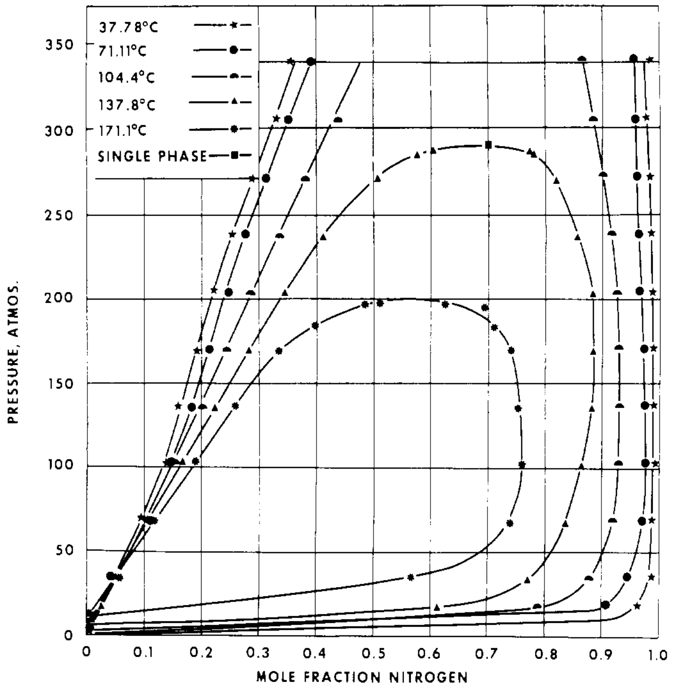

Figure 1. Vapor-liquid equilibria for the nitrogen–*n*-hexane system

air bath. This procedure prevented the possibility of condensation of the *n*-hexane, since the air bath was maintained above 66° C. (150° F.) and sample pressure in the flask was below 1 atm.

A unique two-column arrangement was employed utilizing an 8.0-foot Ansul ether column and a 3.5-foot molecular sieve column in series with switching valves, so that a complete analysis could be made in 8.5 minutes including a correction for any air leakage. No pressure or volume measurements were needed, once the instrument had been calibrated to analyze each sample and only one run per sample was necessary.

Many reruns and checks were made to ascertain that the instrument was properly calibrated and that the analysis was consistent. A mass spectrometer was used as an independent analytical instrument to check the gas chromatograph.

Materials Used. The *n*-hexane was research grade with a stated purity of 99.9%. The nitrogen was dry research grade with a purity of 99.85%. These purities were ascertained on both the gas chromatograph and the mass spectrometer.

RESULTS

The experimentally determined compositions of the coexisting vapor and liquid phases are listed in Table I and plotted in a pressure-composition diagram in Figure 1. The solubility of nitrogen in the liquid hydrocarbon phase increases with pressure, as was reported by several investigators (*1, 2, 3*).

ACCURACY

The over-all analytical procedure is thought to be reliable to ±0.002 mole fraction. Temperature variations within the cell were ±0.11° C. (0.2° F.) during circulation and ±0.028° C. (0.05° F.) during sampling and settling. The accuracy of the reported pressures is ±0.14 atm. (2 p.s.i.a.) during circulation, settling, and sampling.

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Vapor-Liquid Equilibrium Constants for the Ethane–*n*-Butane–*n*-Heptane System at 150°, 200°, and 250° F.

VINOD S. MEHRA and GEORGE THODOS
Northwestern University, Evanston, Ill.

Vapor-liquid equilibrium constants for the system, ethane–*n*-butane–*n*-heptane have been established at 150°, 200°, and 250° F. for pressures ranging 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 each temperature investigated.

CONSIDERABLE vapor-liquid equilibrium data extending into the critical region are presented in the literature for binary systems, but such information for mixtures containing more than two components is limited. To extend this information to the behavior of three-component systems, Herlihy and Thodos (*3*) and Mehra and Thodos (*7*) experimentally determined vapor-liquid equilibrium constants for the ethane-*n*-butane-*n*-pentane system at 150°, 200°, 250°, and 300° F. This type of study is being continued in the present investigation and deals with the ethane-*n*-butane-*n*-heptane system, which was selected for investigation because the three binaries of this ternary system have been comprehensively studied by Kay (*4,5,6*). Recent experimental vapor-liquid equilibrium constants are also reported by Mehra and Thodos for the ethane-*n*-butane and the ethane-*n*-heptane systems (*8,9*). Experimental K values for the ethane-*n*-butane-*n*-heptane system have been established in this investigation at 150°, 200°, and 250° F.

APPARATUS AND PROCEDURE

The experimental equipment is the same as that used for the ethane–*n*-butane–*n*-pentane system, and consists of a stainless steel equilibrium cell provided with a movable piston for varying the volume of the equilibrium chamber. This piston was actuated with mercury supplied from a positive displacement pump. The pressure of the system was measured with two Heise gages which were connected to this mercury system. These gages were calibrated periodically against a dead-weight gage and found to be reproducible to within 3 p.s.i. for the pressure range encountered in this study. The cell was surrounded with a constant temperature air bath, which was capable of maintaining the over-all temperature of the cell to within 0.3° F. of the desired temperature. Under these conditions, the temper-

Table I. Experimental Vapor-Liquid Equilibrium Data for the Ethane–*n*-Butane–*n*-Heptane System at 150° F.

Pressure, 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	
					CHARGE I					
511	0.966	0.0206	0.0134	0.546	0.0553	0.399	1.769	0.373	0.0336	0.122
615	0.964	0.0205	0.0155	0.618	0.0520	0.330	1.560	0.394	0.0469	0.158
733	0.962	0.0205	0.0175	0.720	0.0500	0.230	1.336	0.410	0.0761	0.217
819	0.958	0.0208	0.0210	0.784	0.0457	0.170	1.222	0.455	0.124	0.212
898	0.954	0.0222	0.0240	0.848	0.0390	0.113	1.125	0.569	0.212	0.257
948[a]				0.891	0.0345	0.0745				
952[b]	0.945	0.0242	0.0312							
					CHARGE II					
522	0.933	0.0532	0.0142	0.532	0.154	0.314	1.754	0.345	0.0452	0.329
619	0.940	0.0462	0.0142	0.614	0.1285	0.2575	1.531	0.360	0.0551	0.333
727	0.941	0.0434	0.0154	0.704	0.112	0.184	1.337	0.388	0.0837	0.378
808	0.940	0.0424	0.0173	0.770	0.0965	0.1335	1.221	0.439	0.130	0.419
878	0.938	0.0432	0.0191	0.831	0.0812	0.0873	1.129	0.532	0.219	0.482
918[a]				0.864	0.0700	0.0660				
920[b]	0.930	0.0460	0.0244							
					CHARGE III					
528	0.902	0.0870	0.0110	0.513	0.246	0.241	1.758	0.354	0.0456	0.505
633	0.906	0.0830	0.0110	0.612	0.217	0.171	1.480	0.382	0.0643	0.559
715	0.910	0.0792	0.0111	0.688	0.1885	0.1235	1.323	0.420	0.0899	0.604
799	0.914	0.0741	0.0121	0.752	0.1622	0.0862	1.215	0.457	0.140	0.654
849[b]	0.911	0.0750	0.0140							
852[a]				0.797	0.141	0.0617				

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

Table II. Experimental Vapor-Liquid Equilibrium Data for the Ethane–*n*-Butane–*n*-Heptane System at 200° F.

Pressure, 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	
					CHARGE I					
506	0.926	0.0355	0.0385	0.424	0.0693	0.507	2.184	0.512	0.0759	0.120
625	0.929	0.0335	0.0375	0.512	0.0673	0.421	1.814	0.497	0.0891	0.138
735	0.930	0.0337	0.0365	0.567	0.0661	0.367	1.640	0.510	0.0994	0.153
860	0.930	0.0315	0.0385	0.642	0.0613	0.297	1.449	0.514	0.130	0.171
968	0.925	0.0316	0.0435	0.710	0.0559	0.234	1.303	0.565	0.147	0.193
1045	0.919	0.0314	0.0495	0.754	0.0524	0.194	1.219	0.599	0.255	0.213
1088[a]				0.788	0.0502	0.162				
1090[b]	0.908	0.0333	0.0583							
					CHARGE II					
503	0.874	0.0940	0.0324	0.392	0.1795	0.428	2.230	0.524	0.0757	0.295
625	0.881	0.0855	0.0332	0.484	0.1655	0.350	1.820	0.517	0.0949	0.321
746	0.887	0.0794	0.0333	0.576	0.154	0.270	1.540	0.516	0.123	0.363
859	0.885	0.0791	0.0358	0.635	0.142	0.223	1.394	0.557	0.161	0.389
954	0.882	0.0767	0.0410	0.689	0.130	0.181	1.280	0.590	0.227	0.418
1037[b]	0.877	0.0764	0.0464							
1040[a]				0.744	0.116	0.140				
					CHARGE III					
502	0.821	0.149	0.0303	0.390	0.266	0.344	2.105	0.560	0.0881	0.436
622	0.830	0.141	0.0286	0.457	0.262	0.281	1.816	0.538	0.102	0.483
744	0.838	0.133	0.0287	0.536	0.252	0.212	1.563	0.528	0.135	0.543
867	0.840	0.128	0.0317	0.611	0.224	0.165	1.375	0.571	0.192	0.576
936[b]	0.838	0.128	0.0340							
942[a]				0.670	0.204	0.126				
					CHARGE IV					
485	0.751	0.225	0.0240	0.355	0.398	0.247	2.115	0.565	0.0972	0.617
605	0.768	0.210	0.0220	0.419	0.385	0.196	1.833	0.545	0.112	0.663
715	0.781	0.198	0.0207	0.500	0.356	0.144	1.562	0.556	0.144	0.712
805	0.790	0.188	0.0220	0.559	0.323	0.118	1.413	0.582	0.186	0.732
883	0.794	0.181	0.0247	0.619	0.290	0.0914	1.283	0.624	0.270	0.760

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

Table III. Experimental Vapor-Liquid Equilibrium Data for the Ethane–*n*-Butane–*n*-Heptane System at 250° F.

Pressure, P.S.I.A.	y, Vapor Mole Fraction			x, Liquid Mole Fraction			$K = y/x$			
	Ethane	*n*-Butane	*n*-Heptane	Ethane	*n*-Butane	*n*-Heptane	Ethane	*n*-Butane	*n*-Heptane	C
					CHARGE I					
520	0.874	0.0524	0.0737	0.365	0.0760	0.559	2.394	0.689	0.132	0.120
658	0.881	0.0505	0.0684	0.441	0.0771	0.482	1.998	0.655	0.142	0.138
816	0.883	0.0485	0.0685	0.517	0.0775	0.405	1.708	0.626	0.169	0.161
965	0.878	0.0481	0.0743	0.592	0.0740	0.334	1.483	0.650	0.222	0.181
1094	0.868	0.0475	0.0847	0.657	0.0700	0.273	1.321	0.679	0.310	0.204
1185[a]	0.855	0.0490	0.0962							
1184[b]				0.709	0.0650	0.226				
					CHARGE II					
488	0.810	0.120	0.0695	0.332	0.164	0.504	2.440	0.732	0.138	0.246
627	0.824	0.112	0.0638	0.406	0.159	0.435	2.030	0.704	0.147	0.267
765	0.829	0.108	0.0633	0.472	0.163	0.365	1.756	0.663	0.173	0.309
916	0.830	0.104	0.0663	0.545	0.158	0.297	1.523	0.658	0.223	0.347
1052	0.818	0.104	0.0780	0.613	0.149	0.238	1.334	0.698	0.328	0.385
1152	0.803	0.108	0.0890	0.650	0.144	0.206	1.235	0.750	0.432	0.411
1148[b]				0.675	0.138	0.187				
1150[a]	0.790	0.111	0.0990							
					CHARGE III					
455	0.715	0.220	0.0648	0.277	0.288	0.435	2.581	0.764	0.149	0.398
614	0.736	0.206	0.0580	0.351	0.298	0.351	2.097	0.691	0.165	0.459
755	0.751	0.195	0.0540	0.436	0.293	0.271	1.722	0.666	0.199	0.520
913	0.750	0.191	0.0585	0.508	0.274	0.218	1.476	0.697	0.268	0.557
1024	0.742	0.190	0.0675	0.573	0.255	0.172	1.295	0.745	0.392	0.597
1065	0.730	0.194	0.0760	0.598	0.246	0.156	1.221	0.789	0.487	0.612
					CHARGE IV					
453	0.594	0.354	0.0523	0.222	0.454	0.324	2.676	0.780	0.161	0.584
604	0.621	0.335	0.0435	0.301	0.463	0.236	2.064	0.724	0.184	0.662
733	0.643	0.316	0.0410	0.375	0.446	0.179	1.715	0.709	0.229	0.714
835[b]				0.440	0.423	0.137				
914	0.643	0.302	0.0552	0.483	0.398	0.119	1.331	0.759	0.464	0.770
953	0.625	0.315	0.0598	0.502	0.387	0.111	1.245	0.814	0.539	0.777

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

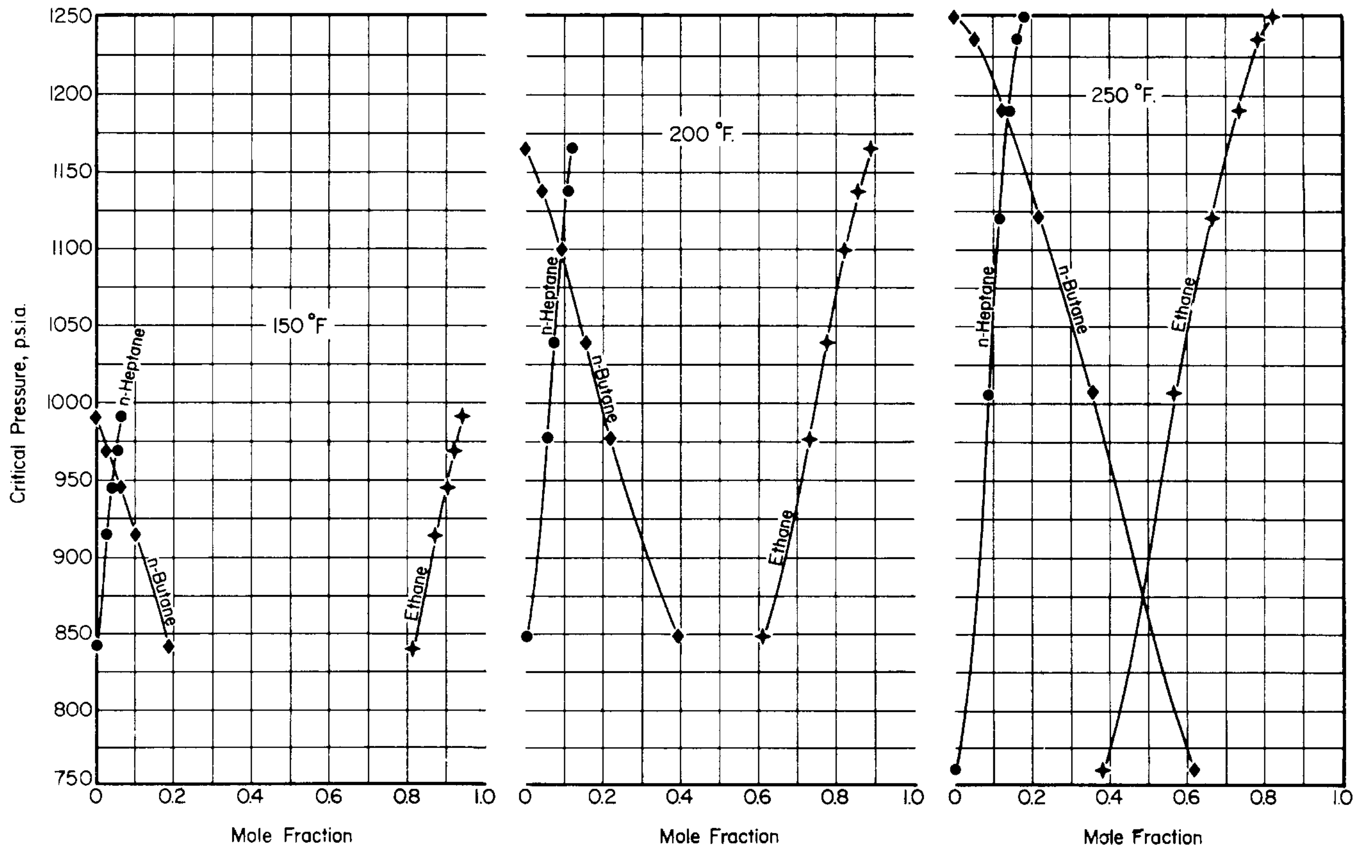

Figure 1. Relation between critical pressure and composition at 150°, 200°, and 250° F. for ethane–*n*-butane–*n*-heptane system

Table IV. Final *K* Values for the System Ethane–*n*-Butane–*n*-Heptane at 150° F.

Pressure, P.S.I.A.	Vapor-Liquid Equilibrium Constant, $K = y/x$		
	Ethane	*n*-Butane	*n*-Heptane
	$C = 0.000$		
450	1.932		0.0340
500	1.774		0.0373
550	1.650		0.0391
600	1.540		0.0443
650	1.451		0.0498
700	1.372		0.0595
750	1.307		0.0685
800	1.247		0.0849
850	1.191		0.113
900	1.140		0.161
920	1.122		0.191
950	1.092		0.255
970	1.064		0.376
991[a]	1.000		1.000
	$C = 0.200$		
450	1.920	0.342	0.0369
500	1.763	0.345	0.0400
550	1.640	0.350	0.0440
600	1.534	0.356	0.0492
650	1.445	0.364	0.0565
700	1.367	0.375	0.0670
750	1.300	0.392	0.0800
800	1.230	0.421	0.100
850	1.182	0.469	0.137
900	1.127	0.550	0.200
920	1.105	0.597	0.238
940	1.085	0.657	0.294
960	1.061	0.752	0.412
979[a]	1.000	1.000	1.000
	$C = 0.400$		
450	1.907	0.349	0.0400
500	1.755	0.352	0.0439
550	1.632	0.356	0.0487
600	1.526	0.364	0.0545
650	1.438	0.371	0.0627
700	1.360	0.385	0.0753
750	1.292	0.400	0.0920
800	1.230	0.430	0.119
850	1.170	0.477	0.165
900	1.113	0.565	0.248
920	1.090	0.617	0.300
940	1.066	0.690	0.398
960	1.030	0.855	0.692
965[a]	1.000	1.000	1.000
	$C = 0.600$		
450	1.883	0.360	0.0441
500	1.739	0.364	0.0486
550	1.618	0.370	0.0540
600	1.515	0.377	0.0615
	$C = 0.600$ (*continued*)		
650	1.427	0.389	0.0713
700	1.350	0.404	0.0850
750	1.280	0.424	0.105
800	1.218	0.453	0.136
840	1.170	0.490	0.182
860	1.145	0.514	0.217
880	1.120	0.549	0.290
900	1.094	0.599	0.323
920	1.067	0.678	0.363
940	1.030	0.875	0.720
944[a]	1.000	1.000	1.000
	$C = 0.800$		
450	1.851	0.389	0.0508
500	1.710	0.390	0.0569
550	1.618	0.395	0.0640
600	1.515	0.402	0.0736
650	1.405	0.417	0.0860
700	1.327	0.437	0.103
750	1.258	0.468	0.128
800	1.192	0.509	0.173
840	1.142	0.559	0.240
860	1.117	0.598	0.293
880	1.088	0.658	0.376
900	1.052	0.794	0.570
909[a]	1.000	1.000	1.000
	$C = 0.900$		
450	1.824		
500	1.682		
550	1.567		
600	1.468		
650	1.383		
700	1.306		
750	1.235		
800	1.167		
820	1.141		
840	1.112		
860	1.080		
882[a]	1.000		
	$C = 1.000$		
450	1.791	0.425	
500	1.647	0.426	
550	1.532	0.431	
600	1.438	0.438	
650	1.353	0.455	
700	1.280	0.479	
750	1.203	0.530	
800	1.130	0.615	
820	1.087	0.706	
841[a]	1.000	1.000	

[a] Critical point.

ature across the cell varied from 0.2° F. at 150° F. to 0.4° F. at 250° F. Agitation within the equilibrium chamber was provided with a stirrer, coupled magnetically to an external mechanical drive. Complete details of the cell and associated equipment are available elsewhere (*10*).

In the present study, each component was charged to the cell from individual charging reservoirs. With this arrangement, the desired amount of each component could be conveniently introduced into the cell. Approximately 3 hours were required for the system to attain equilibrium. However, for conditions in the vicinity of the critical point, more time was necessary. After reaching equilibrium, microsamples of the vapor and liquid phases in equilibrium were withdrawn by first freezing each of them with liquid nitrogen in a sampling bulb and then allowing them to vaporize and expand in their respective bulbs. The volumes of the sampling bulbs were selected so that the partial pressure of the *n*-heptane in the bulb was always considerably less than its vapor pressure at room temperature.

The vapor and liquid samples were analyzed with a gas chromatography unit equipped with a thermal conductivity cell as detector. This unit was calibrated by preparing standards consisting of several mixtures of the binary systems, ethane–*n*-butane and ethane–*n*-heptane, whose compositions were determined with a mass spectrometer. The ratio of *n*-butane to ethane and *n*-heptane to ethane in the ternary mixture provided means for completely determining the composition of the ternary samples. Analyses carried out on the gas chromatograph were reproducible in a series of several measurements to within 1 mole % of a component based on the assumption that the mass spectrometer results represented the true composition.

MATERIALS

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

Table V. Final K values for the System Ethane–n-Butane–n-Heptane at 200° F.

Pressure, P.S.I.A.	Vapor-Liquid Equilibrium Constant, $K = y/x$ Ethane	n-Butane	n-Heptane
	$C = 0.000$		
450	2.435		0.0708
500	2.225		0.0721
550	2.056		0.0750
600	1.922		0.0780
650	1.803		0.0835
700	1.700		0.0876
750	1.610		0.0968
800	1.531		0.107
850	1.457		0.120
900	1.392		0.135
950	1.329		0.161
1000	1.273		0.194
1050	1.222		0.233
1100	1.166		0.302
1120	1.140		0.354
1140	1.104		0.456
1165[a]	1.000		1.000
	$C = 0.200$		
450	2.834	0.524	0.0760
500	2.183	0.513	0.0776
550	2.030	0.506	0.0810
600	1.899	0.503	0.0860
650	1.780	0.502	0.0919
700	1.678	0.504	0.0989
750	1.588	0.508	0.108
800	1.511	0.514	0.118
850	1.444	0.524	0.132
900	1.378	0.535	0.150
950	1.316	0.550	0.176
1000	1.260	0.572	0.211
1050	1.209	0.606	0.265
1100	1.147	0.678	0.370
1120	1.117	0.740	0.470
1140	1.069	0.871	0.705
1148[a]	1.000	1.000	1.000
	$C = 0.400$		
450	2.336	0.540	0.0839
500	2.150	0.530	0.0860
550	2.000	0.523	0.0899
600	1.874	0.520	0.0953
650	1.759	0.518	0.102
700	1.658	0.519	0.112
750	1.570	0.522	0.124
800	1.490	0.529	0.137
850	1.420	0.541	0.156
900	1.353	0.557	0.180
950	1.291	0.580	0.210
1000	1.233	0.607	0.252
1040	1.189	0.643	0.305
1060	1.163	0.674	0.350
1080	1.134	0.720	0.422
1100	1.100	0.800	0.554
1118[a]	1.000	1.000	1.000
	$C = 0.600$		
450	2.290	0.560	0.0918
500	2.105	0.549	0.0959
550	1.957	0.543	0.102
	$C = 0.600$ (*continued*)		
600	1.836	0.541	0.107
650	1.722	0.540	0.116
700	1.620	0.541	0.127
750	1.532	0.545	0.142
800	1.457	0.554	0.160
850	1.388	0.567	0.186
900	1.310	0.586	0.222
950	1.241	0.625	0.274
1000	1.174	0.683	0.359
1020	1.148	0.720	0.411
1040	1.123	0.775	0.492
1060	1.080	0.878	0.658
1069[a]	1.000	1.000	1.000
	$C = 0.800$		
450	2.237	0.581	0.107
500	2.052	0.572	0.114
550	1.902	0.567	0.120
600	1.779	0.565	0.128
650	1.661	0.566	0.141
700	1.560	0.571	0.157
750	1.468	0.582	0.178
800	1.383	0.600	0.207
850	1.310	0.627	0.251
900	1.230	0.673	0.320
920	1.198	0.701	0.363
940	1.160	0.736	0.423
960	1.120	0.786	0.510
980	1.079	0.867	0.668
992[a]	1.000	1.000	1.000
	$C = 0.900$		
450	2.205		
500	2.011		
550	1.852		
600	1.730		
650	1.611		
700	1.509		
750	1.411		
800	1.320		
840	1.242		
860	1.201		
880	1.160		
900	1.114		
920	1.070		
933[a]	1.000		
	$C = 1.000$		
450	2.173	0.613	
500	1.972	0.605	
550	1.809	0.601	
600	1.670	0.606	
650	1.546	0.620	
700	1.448	0.635	
750	1.351	0.663	
800	1.243	0.721	
820	1.183	0.770	
830	1.147	0.805	
848[a]	1.000	1.000	

[a] Critical point.

EXPERIMENTAL INVESTIGATION

For a ternary system, the vapor-liquid equilibrium constant, $K = y/x$ is a function of temperature, pressure, and the composition of the three-component mixture. Therefore, if the temperature and pressure are fixed, one other intensive quantity which depends on composition must be specified in order to define the system. Such an intensive quantity which has found widespread use is the composition parameter, defined as follows (*1*):

$$C = \frac{x_i}{x_i + x_h} \tag{1}$$

Throughout the entire range of compositions of the ternary system of the study, the composition parameter varies from zero for the ethane–n-heptane system to unity for the ethane–n-butane system.

For temperatures of 150°, 200°, and 250° F., charges were prepared with composition parameters, C, ranging from zero to unity. The charge compositions were selected so that they corresponded to critical temperatures very close to 150°, 200°, and 250° F. These compositions were established by the method described by Grieves and Thodos (*2*). 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

Table VI. Final K Values for the System Ethane–n-Butane–n-Heptane at 250° F.

Pressure, P.S.I.A.	Vapor-Liquid Equilibrium Constant, $K = y/x$		
	Ethane	n-Butane	n-Heptane
	$C = 0.000$		
450	2.755		0.135
500	2.550		0.135
550	2.378		0.134
600	2.217		0.137
650	2.074		0.139
700	1.958		0.144
750	1.850		0.150
800	1.755		0.159
850	1.674		0.170
900	1.598		0.184
950	1.533		0.200
1000	1.471		0.218
1050	1.410		0.244
1100	1.349		0.279
1150	1.285		0.329
1200	1.212		0.422
1220	1.172		0.488
1250[a]	1.000		1.000
	$C = 0.200$		
450	2.709	0.740	0.143
500	2.503	0.712	0.141
550	2.334	0.693	0.142
600	2.175	0.676	0.145
650	2.032	0.661	0.150
700	1.916	0.649	0.154
750	1.811	0.640	0.161
800	1.723	0.636	0.170
850	1.643	0.635	0.184
900	1.570	0.636	0.200
950	1.505	0.640	0.220
1000	1.442	0.648	0.244
1050	1.378	0.662	0.275
1100	1.317	0.679	0.311
1140	1.266	0.701	0.355
1180	1.210	0.735	0.422
1200	1.180	0.763	0.478
1220	1.129	0.818	0.572
1239[a]	1.000	1.000	1.000
	$C = 0.400$		
450	2.660	0.759	0.153
500	2.457	0.732	0.152
550	2.291	0.711	0.154
600	2.140	0.693	0.156
650	2.000	0.678	0.160
700	1.881	0.666	0.167
750	1.780	0.659	0.176
800	1.693	0.657	0.189
850	1.610	0.660	0.205
900	1.536	0.664	0.225
950	1.467	0.670	0.250
1000	1.398	0.679	0.283
1050	1.334	0.695	0.330
1100	1.270	0.726	0.388
1140	1.209	0.767	0.465
1160	1.176	0.795	0.526
1180	1.133	0.835	0.612
1206[a]	1.000	1.000	1.000
	$C = 0.600$		
450	2.590	0.782	0.170
500	2.390	0.757	0.170
550	2.228	0.734	0.171
600	2.086	0.715	0.175
650	1.953	0.700	0.182
700	1.833	0.690	0.192
750	1.728	0.685	0.206
800	1.636	0.685	0.224
850	1.556	0.690	0.247
900	1.479	0.700	0.275
950	1.404	0.714	0.315
1000	1.330	0.736	0.364
1040	1.272	0.760	0.420
1080	1.213	0.801	0.514
1100	1.177	0.832	0.582
1120	1.133	0.872	0.682
1145[a]	1.000	1.000	1.000
	$C = 0.800$		
450	2.483	0.811	0.208
500	2.279	0.788	0.210
550	2.119	0.767	0.220
600	1.980	0.751	0.235
650	1.850	0.740	0.254
700	1.730	0.733	0.278
750	1.609	0.732	0.310
800	1.503	0.735	0.352
850	1.410	0.746	0.411
900	1.319	0.772	0.486
940	1.237	0.805	0.562
960	1.198	0.829	0.615
980	1.150	0.860	0.685
1000	1.100	0.903	0.790
1016[a]	1.000	1.000	1.000
	$C = 0.900$		
450	2.391		
500	2.177		
550	2.013		
600	1.872		
650	1.748		
700	1.621		
750	1.481		
800	1.335		
840	1.232		
860	1.183		
880	1.127		
903[a]	1.000		
	$C = 1.000$		
450	2.272	0.854	
500	2.022	0.836	
550	1.844	0.823	
600	1.705	0.813	
650	1.585	0.807	
700	1.470	0.811	
720	1.401	0.827	
740	1.292	0.859	
750	1.215	0.889	
761[a]	1.000	1.000	

[a] Critical point.

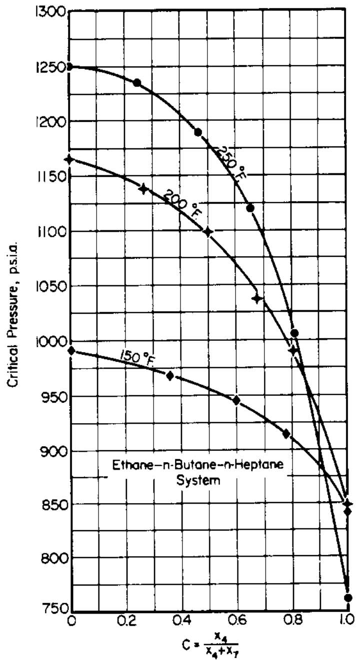

Figure 2. Relationship between critical pressure and composition parameter for ethane–n-butane–n-heptane system at 150°, 200°, and 250° F.

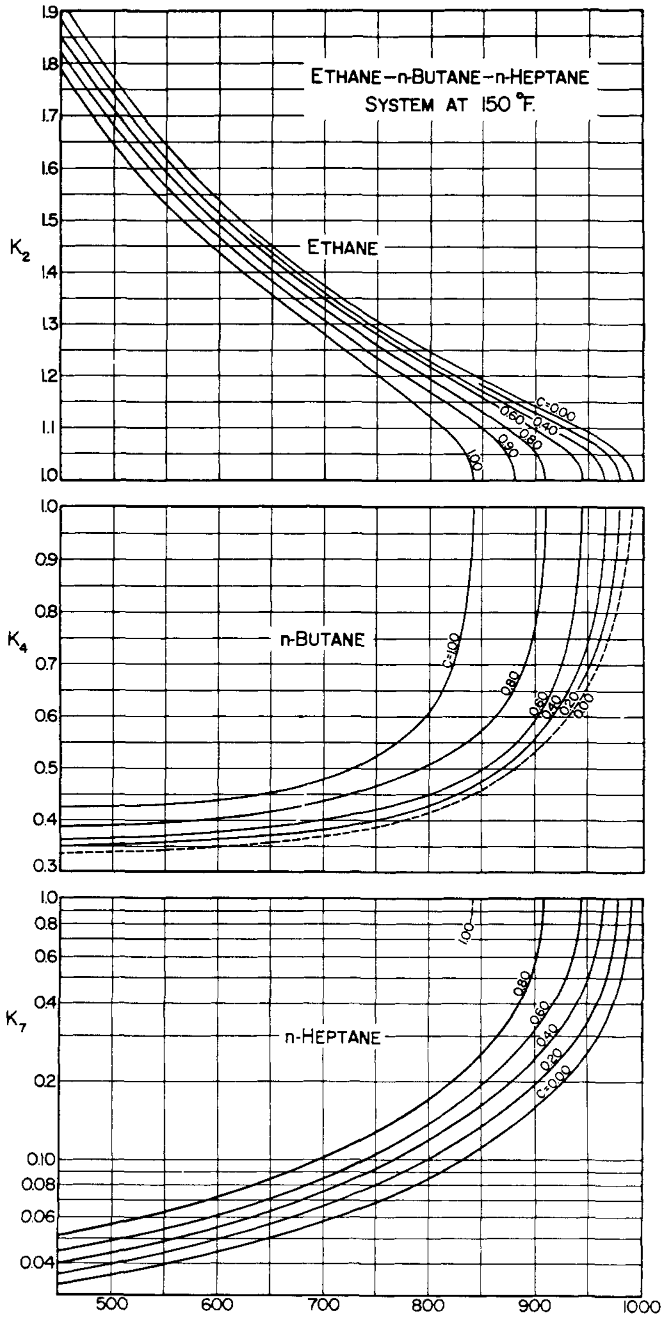

Figure 3. Vapor-liquid equilibrium constants for ethane–*n*-butane–*n*-heptane system at 150° F.

all charges studied are presented in Tables I, II, and III for temperatures of 150°, 200°, and 250° F., respectively. In the vicinity of the critical point, it frequently became necessary to withdraw a sample of the vapor phase first and allow equilibrium again to be reached before withdrawing the liquid sample, in order to eliminate possible contamination of the vapor phase with the liquid phase.

For each charge, the experimental data were smoothed by plotting compositions against pressure and equilibrium constants, $K = y/x$, were obtained from these smoothed curves. The vapor and liquid composition lines were then extended beyond the highest pressure to their point of convergence which represents the critical pressure of the charge. Using this approach, the composition of the charge mixture having this critical pressure was established. This procedure was followed to establish to composition and critical pressure of each charge at 150°, 200°, and 250° F. The final value of the critical pressure for each charge was

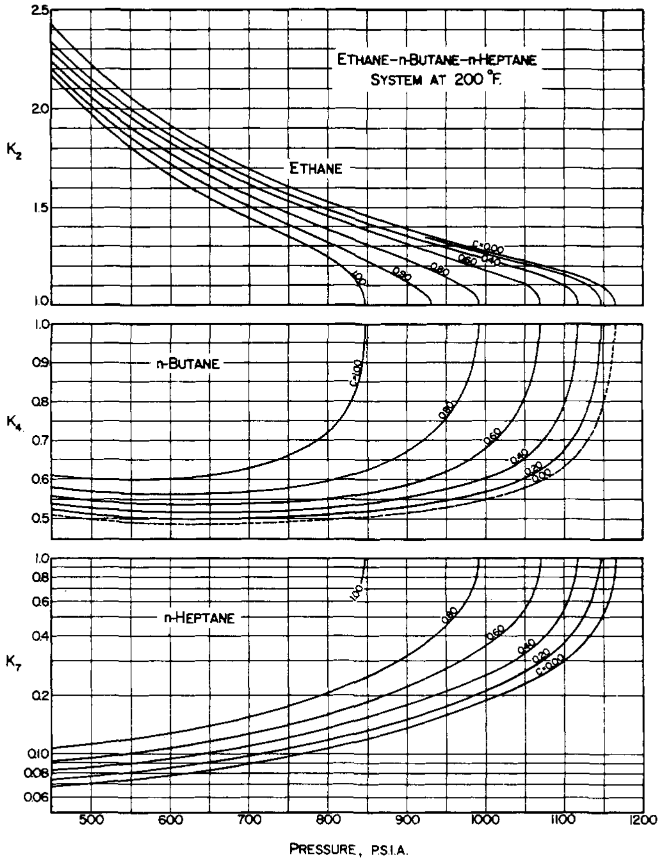

Figure 4. Vapor-liquid equilibrium constants for ethane–*n*-butane–*n*-heptane system at 200° F.

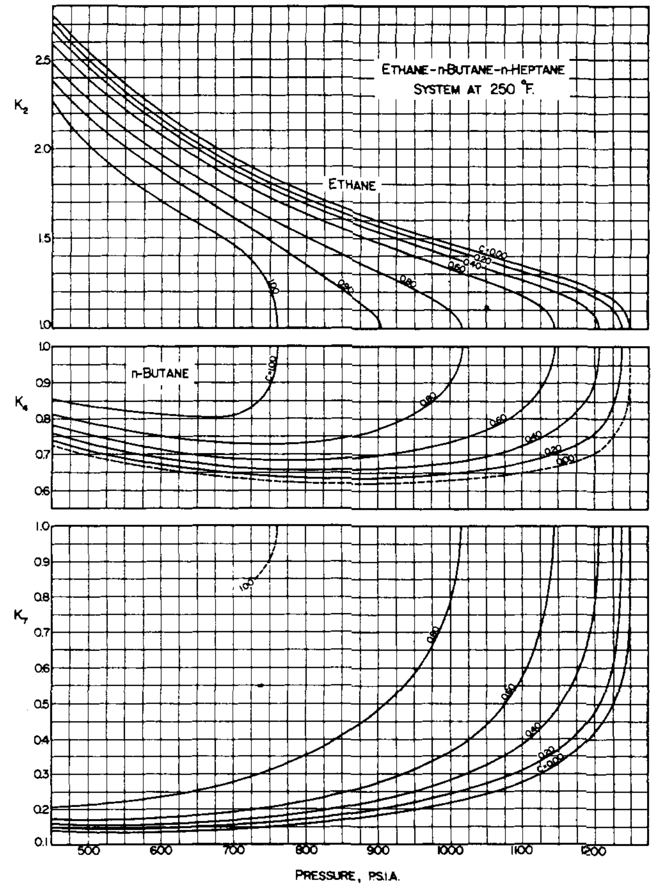

Figure 5. Vapor-liquid equilibrium constants for ethane–*n*-butane–*n*-heptane system at 250° F.

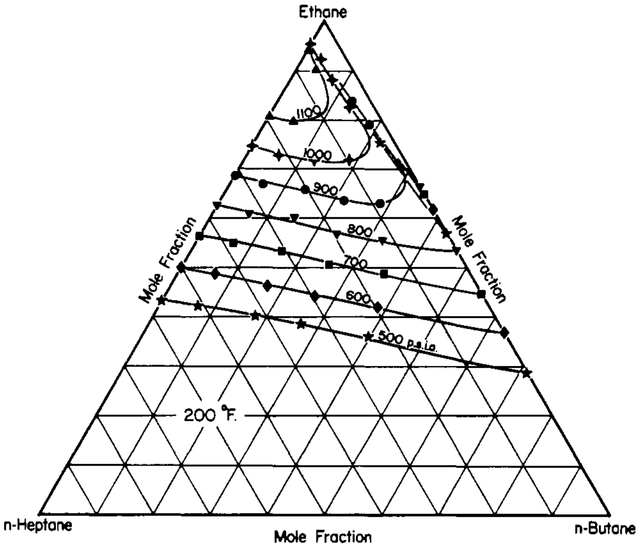

Figure 6. Vapor-liquid equilibrium behavior for ethane–n-butane–n-heptane system at 200° F.

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 critical pressures are plotted against the corresponding compositions of each charge to produce, for each temperature, the relationships presented in Figure 1. The critical pressures of the charges and corresponding binaries were also plotted against the composition parameter, C, to obtain a single relationship for each temperature as shown in Figure 2. The binary data for the systems, ethane–n-butane and ethane–n-heptane presented by Mehra and Thodos (*8,9*) have been used.

Vapor-liquid equilibrium constants obtained from the smoothed curves of each charge were plotted against the composition parameter for convenient pressures and cross-plotted as K against pressure for constant composition parameters. The resulting curves are presented in Figures 3, 4, and 5 for 150°, 200°, and 250° F., respectively. Final K values for this ternary system obtained from Figures 3, 4, and 5 are presented in Tables IV, V, and VI for 150°, 200°, and 250° F., respectively.

The vapor-liquid equilibrium behavior of this system can be presented in the form of triangular plots as shown for 200° F. in Figure 6. This figure presents the dew point and bubble point curves at 200° F. for convenient pressures and permits the establishment of the two-phase region for pressures above 500 p.s.i.a.

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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 compnent in vapor phase

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Lithium Hydride Systems

Solid-Liquid Phase Equilibria for the Ternary Lithium Hydride–Lithium Chloride–Lithium Fluoride System

CARL E. JOHNSON, ELLEN HATHAWAY, and CARL E. CROUTHAMEL
Argonne National Laboratory, Argonne, Ill.

THE phase equilibrium relationship among the hydride, chloride, and fluoride of lithium metal has been studied. This fused salt system is of interest because of its potential application as the electrolyte in the lithium hydride regenerative galvanic cell. Two of the lateral sides of this ternary system are simple eutectics with no apparent solid solution formation (LiF-LiCl and LiCl-LiH), while the third (LiH-LiF) consists of a complete series of solid solutions. The diagram of the crystallization surface consists of two areas, one comprising mainly a crystallization field of solid solutions continuous between LiH and LiF, with an undetermined possible LiCl content, and a smaller field of pure lithium chloride.

EXPERIMENTAL

The data to determine the crystalline surface were obtained by thermal analysis techniques; the compositions of the solid solutions in equilibrium with the liquid were not determined. The apparatus used has been described in detail (*4*). All experiments were run under a hydrogen pressure of 1 atm.

Reagent grade lithium chloride and lithium fluoride were obtained from J. T. Baker Chemical Co., Phillipsburg, N. J. The lithium chloride was purified with chlorine gas, using the method of Maricle and Hume (*5*). The lithium chloride melting point was 606.8° C. The lithium fluoride was in the