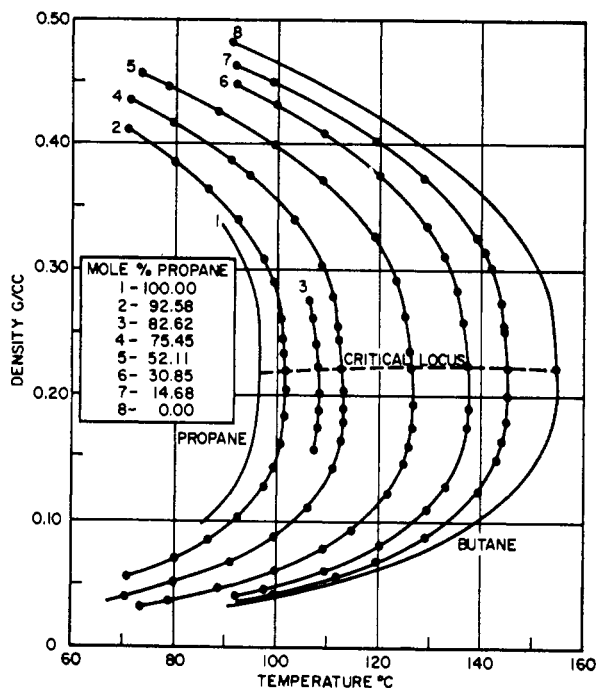


Figure 2. Temperature-density-composition diagram for propane- $n$ -butane system

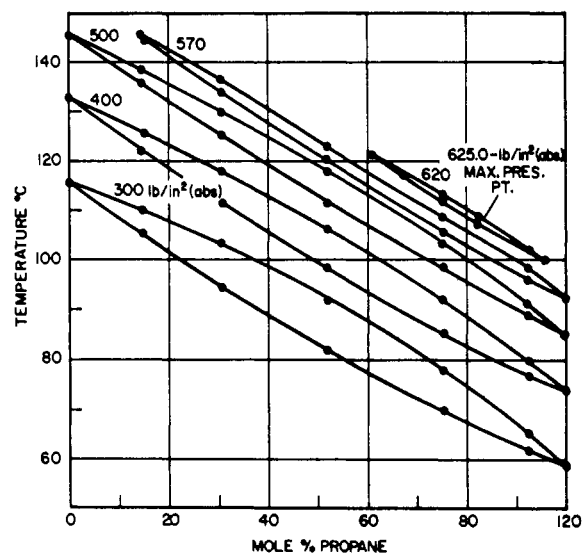


Figure 3. Isobaric temperature-composition diagram for propane- $n$ -butane system

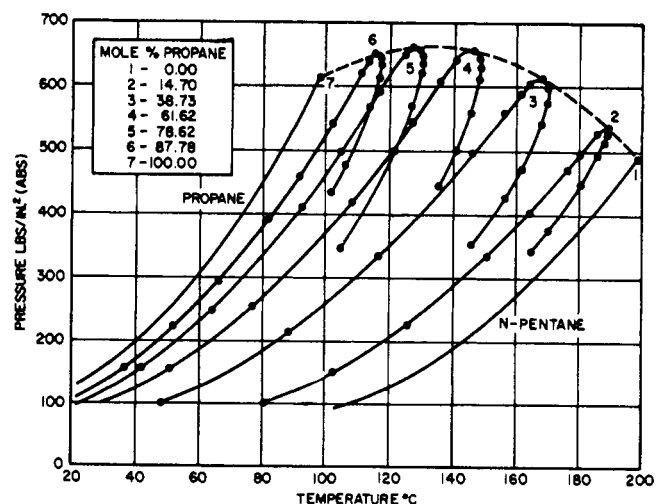


Figure 4. Pressure-temperature-composition diagram for propane- $n$ -pentane system

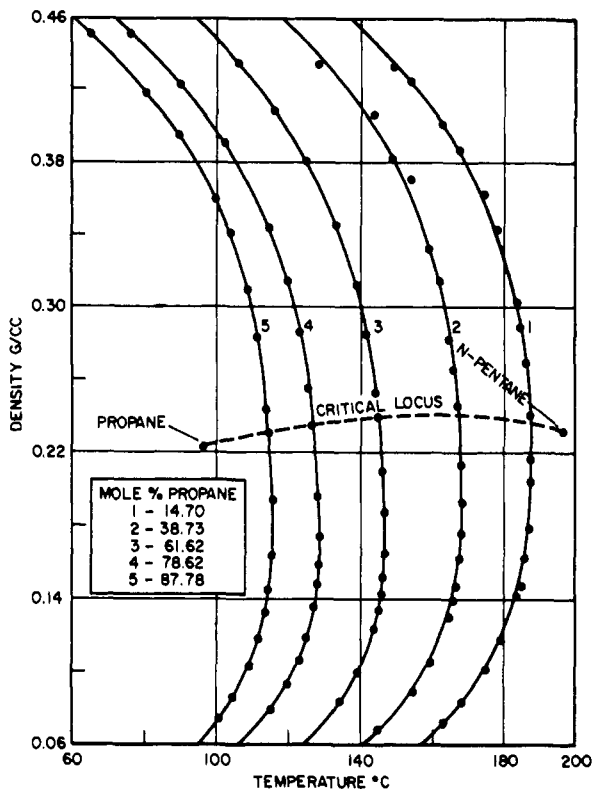


Figure 5. Temperature-density-composition diagram for propane-n-pentane system

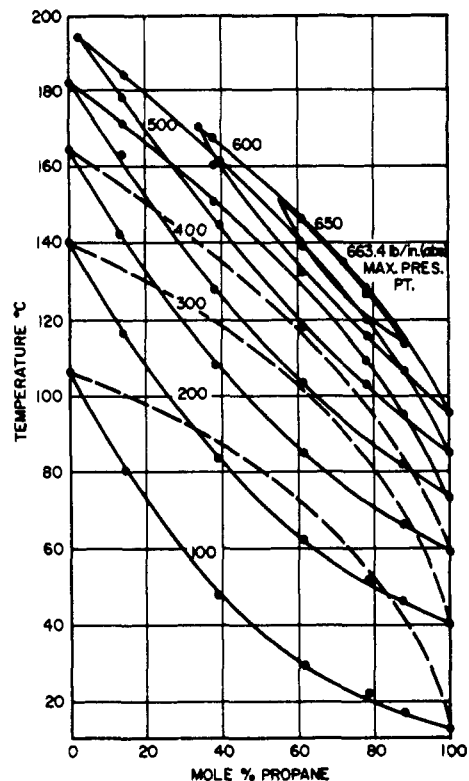


Figure 6. Isobaric temperature-composition diagram for propane-n-pentane system

Table I. Summary of Temperature, Pressure, and Density Relations of the Propane-n-Butane System at the Phase Boundaries (1)

Pressure, P.S.I.A.	Liquid		Vapor		Pressure, P.S.I.A.	Liquid		Vapor	
	Temp., °C.	Density, g./cc.	Temp., °C.	Density, g./cc.		Temp., °C.	Density, g./cc.	Temp., °C.	Density, g./cc.
Composition. 14.68 Mole % Propane					Composition. 52.11 Mole % Propane				
225.0	89.9	...	95.8	0.0382	250.0	71.0 <sup>a</sup>	...	82.8	0.0402
250.0	95.6	0.4556	101.1	0.0436	300.0	81.8	0.4397	91.7	0.0499
300.0	105.3	0.4372	110.0	0.0480	350.0	90.4	0.4213	99.4	0.0603
350.0	114.1	0.4171	118.3	0.0660	400.0	98.1	0.4030	106.2	0.0724
400.0	122.1	0.3950	125.8	0.0796	450.0	105.1	0.3844	112.3	0.0863
450.0	129.5	0.3719	132.5	0.0968	500.0	111.7	0.3629	117.8	0.1034
500.0	136.0	0.3450	138.6	0.1191	525.0	114.9	0.3504	120.3	0.1142
525.0	139.2	0.3279	141.4	0.1337	550.0	117.9	0.3361	122.7	0.1266
540.0	141.1	0.3140	142.9	0.1449	570.0	120.3	0.3221	124.4	0.1380
550.0	142.4	0.3029	143.9	0.1554	590.0	122.7	0.3034	126.0	0.1562
560.0	143.6	0.2890	144.8	0.1710	600.0	124.0	0.2899	126.6	0.1674
565.0	144.2	0.2783	145.2	0.1806	605.0	124.6	0.2820	126.9	0.1726
567.5	144.5	0.2720	145.4	0.1870	610.0	125.35	0.2696	127.1	0.1880
570.0	144.9	0.2616	145.5	0.196	614.8 max. p.	126.5	0.2482	...	...
Composition. 30.85 Mole % Propane					Composition. 75.45 Mole % Propane				
250.0	84.9 <sup>a</sup>	...	94.1	0.0421	300.0	69.9 <sup>a</sup>	0.4364	78.2	0.0484
300.0	94.8	0.4418	103.4	0.0522	350.0	77.9	0.4199	85.3	0.0584
350.0	103.5	0.4227	111.0	0.0631	400.0	85.5	0.4019	91.9	0.0696
400.0	111.5	0.4029	117.9	0.0758	450.0	92.3	0.3832	97.9	0.0830
450.0	118.7	0.3800	124.2	0.0914	500.0	98.4	0.3625	103.2	0.0984
500.0	125.3	0.3559	129.9	0.1114	525.0	101.4	0.3498	105.6	0.1084
525.0	128.6	0.3407	132.5	0.1234	550.0	104.2	0.3360	108.0	0.1198
550.0	131.6	0.3238	134.8	0.1385	570.0	106.4	0.3240	109.8	0.1308
560.0	132.8	0.3148	135.7	0.1460	590.0	108.6	0.3079	111.4	0.1441
570.0	134.0	0.3042	136.6	0.1562	600.0	109.7	0.2974	112.1	0.1530
580.0	135.2	0.2916	137.5	0.1710	610.0	110.8	0.2844	112.8	0.1662
585.0	135.9	0.2820	137.8	0.1804					
590.0	136.8	0.2646	137.9	0.1876					

Table I. (Continued)

Pressure, P.S.I.A.	Liquid		Vapor		Pressure, P.S.I.A.	Liquid		Vapor	
	Temp., ° C.	Density, g./cc.	Temp., ° C.	Density, g./cc.		Temp., ° C.	Density, g./cc.	Temp., ° C.	Density, g./cc.
615.0	111.3	0.2766	113.1	0.1750	525.0	91.6	0.3440	93.5	0.1072
620.0	112.0	0.2630	113.3	0.1868	550.0	94.3	0.3298	96.0	0.1184
622.5	112.4	0.2524	113.36	0.1960	570.0	96.4	0.3165	97.8	0.1292
Composition, 92.58 Mole % Propane					590.0	98.4	0.3011	99.6	0.1424
350.0	69.6 <sup>a</sup>	...	72.9	0.0577	600.0	99.4	0.2911	100.4	0.1523
400.0	76.6	0.3948	79.6	0.0694	610.0	100.4	0.2764	101.2	0.1656
450.0	83.1	0.3755	85.5	0.0824	615.0	100.9	0.2658	101.6	0.1768
500.0	88.8	0.3563	91.0	0.0980	620.0	101.4	0.2514	101.9	0.1822

<sup>a</sup> Extrapolated value.

sistance thermometer which had been calibrated by the National Bureau of Standards, and the latter by comparison with a calibrated dead weight gage. A previous calibration of the tube made it possible to determine the volume of the sample by measuring the length of the tube which it occupied with a cathetometer reading to 0.02 mm. 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. Pressure and volume were observed at a series of constant temperatures covering the range desired.

#### MATERIALS AND PREPARATION OF MIXTURES

The propane, *n*-butane, and *n*-pentane from which the mixtures were prepared were supplied with a purity of 99.9 mole % or better by the Phillips Petroleum Co. and

used without further purification except for the removal of air. Deaeration was accomplished by a series of operations which involved freezing with liquid nitrogen and pumping off residual gas over the solid, followed by melting of the solid sample and distillation at low pressure. The purity of the components was checked by measuring the difference between their isothermal dew and bubble points. The maximum pressure difference was less than 2.0 p.s.i. Mixtures of propane with *n*-butane were prepared by injecting measured amounts of each gas into the experimental tube, previously filled with pure air-free mercury. For mixtures containing *n*-pentane, a measured amount of the air-free liquid component was transferred by molecular distillation to the experimental tube, which was attached to a high-vacuum line. Measured quantities of pure propane gas were then injected to make a mixture of the desired composition.

Table II. Isobaric Temperature-Composition Relations of Propane-*n*-Butane System

Composition, Mole % Propane	Temperature, ° C.		Composition, Mole % Propane	Temperature, ° C.		Composition, Mole % Propane	Temperature, ° C.	
	Liquid	Vapor		Liquid	Vapor		Liquid	Vapor
Pressure. 300 P.S.I.A.			Pressure. 500 P.S.I.A.			Pressure. 570 P.S.I.A.		
0	116.2	116.2	0	146.0	146.0	20	140.7	142.6
10	108.6	112.0	10	139.2	141.1	30	134.4	137.0
20	101.7	107.8	20	132.5	135.8	40	128.2	131.4
30	95.2	103.4	30	125.85	130.4	50	121.9	125.6
40	88.9	98.7	40	119.25	124.8	60	115.6	119.7
50	82.9	93.6	50	113.0	119.1	70	109.4	113.5
60	77.4	88.1	60	107.0	113.1	80	103.5	106.8
70	72.4	81.9	70	101.2	106.8	90	97.8	100.0
80	67.8	75.1	80	95.55	100.0	100	92.7	92.7
90	63.3	67.5	90	90.25	92.9			
100	59.3	59.3	100	85.5	85.5			
Pressure. 400 P.S.I.A.			Pressure. 550 P.S.I.A.			Pressure. 590 P.S.I.A.		
0	132.7	132.7	0	152.2	152.2	30.85	136.8	137.9
10	125.4	128.1	10	145.5	146.5	40	130.7	132.8
20	118.6	123.3	20	138.8	140.9	50	124.1	127.2
30	112.0	118.3	30	132.3	135.3	60	117.8	121.2
40	105.6	113.0	40	125.6	129.7	70	111.8	115.0
50	99.4	107.4	50	119.3	124.0	80	105.9	108.4
60	93.7	101.6	60	113.2	118.0	90	99.9	101.4
70	88.3	95.5	70	107.2	111.6	100	94.6	94.6
80	83.05	88.8	80	101.4	104.8			
90	77.9	81.5	90	95.8	97.7			
100	73.5	73.5	100	90.4	90.4			
						Pressure. 625.0 <sup>a</sup> P.S.I.A.		
						82.6	108.1	108.1

<sup>a</sup> Maximum critical pressure for propane-*n*-butane system.

Table III. Vapor-Liquid Equilibrium Ratios for Propane-*n*-Butane System

Temp., ° C.	Pressure, P.S.I.A.	$K_{C_2}$	$K_{C_4}$	Temp., ° C.	Pressure, P.S.I.A.	$K_{C_3}$	$K_{C_4}$	
90	300	1.48	0.70	110	350	1.58	0.85	
	350	1.30	0.66		400	1.37	0.82	
	400	1.17	0.65		450	1.26	0.79	
	450	1.09	0.66		500	1.18	0.78	
100	300	1.65	0.81	120	550	1.11	0.79	
	350	1.42	0.76		590	1.07	0.83	
	400	1.28	0.73		350	1.83	0.94	
	450	1.18	0.71			400	1.49	0.89
	500	1.11	0.72			450	1.33	0.87
	550	1.05	0.75			500	1.25	0.84
110	300	1.84	0.93	550	1.16	0.84		
				590	1.10	0.87		

Table IV. Composition and Critical Constants of Propane-*n*-Butane Mixtures

Mole % $C_3$	Critical Point			Point of Maximum Pressure			Point of Maximum Temperature		
	Temp., $T_c$ , ° C.	Pressure, $P_c$ , P.S.I.A.	Density, $\rho_c$ , g./cc.	Temp., $T_{P,max}$ , ° C.	Pressure, $P_{P,max}$ , P.S.I.A.	Density, $\rho_{P,max}$ , g./cc.	Temp., $T_{T,max}$ , ° C.	Pressure, $P_{T,max}$ , P.S.I.A.	Density, $\rho_{T,max}$ , g./cc.
	0	152.2 <sup>a</sup>	550.8 <sup>a</sup>	0.228					
14.7	145.4	570.8	0.225	145.2	571.0	0.251	145.5	570.0	0.201
30.9	137.7	590.9	0.223	137.5	591.7	0.241	138.0	587.7	0.190
52.1	126.6	614.4	0.222	126.4	614.8	0.235	127.1	609.8	0.184
75.5	113.0	624.5	0.223	113.0	624.5	0.222	113.4	622.8	0.192
82.6	108.3	624.7	0.223	108.4	624.7	0.233	108.6	623.6	0.196
92.6	101.8	621.5	0.225	101.9	621.5	0.220	101.9	620.4	0.204
100	96.87 <sup>b</sup>	617.9 <sup>b</sup>	0.226 <sup>b</sup>						

<sup>a</sup> (3). <sup>b</sup> (2).Table V. Summary of Temperature, Pressure, and Density Relations for the Propane-*n*-Pentane System at the Phase Boundaries (8)

Pressure, P.S.I.A.	Liquid		Vapor		Pressure, P.S.I.A.	Liquid		Vapor	
	Temp., ° C.	Density, g./cc.	Temp., ° C.	Density, g./cc.		Temp., ° C.	Density, g./cc.	Temp., ° C.	Density, g./cc.
Composition. 14.70 Mole % Propane					Composition. 61.62 Mole % Propane				
100			103.4		300	85.3	0.480	118.2	...
150	101.0	0.520	121.2	...	350	95.1	0.462	124.6	...
200	117.0	0.497	134.8	...	400	103.5	0.444	...	...
250	131.5	0.474	146.5	...	450	111.5	0.424	134.8	0.085
300	143.4	0.451	155.8	...	500	118.8	0.404	139.4	0.100
350	153.2	0.430	164.4	0.075	550	126.2	0.380	143.2	0.119
400	162.1	0.406	172.0	0.093	600	132.9	0.352	146.2	0.145
450	170.8	0.378	179.0	0.117	650	140.8	0.299	146.8	0.155
500	179.2	0.341	184.7	0.147					
510	180.8	0.332	185.8	0.157	Composition. 78.62 Mole % Propane				
520	182.5	0.320	186.6	0.170	150			71.2	...
530	184.2	0.302	187.2	0.186	200	52.2	0.491	81.6	...
					250	63.5	0.474	90.2	...
					300	73.2	0.458	97.5	...
Composition. 38.73 Mole % Propane					350	81.6	0.442	104.0	0.056
100			90.9	...	400	89.3	0.426	109.8	0.067
150	67.9	0.5396	106.8	...	450	96.5	0.408	115.2	0.079
200	83.7	0.518	118.5	...	500	103.2	0.389	119.9	0.094
250	96.7	0.499	128.1	...	550	109.8	0.367	124.0	0.112
300	108.4	0.4805	136.7	...	600	115.9	0.341	127.1	0.135
350	119.1	0.461	144.0	...	650	122.8	0.287	128.5	0.173
400	128.3	0.441	151.2	0.082	Composition. 87.78 Mole % Propane				
450	136.8	0.421	156.9	0.097	250	56.9	0.467	79.7	...
500	144.8	0.398	162.0	0.115	300	66.3	0.449	86.3	...
550	152.8	0.371	166.5	0.143	350	74.5	0.433	92.2	...
600	161.2	0.325	168.4	0.178	400	82.2	0.415	97.0	...
610	163.3	0.305	167.7	0.158	450	89.2	0.398	102.1	0.078
Composition. 61.62 Mole % Propane					500	95.4	0.379	106.5	0.092
100			80.1	...	550	101.3	0.357	110.5	0.110
150	48.2	0.539	93.5	...	600	107.1	0.328	113.9	0.135
200	62.3	0.518	103.2	...	650	113.4	0.255	115.5	0.200
250	74.5	0.499	111.6	...					

Table VI. Isobaric Temperature-Composition Relations of Propane-*n*-Pentane System

Composition, Mole % Propane	Liquid, ° C.	Vapor, ° C.	Composition, Mole % Propane	Liquid, ° C.	Vapor, ° C.	Composition, Mole % Propane	Liquid, ° C.	Vapor, ° C.
0	165.2	165.2	50	114.9	140.9	33.7	171.1	171.1
10	150.4	157.94	60	105.0	131.1	38.73	161.4	168.4
20	135.7	150.6	70	96.1	120.6	40	159.4	167.2
30	121.1	142.8	80	88.1	108.1	50	146.1	158.0
40	106.6	134.7	90	80.4	92.9	60	134.5	148.2
50	95.4	126.7	100	73.0	73.0	70	124.3	137.2
60	86.6	118.1	Pressure, 500 P.S.I.A.			80	114.6	125.0
70	78.9	108.3	3.2	194.6	194.6	90	105.0	110.6
80	71.9	96.7	10	185.0	188.7	100	95.2	95.2
90	65.3	81.7	20	171.1	179.9	Pressure, 650 P.S.I.A.		
100	58.8	58.8	30	157.1	170.6	55	151.7	151.7
Pressure, 400 P.S.I.A.			40	143.2	160.7	60	142.7	148.3
0	183.3	183.3	50	131.3	150.8	70	131.7	138.6
10	168.9	175.8	60	120.1	140.9	80	121.6	126.9
20	154.4	167.7	70	110.6	130.4	87.76	113.3	115.6
30	140.2	158.9	80	101.9	117.9	88.6	113.3	113.3
40	126.4	150.0	90	93.3	103.2			
			100	85.00	85.0			

Table VII. Vapor-Liquid Equilibrium Ratios for Propane-*n*-Pentane System

Temp., ° C.	Pressure, P.S.I.A.	$K_{C_3}$	$K_{C_5}$	Temp., ° C.	Pressure, P.S.I.A.	$K_{C_3}$	$K_{C_5}$	Temp., ° C.	Pressure, P.S.I.A.	$K_{C_3}$	$K_{C_5}$
90	300	1.52	0.342	110	300	1.82	0.506	120	650	1.044	0.808
	400	1.18	0.371		400	1.44	0.472	150	300	2.03	0.882
	500	1.036	0.425		500	1.21	0.490		400	1.74	0.779
					600	1.067	0.627		500	1.45	0.757
100	300	1.69	0.416	120	300	1.88	0.609		600	1.24	0.791
	400	1.31	0.417		400	1.55	0.541		650	1.05	0.933
	500	1.12	0.458		500	1.30	0.544	180	400	1.96	0.976
	600	1.02	0.626		600	1.125	0.634		500	1.46	0.928

Table VIII. Critical Constants of Propane-*n*-Pentane Mixtures

Mole % Propane	Critical Point			Point of Maximum Pressure			Point of Maximum Temperature		
	Temp., ° C.	Pressure, P.S.I.A.	Density, g./cc.	$T_{P \max}$ temp., ° C.	$P_{P \max}$ pressure, P.S.I.A.	Density, g./cc.	Temp., ° C. $T_{T \max}$	$P_{T \max}$ P.S.I.A.	Density, g./cc.
0	196.6 <sup>a</sup>	489.7 <sup>a</sup>	0.232 <sup>a</sup>	...	...	...	...	...	...
14.7	187.0	538.1	0.241	186.3	539.1	0.326	187.4	533.7	0.190
38.7	166.8	614.0	0.244	165.4	616.3	0.278	168.5	595.0	0.190
61.6	144.7	657.7	0.240	144.3	658.0	0.259	147.3	636.0	0.180
78.6	126.1	662.0	0.235	126.5	662.0	0.242	128.6	650.0	0.170
87.8	114.3	651.8	0.231	115.0	652.0	0.246	115.7	643.0	0.180
100	96.87 <sup>b</sup>	617.9 <sup>b</sup>	0.226 <sup>b</sup>	...	...	...	...	...	...

<sup>a</sup> (3). <sup>b</sup> (2).

The estimated error in the composition of the mixture prepared in this manner was about 0.5%.

#### EQUILIBRIUM DATA

The pressure-temperature and density-temperature diagrams for mixtures of constant composition, and the isobaric temperature-composition diagrams for propane-*n*-butane and propane-*n*-pentane systems are shown in Figures 1 through 6. From large plots of these figures, Tables I through VIII were constructed, giving smoothed values of the temperatures and densities at the bubble and dew points for mixtures of constant composition at regular intervals of pressure, the bubble and dew points

at regular intervals of the composition at a series of constant pressures, the vapor-liquid equilibrium ratio  $K = y/x$ , as a function of pressure at a series of selected temperatures, and the pressure, temperature, and density at the critical point, maximum pressure point, and maximum temperature points on the  $P$ - $T$  border curves for each of the mixtures of the two binary systems that were studied. The tables for each system are grouped together and appropriately marked. 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 accuracy of the tabulated data is estimated as follows: temperature,  $\pm 0.5^\circ\text{C}$ .; pressure,  $\pm 2.0$  p.s.i.; density,  $\pm 0.001$  gram per cc. for the liquid and  $\pm 0.0001$  gram per 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 measurements in this region.

#### COMPARISON OF RESULTS WITH LITERATURE DATA

The propane-*n*-butane system was studied by Nysewander *et al.* (7) and the propane-*n*-pentane system by Sage and Lacey (9). An apparatus similar to that employed in this study was used. In Table IX (deposited with ASIS) a comparison is made between the values of the temperature and pressure at the critical point, maximum pressure point, and maximum temperature point reported for these systems and those found in this study. The agreement is moderately good for both systems, but noticeably better for the propane-*n*-pentane system. Table X (deposited with ASIS) compares bubble and dew point data for the propane-*n*-butane system. The dew point pressures of mixtures of low propane content agree moderately well with those found in this study; for mixtures of high propane content, the agreement is less satisfactory. The bubble point pressures show fairly large deviations. This is due to the greater sensitivity of the bubble point pressure, compared to the dew point pressure, to small traces of noncondensable gas in the sample.

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#### LITERATURE CITED

- (1) Barber, J. R., M.S. thesis, Ohio State University, Columbus, Ohio, 1964.
- (2) Barber, J. R., Ph.D. thesis, Ohio State University, Columbus, Ohio, 1968.
- (3) Hoffman, R. L., M.S. thesis, Ohio State University, Columbus, Ohio, 1962.
- (4) Kay, W. B., *Ind. Eng. Chem.* **32**, 358 (1940).
- (5) Kay, W. B., *J. Am. Chem. Soc.* **69**, 1273 (1947).
- (6) Kay, W. B., Rambossek, G. M., *Ind. Eng. Chem.* **45**, 221 (1953).
- (7) Nysewander, C. N., Sage, B. H., Lacey, W. N., *Ibid.*, **32**, 118 (1940).
- (8) Oxley, J. A., M.S. thesis, Ohio State University, Columbus, Ohio, 1963.
- (9) Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.* **32**, 992 (1940).

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## Low Temperature Heat Capacities of 15 Inorganic Compounds

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Smoothed low temperature heat capacities and derived thermodynamic functions for KOH,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{SiO}_3$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{KBH}_4$ , LiCl,  $\text{LiBO}_2$ ,  $\text{Li}_2\text{SiO}_3$ , MgS,  $\text{Mg}(\text{CO}_2\text{H})_2$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{BPO}_4$ ,  $\text{SnSO}_4$ ,  $\text{Na}_2\text{SiF}_6$ , and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  are presented at even temperatures. Comparisons with literature data indicate the entropies at  $298.15^\circ\text{K}$ . are accurate to at least 1%. Such values are useful in thermodynamic calculations, as evidenced by comparison with estimates based on ion contributions.

DURING THE PAST DECADE and a half, the pioneer automatic adiabatic low-temperature calorimeter described by Stull (13) was used for the measurement of the heat capacity of a number of inorganic solids. The precision of measurement attained with this calorimeter was somewhat less than could be achieved with manually operated apparatus. Samples used were the best available within the time limitations of an industrial laboratory; in some cases this meant relatively low purity and in others incomplete characterization. Heat capacity measurements are not highly sensitive to impurities, however, and the smoothed heat capacity

data led to third-law entropies of good accuracy as shown by some comparisons with data from other laboratories. Therefore, although the measurements may not warrant a detailed account of individual data points, smoothed tables of thermodynamic functions at even temperatures should prove useful in thermodynamic calculations.

#### MATERIALS

Reagent grade potassium hydroxide was dried under vacuum at  $425^\circ\text{C}$ . Analysis by acid titration indicated 97.8% KOH and 2.2%  $\text{K}_2\text{CO}_3$ .

Reagent grade potassium carbonate was dried at  $300^\circ\text{C}$ . The manufacturer's analysis indicating 99.9% purity was accepted.

A sample of potassium metasilicate was prepared from

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