Vapor-Liquid Equilibrium Constants for the Ethane–*n*-Butane–*n*-Heptane System at 300° and 350° F.

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Experimental studies concerned with the determination of vapor-liquid equilibrium constants have been extended for the ethane–*n*-butane–*n*-heptane system reported in a previous study for 150°, 200°, and 250° F., to include in this investigation the temperatures of 300° and 350° F. The pressures studied ranged from 450 p.s.i.a. up to the critical region. Values of critical pressure and composition have been obtained from these data and are presented for 300° and 350° F.

RECENTLY the vapor liquid equilibrium behavior of the ethane–*n*-butane–*n*-heptane system was reported in the literature (*7*) for 150°, 200°, and 250° F. In the present study, the vapor-liquid equilibrium behavior of this system has been extended to include the temperatures of 300° and 350° F. Because of the limiting properties of the rubber O-rings used in the equilibrium cell, it was not possible to obtain data for higher temperatures. The three binaries of this ternary system have been comprehensively studied by Kay (*2–4*). Furthermore, recent vapor-liquid equilibrium studies are reported by Mehra and Thodos for the ethane–*n*-butane (*6*) and the ethane–*n*-heptane (*5*) systems and have been utilized in the analysis of the data of the present investigation.

APPARATUS AND PROCEDURE

The experimental equipment used in this study is the same as that used for obtaining data for the ethane–*n*-butane–*n*-heptane system at 150°, 200°, and 250° F. The descriptive details of the equilibrium cell and auxiliary equipment have been described (*7, 8*), and only the salient features of the experimental equipment will be presented here.

The equilibrium cell was constructed of stainless steel and was provided with a movable piston which could be actuated with mercury for varying the volume of the equilibrium chamber. The pressure of the system was measured by two calibrated Heise gages which were reproducible to within 3 p.s.i. for the pressure range of the present study. The cell was surrounded with a constant temperature air bath, capable of maintaining its over-all temperature to within 0.4° F. of the desired temperature. Agitation within the equilibrium chamber was provided with a stirrer, which was coupled magnetically to an external mechanical drive. Each component was introduced into the cell from individual charging reservoirs. After reaching equilibrium, micro-samples of the liquid and vapor phases in equilibrium were withdrawn and were analyzed in a gas chromatography unit. The analyses carried out in the gas chromatograph were reproducible in a series of several measurements to within one mole per cent of a component. The procedure used for the calibration of the gas chromatograph has been described (*7*).

MATERIALS

The hydrocarbons used were reagent grade and were supplied by the Phillips Petroleum Co. The purities of these hydrocarbons were claimed by the supplier to be: ethane, 99.91 mole %; *n*-butane, 99.90 mole %; and *n*-heptane, 99.78 mole %.

EXPERIMENTAL INVESTIGATION

For the temperatures of 300° and 350° F., charges were prepared with composition parameters, C, ranging from zero to unity. The charge mixtures were selected so their compositions corresponded to critical temperatures which were very close to 300° and 350° F. These compositions were established by the method described by Grieves and Thodos (*1*). Thus it became possible to obtain the vapor and liquid phases for a given charge for pressures ranging from approximately 450 p.s.i.a. up to the critical region. For each charge, the compositions of the vapor and liquid phases were determined at several pressures above 450 p.s.i.a. The experimental vapor and liquid compositions for all charges studied are presented in Table I for temperatures of 300° and 350° F.

For each charge, the experimental data were smoothed by plotting compositions against pressure as shown in Figure 1 for charge II at 350° F. For this charge, the vapor and liquid samples were obtained for pressures up to 1109 p.s.i.a., and the resulting bubble and dew point curves of each component were extended to their point of convergence, the critical pressure. For the charge, shown in Figure 1, the critical pressure was 1140 p.s.i.a. for a mole fraction composition of 0.559 ethane, 0.169 *n*-butane, and 0.272 *n*-heptane. For the remaining charges, plots similar to Figure 1 were prepared and the critical pressures and compositions were estimated. Equilibrium constants, $K = y/x$,

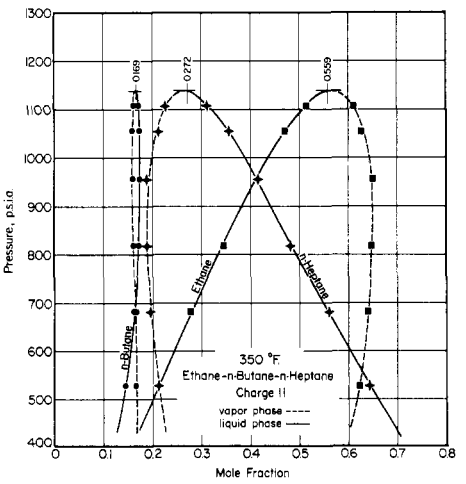

Figure 1. Vapor-liquid equilibrium behavior for a mixture of ethane, *n*-butane, and *n*-heptane at 350° F. (charge II)

Table I. Experimental Vapor-Liquid Equilibrium Data for the Ethane–*n*-Butane–*n*-Heptane System

Press., P.S.I.A.	*y*, Vapor Mole Fraction			*x*, Liquid Mole Fraction			$K = y/x$			C
	Ethane	*n*-Butane	*n*-Heptane	Ethane	*n*-Butane	*n*-Heptane	Ethane	*n*-Butane	*n*-Heptane	
					At 300° F.					
					Charge I					
535	0.804	0.0615	0.134	0.319	0.0725	0.608	2.520	0.848	0.220	0.107
690	0.814	0.0603	0.126	0.382	0.0740	0.544	2.131	0.815	0.232	0.120
840	0.820	0.0588	0.121	0.460	0.0770	0.463	1.783	0.764	0.261	0.143
983	0.816	0.0578	0.126	0.528	0.0716	0.400	1.545	0.807	0.315	0.152
1102	0.803	0.0577	0.139	0.590	0.0730	0.337	1.361	0.790	0.412	0.178
1206	0.772	0.0580	0.170	0.655	0.0755	0.269	1.179	0.768	0.632	0.219
					Charge V					
520	0.695	0.176	0.129	0.265	0.186	0.549	2.623	0.946	0.235	0.253
664	0.711	0.173	0.116	0.325	0.202	0.473	2.188	0.856	0.245	0.299
795	0.717	0.168	0.115	0.382	0.210	0.408	1.877	0.800	0.282	0.340
903	0.718	0.167	0.115	0.430	0.208	0.362	1.670	0.803	0.318	0.365
1000	0.694	0.173	0.133	0.489	0.200	0.311	1.419	0.865	0.428	0.391
1087	0.682	0.171	0.147	0.544	0.192	0.264	1.254	0.891	0.557	0.421
1133	0.675	0.170	0.155	0.584	0.187	0.229	1.156	0.909	0.677	0.450
					Charge II					
554	0.604	0.287	0.109	0.251	0.317	0.432	2.406	0.905	0.252	0.423
691	0.619	0.280	0.101	0.318	0.333	0.349	1.947	0.841	0.289	0.488
830	0.624	0.276	0.100	0.371	0.330	0.299	1.682	0.836	0.334	0.525
950	0.615	0.268	0.117	0.437	0.320	0.243	1.407	0.838	0.481	0.568
1021	0.595	0.280	0.125	0.489	0.308	0.203	1.217	0.909	0.616	0.603
1046	0.580	0.283	0.137	0.507	0.304	0.189	1.144	0.931	0.725	0.617
					Charge III					
512	0.501	0.394	0.105	0.190	0.415	0.395	2.637	0.949	0.266	0.512
627	0.524	0.383	0.0928	0.239	0.436	0.325	2.192	0.878	0.286	0.573
755	0.540	0.372	0.0880	0.299	0.442	0.259	1.806	0.842	0.340	0.631
852	0.543	0.366	0.0910	0.354	0.433	0.213	1.534	0.845	0.427	0.670
924	0.517	0.375	0.108	0.401	0.421	0.178	1.289	0.891	0.607	0.703
962	0.513	0.375	0.112	0.426	0.410	0.164	1.204	0.915	0.683	0.714
					Charge IV					
514	0.365	0.551	0.0837	0.143	0.569	0.288	2.552	0.968	0.291	0.664
629	0.389	0.540	0.0712	0.193	0.595	0.212	2.016	0.908	0.336	0.737
726	0.403	0.528	0.0693	0.238	0.598	0.164	1.693	0.883	0.423	0.785
809	0.394	0.529	0.0770	0.287	0.585	0.128	1.373	0.904	0.602	0.820
837	0.392	0.528	0.0800	0.304	0.575	0.121	1.289	0.918	0.661	0.826
					At 350° F.					
					Charge I					
542	0.698	0.0775	0.224	0.236	0.0682	0.696	2.958	1.136	0.322	0.0892
685	0.719	0.0745	0.206	0.304	0.0745	0.621	2.365	1.000	0.332	0.107
832	0.732	0.0723	0.196	0.373	0.0780	0.549	1.962	0.927	0.357	0.124
965[b]	0.725	0.0717	0.203							
970[a]				0.443	0.0800	0.477				
1080	0.705	0.0730	0.222	0.498	0.0793	0.423	1.416	0.921	0.525	0.158
1153	0.683	0.0735	0.243	0.552	0.0788	0.369	1.237	0.933	0.659	0.176
					Charge II					
528	0.622	0.166	0.212	0.214	0.144	0.642	2.907	1.153	0.330	0.183
682	0.640	0.165	0.195	0.278	0.162	0.560	2.302	1.019	0.348	0.224
819	0.649	0.162	0.189	0.347	0.171	0.482	1.870	0.947	0.392	0.262
956	0.651	0.160	0.189	0.410	0.175	0.415	1.588	0.916	0.455	0.296
1054	0.628	0.159	0.213	0.470	0.172	0.358	1.336	0.924	0.595	0.325
1109	0.612	0.161	0.227	0.517	0.172	0.311	1.184	0.936	0.730	0.356
					Charge III					
528	0.532	0.289	0.179	0.188	0.257	0.555	2.830	1.125	0.323	0.317
669	0.540	0.286	0.174	0.243	0.284	0.473	2.222	1.007	0.368	0.375
795	0.545	0.283	0.172	0.299	0.299	0.402	1.823	0.946	0.428	0.427
893	0.543	0.282	0.175	0.339	0.302	0.359	1.602	0.934	0.487	0.457
975	0.529	0.280	0.191	0.392	0.300	0.308	1.349	0.933	0.620	0.493
1021	0.516	0.282	0.202	0.416	0.297	0.287	1.240	0.949	0.703	0.509
					Charge IV					
536	0.405	0.441	0.154	0.143	0.406	0.451	2.832	1.086	0.341	0.474
643	0.410	0.439	0.151	0.179	0.427	0.394	2.291	1.028	0.383	0.520
759	0.414	0.437	0.149	0.228	0.446	0.326	1.816	0.980	0.457	0.578
854	0.413	0.435	0.152	0.277	0.455	0.268	1.491	0.956	0.567	0.629
923	0.405	0.438	0.157	0.317	0.456	0.227	1.278	0.961	0.692	0.668

[a] Liquid sample only. [b] Vapor sample only.

Table II. Critical Pressures and Compositions for Each Temperature Investigated

	Critical Pressure, P.S.I.A.	Composition at Critical Point, Mole Fraction			
		Ethane	*n*-Butane	*n*-Heptane	*C*
		Critical Temperature, 300° F.			
Ethane–*n*-Heptane	1275	0.760	0.000	0.240	0.000
Charge I	1250	0.705	0.069	0.226	0.234
Charge V	1169	0.636	0.173	0.191	0.475
Charge II	1076	0.544	0.293	0.163	0.643
Charge III	995	0.474	0.390	0.136	0.741
Charge IV	877	0.356	0.547	0.097	0.849
Ethane–*n*-Butane	591	0.075	0.925	0.000	1.000
		Critical Temperature, 350° F.			
Ethane–*n*-Heptane	1219	0.681	0.000	0.319	0.000
Charge I	1195	0.625	0.077	0.298	0.205
Charge II	1140	0.559	0.169	0.272	0.383
Charge III	1066	0.466	0.290	0.244	0.543
Charge, IV	965	0.360	0.448	0.192	0.700
n-Butane–*n*-Heptane[a]	591	0.000	0.910	0.090	0.910

[a] Obtained by extrapolation of data of this investigation; Kay (*4*) reports a value of 592 p.s.i.a. for the critical pressure of the binary composition $x_4 = 0.863$ and $x_7 = 0.137$.

were determined from the smoothed curves of each charge. The final value of the critical pressure for each charge was established as the pressure at which the curves for the three components converged at $K = 1.00$ in a plot of equilibrium constant *vs.* pressure. The resulting values of the critical pressure are presented in Table II with the corresponding temperatures and compositions and the critical values of the related binaries.

The resulting critical pressures are plotted against the corresponding compositions to produce the relationships for each temperature (Figure 2). The critical pressures of the charges and related binaries are also plotted against the composition parameter to obtain a single relationship for each temperature (Figure 3). In this figure, the 300° F. critical isotherm terminates at the ethane–*n*-butane binary system whose composition is $x_2 = 0.075$ and $x_4 = 0.925$ ($C = 1.00$) for which $P_c = 591$ p.s.i.a. On the other hand, the 350° F. critical isotherm terminates on the *n*-butane–*n*-heptane binary system at a composition $x_4 = 0.910$ and $x_7 = 0.090$ ($C = 0.910$) for which the critical pressure also happens to be 591 p.s.i.a. Vapor-liquid equilibrium constants obtained from the smoothed curves of each charge, of the form of Figure 1, were plotted against the composition parameter, C, and were cross-plotted as K against pressure

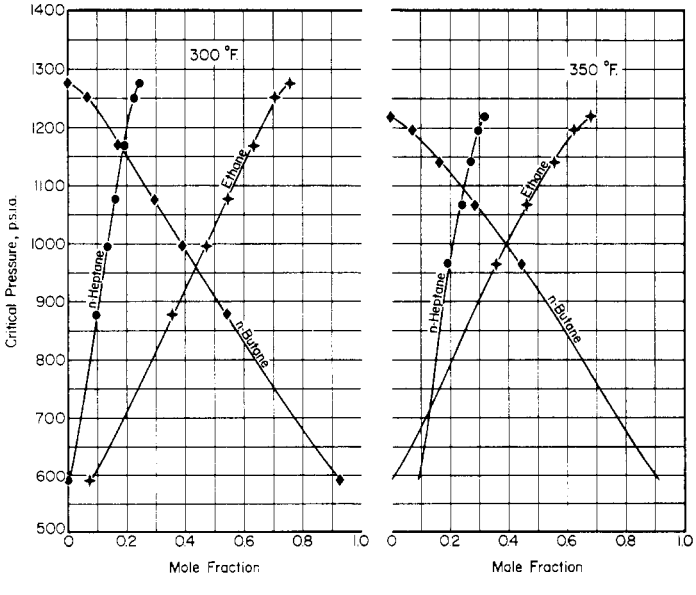

Figure 2. Relationships between critical pressure and composition at 300° and 350° F. for the ethane–*n*-butane–*n*-heptane system

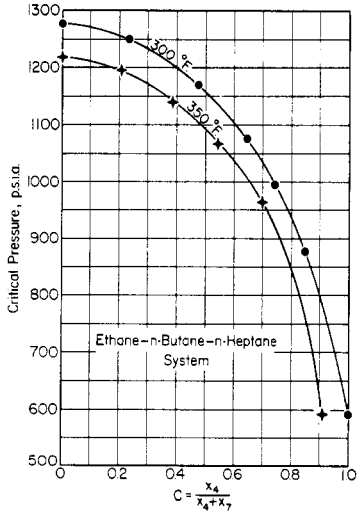

Figure 3. Relationships between critical pressure and composition parameter for the ethane–*n*-butane–*n*-heptane system at 300° and 350° F.

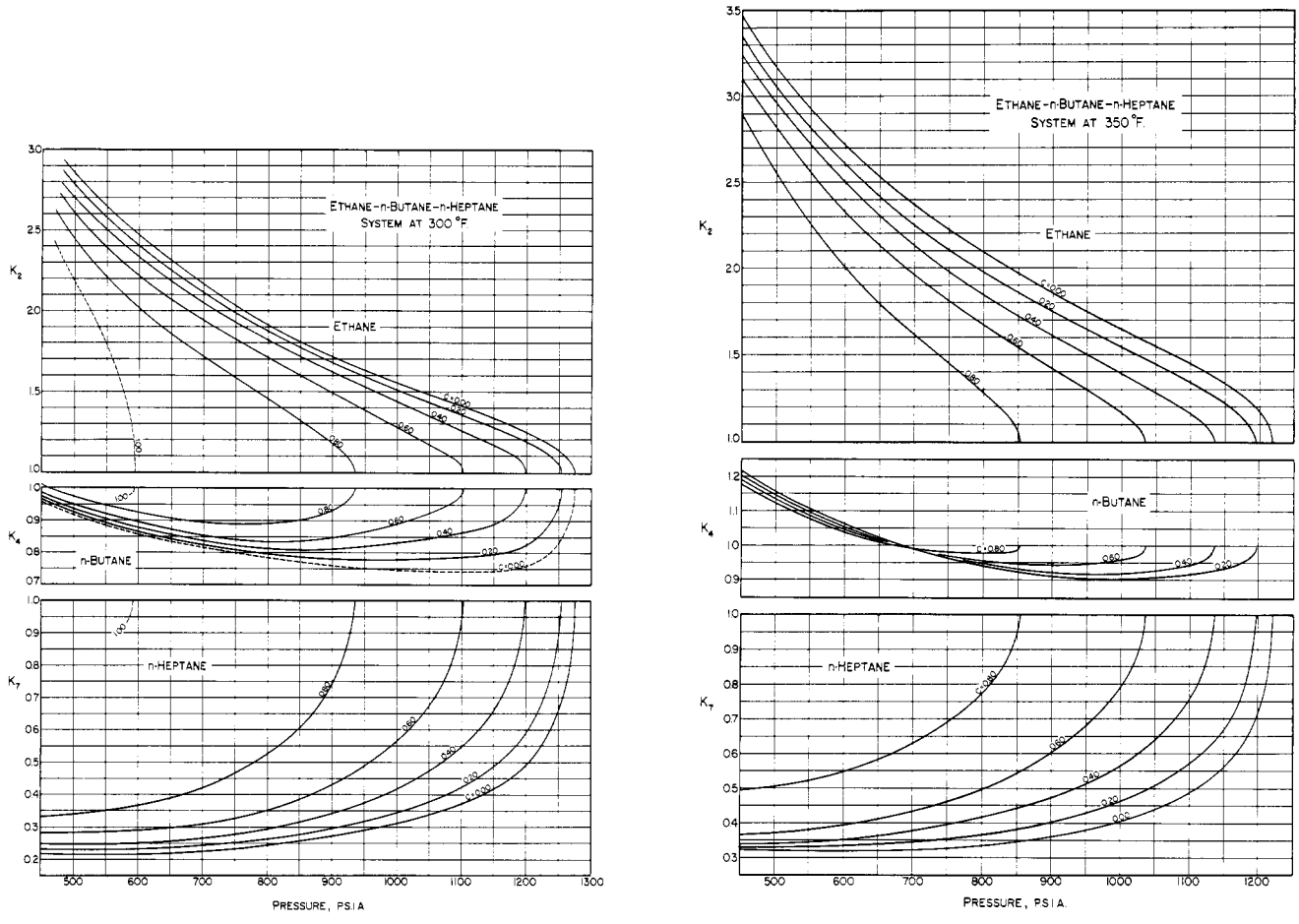

Figure 4. Vapor-liquid equilibrium constants for the ethane–*n*-butane–*n*-heptane system

300° F.

350° F.

Table III. Final *K* Values for the System Ethane–*n*-Butane–*n*-Heptane

Press., P.S.I.A.	Equilibrium Constant, $K = y/x$ Ethane	*n*-Butane	*n*-Heptane
	At 300° F.		
	$C = 0.000$		
450	3.118		0.220
500	2.861		0.217
550	2.644		0.216
600	2.478		0.215
650	2.314		0.219
700	2.165		0.223
750	2.030		0.232
800	1.914		0.243
850	1.810		0.259
900	1.718		0.274
950	1.633		0.292
1000	1.555		0.313
1050	1.484		0.336
1100	1.414		0.369
1150	1.338		0.415
1200	1.255		0.489
1230	1.188		0.581
1250	1.136		0.671
1275[a]	1.000		1.000
	$C = 0.200$		
450	3.065	0.966	0.230
500	2.785	0.925	0.228
550	2.579	0.893	0.229
600	2.403	0.865	0.230
650	2.252	0.843	0.235
700	2.113	0.823	0.242
750	1.984	0.809	0.250
800	1.872	0.796	0.262
850	1.772	0.787	0.276
900	1.680	0.781	0.291
950	1.596	0.777	0.315
1000	1.513	0.777	0.342
1050	1.435	0.782	0.379
1100	1.360	0.790	0.426
1140	1.297	0.794	0.475
1180	1.226	0.807	0.540
1200	1.189	0.825	0.589
1220	1.147	0.853	0.661
1255[a]	1.000	1.000	1.000
	$C = 0.400$		
450	3.008	0.975	0.248
500	2.701	0.935	0.247
550	2.500	0.904	0.249
600	2.329	0.876	0.252

[a] Critical point.

(*Continued*)

Table III. Final K Values for the System Ethane–*n*-Butane–*n*-Heptane (*Continued*)

Press., P.S.I.A.	Equilibrium Constant, $K = y/x$ Ethane	*n*-Butane	*n*-Heptane
	$C = 0.400$		
650	2.183	0.854	0.257
700	2.051	0.834	0.265
750	1.929	0.820	0.277
800	1.819	0.811	0.293
850	1.720	0.807	0.315
900	1.625	0.810	0.339
950	1.533	0.818	0.373
1000	1.441	0.832	0.417
1050	1.349	0.846	0.473
1100	1.257	0.862	0.550
1140	1.187	0.881	0.632
1160	1.150	0.898	0.696
1180	1.110	0.927	0.790
1198[a]	1.000	1.000	1.000
	$C = 0.600$		
450	2.932	0.987	0.281
500	2.605	0.950	0.281
550	2.391	0.922	0.284
600	2.220	0.897	0.290
650	2.070	0.874	0.297
700	1.946	0.855	0.307
750	1.829	0.841	0.323
800	1.712	0.835	0.349
850	1.600	0.837	0.384
900	1.494	0.846	0.430
950	1.387	0.865	0.490
1000	1.277	0.891	0.568
1020	1.232	0.904	0.606
1040	1.192	0.918	0.650
1060	1.150	0.933	0.708
1080	1.101	0.951	0.790
1102[a]	1.000	1.000	1.000
	$C = 0.800$		
450	2.810	1.010	0.334
500	2.446	0.975	0.337
550	2.210	0.948	0.350
600	2.014	0.926	0.368
650	1.855	0.907	0.390
700	1.716	0.895	0.421
750	1.585	0.890	0.468
800	1.453	0.890	0.527
840	1.347	0.899	0.589
880	1.238	0.917	0.678
900	1.175	0.933	0.746
920	1.110	0.958	0.842
935[a]	1.000	1.000	1.000
	At 350° F. $C = 0.000$		
450	3.474		0.330
500	3.182		0.325
550	2.931		0.322
600	2.721		0.321
650	2.529		0.319
700	2.376		0.322
750	2.229		0.327
800	2.093		0.336
850	1.973		0.346
900	1.857		0.361
950	1.750		0.381
1000	1.651		0.404
1050	1.549		0.440
1100	1.448		0.487
1150	1.336		0.563
1170	1.288		0.602
1190	1.218		0.673
1219[a]	1.000		1.000

Press., P.S.I.A.	Equilibrium Constant, $K = y/x$ Ethane	*n*-Butane	*n*-Heptane
	$C = 0.200$		
450	3.351	1.218	0.335
500	3.067	1.157	0.331
550	2.827	1.107	0.332
600	2.610	1.063	0.335
650	2.420	1.025	0.340
700	2.254	0.992	0.349
750	2.110	0.964	0.358
800	1.982	0.941	0.370
850	1.863	0.925	0.385
900	1.752	0.914	0.405
950	1.648	0.906	0.430
1000	1.549	0.905	0.463
1050	1.448	0.910	0.508
1100	1.340	0.921	0.573
1120	1.297	0.927	0.607
1140	1.248	0.935	0.647
1160	1.192	0.945	0.702
1180	1.117	0.958	0.802
1195[a]	1.000	1.000	1.000
	$C = 0.400$		
450	3.241	1.204	0.341
500	2.965	1.145	0.341
550	2.720	1.097	0.345
600	2.494	1.053	0.353
650	2.303	1.020	0.365
700	2.137	0.992	0.380
750	1.984	0.968	0.399
800	1.847	0.948	0.420
850	1.724	0.933	0.445
900	1.611	0.923	0.475
950	1.503	0.920	0.514
1000	1.396	0.922	0.565
1040	1.303	0.928	0.624
1080	1.208	0.939	0.703
1100	1.160	0.947	0.756
1120	1.100	0.962	0.838
1135[a]	1.000	1.000	1.000
	$C = 0.600$		
450	3.100	1.190	0.367
500	2.819	1.135	0.372
550	2.561	1.087	0.381
600	2.326	1.046	0.395
650	2.130	1.015	0.413
700	1.961	0.992	0.435
750	1.807	0.972	0.465
800	1.670	0.957	0.500
850	1.542	0.948	0.545
900	1.422	0.945	0.604
940	1.327	0.947	0.665
980	1.220	0.954	0.743
1000	1.160	0.962	0.793
1020	1.100	0.972	0.862
1036[a]	1.000	1.000	1.000
	$C = 0.800$		
450	2.897	1.177	0.495
500	2.558	1.125	0.505
550	2.258	1.078	0.524
600	2.003	1.038	0.550
650	1.792	1.009	0.584
700	1.618	0.992	0.629
740	1.487	0.984	0.677
780	1.350	0.980	0.738
800	1.280	0.979	0.776
820	1.207	0.980	0.821
840	1.127	0.983	0.891
855[a]	1.000	1.000	1.000

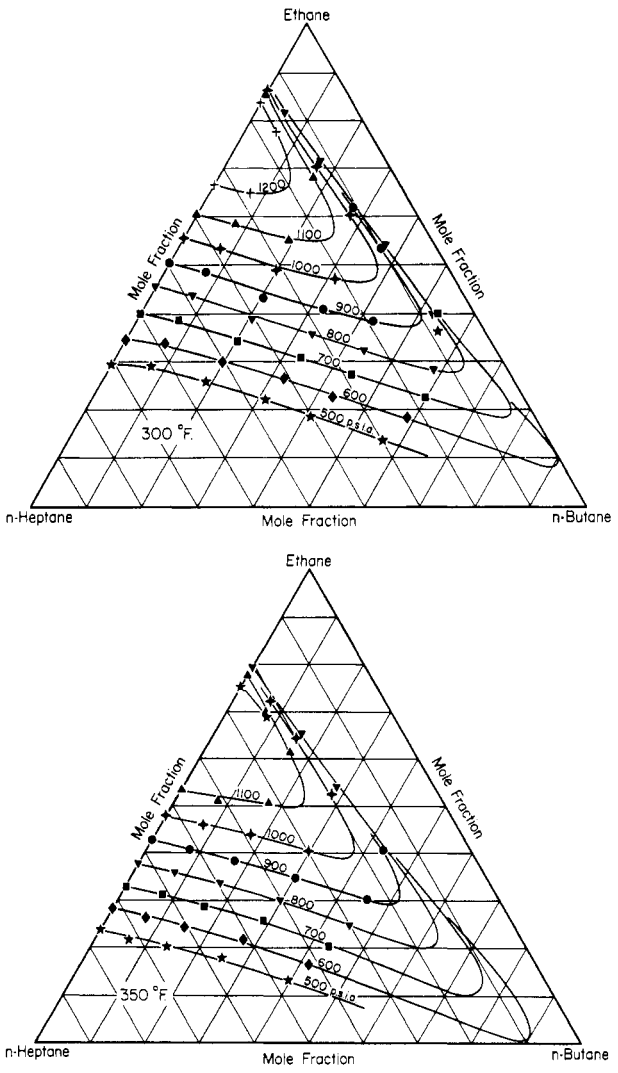

Figure 5. Vapor-liquid equilibrium behavior for the ethane–*n*-butane–*n*-heptane system
Top: 300° F.
Bottom: 350° F.

for constant composition parameters. The resulting curves are presented in Figure 4 for 300° and 350° F. Final K values for this ternary system obtained from Figure 4 are presented in Table III.

The vapor-liquid equilibrium behavior of this system is presented in the form of triangular plots for the two temperatures, 300° and 350° F., (Figure 5). These figures present the bubble point and dew point curves at convenient pressures and permit the establishment of the two phase region for pressures above 500 p.s.i.a. and temperatures of 300° and 350° F.

NOMENCLATURE

- C = composition parameter, $x_i/(x_i + x_h)$
- K = vapor-liquid equilibrium constant, y/x
- x = mole fraction of a component in liquid phase
- x_h = mole fraction in liquid phase of component of lowest volatility
- x_i = mole fraction in liquid phase of component of intermediate volatility
- y = mole fraction of a component in vapor phase

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