

PART II

PHASE EQUILIBRIA MOLECULAR TRANSPORT THERMODYNAMICS

Vapor-Liquid Equilibrium Constants for the Ethane-n-Butane-n-Pentane System at 200°, 250°, and 300° F.

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Vapor-liquid equilibrium constants were established at 200, 250, and 300° F. for a complete range of pressures and compositions. Values of the critical pressure and composition are presented for each temperature investigated.

HERLIHY AND THODOS (3) have recently determined vapor-liquid equilibrium constants for the ethane-n-butane-n-pentane system at 150° F. In the present study, this work has been extended to establish equilibrium constants for this system at 200°, 250°, and 300° F. for a complete range of pressures and compositions.

APPARATUS AND PROCEDURE

The apparatus used is basically the same as that described in detail previously (6), with some modifications. The ternary mixture was charged into an equilibrium cell equipped with a movable piston to control the pressure of the system which was measured with Heise gages, calibrated with a dead weight gage. This procedure is known to reproduce pressures to within 2 p.s.i. In the present study, the charging system consisted of individual reservoirs for each constituent from which they were charged into the cell. The cell was surrounded by an air bath which was capable of maintaining the over-all temperature of the cell to within 0.2° F. of the desired temperature. Under these conditions the temperature across the cell varied from 0.2° to F. at 200° F. to 0.4° F. at 300° F. Agitation was provided by a stirrer coupled magnetically to an external mechanical drive.

The system was found to reach a constant pressure in approximately 2 hours except for conditions near the

critical point, where more time was required. After this equilibrium was attained, microsamples of the vapor and liquid phases were removed and analyzed with a gas chromatography unit, standardized for this system with the aid of a mass spectrometer. 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 were reagent grade. The supplier (Phillips Petroleum Co.) claimed the purity to be as follows: ethane, 99.91 mole %; n-butane, 99.90 mole %; and n-pentane, 99.80 %.

EXPERIMENTAL

Before the ternary system was investigated at each temperature, the apparatus and experimental procedure were tested by obtaining vapor-liquid equilibrium data for the ethane-n-pentane system at that temperature and were compared with the values reported by Reamer, Sage and Lacey (5). At moderate pressure conditions the vapor and liquid compositions for each temperature of this study showed deviations which never exceeded 1.4% of the

Table I. Experimental Vapor-Liquid Equilibrium Data at 200° F.

Pressure, P.s.i.a.	Vapor Mole Fraction			Liquid Mole Fraction			$K = y/x$			C
	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	
Charge I										
553	0.793	0.0338	0.173	0.408	0.0594	0.533	1.944	0.569	0.325	0.100
615	0.807	0.0320	0.161	0.463	0.0584	0.479	1.743	0.548	0.336	0.109
693	0.816	0.0315	0.152	0.515	0.0579	0.427	1.584	0.544	0.356	0.119
764	0.822	0.0304	0.148	0.560	0.0528	0.387	1.468	0.576	0.382	0.120
825	0.825	0.0306	0.144	0.611	0.0503	0.399	1.350	0.608	0.425	0.129
888	0.819	0.0312	0.150	0.663	0.0450	0.292	1.235	0.693	0.514	0.134
942	0.805	0.0315	0.163	0.700	0.0408	0.259	1.150	0.772	0.629	0.136
Charge II										
537	0.779	0.0714	0.150	0.391	0.124	0.485	1.992	0.576	0.309	0.204
614	0.798	0.0655	0.1365	0.450	0.117	0.433	1.773	0.560	0.315	0.213
714	0.804	0.0623	0.134	0.519	0.111	0.370	1.549	0.561	0.362	0.231
815	0.810	0.0596	0.131	0.590	0.102	0.308	0.373	0.584	0.425	0.248
909	0.803	0.0603	0.137	0.660	0.0875	0.252	1.217	0.689	0.544	0.257
Charge III										
545	0.751	0.1165	0.1325	0.385	0.203	0.412	1.951	0.574	0.322	0.330
624	0.772	0.108	0.120	0.458	0.191	0.351	1.686	0.565	0.342	0.352
715	0.786	0.103	0.111	0.533	0.177	0.290	1.475	0.581	0.383	0.379
805	0.795	0.0983	0.107	0.597	0.157	0.246	1.332	0.626	0.435	0.390
845	0.790	0.0970	0.113	0.616	0.148	0.236	1.282	0.655	0.479	0.385
Charge IV										
525	0.692	0.2045	0.1035	0.351	0.354	0.295	1.972	0.578	0.351	0.546
605	0.712	0.191	0.097	0.426	0.317	0.257	1.671	0.603	0.377	0.552
685	0.717	0.188	0.095	0.482	0.294	0.224	1.488	0.639	0.424	0.568
Charge V										
577	0.725	0.174	0.101	0.396	0.314	0.290	1.831	0.554	0.348	0.520
625	0.731	0.177	0.0924	0.435	0.309	0.256	1.680	0.573	0.361	0.547
710	0.753	0.159	0.088	0.506	0.272	0.222	1.488	0.585	0.396	0.551
785	0.732	0.167	0.101	0.566	0.245	0.189	1.293	0.686	0.534	0.565
848	0.725	0.172	0.103	0.610	0.223	0.167	1.189	0.771	0.617	0.572
Charge VI										
533	0.660	0.288	0.052	0.334	0.510	0.156	1.976	0.565	0.333	0.766
627	0.681	0.271	0.048	0.411	0.467	0.122	1.655	0.578	0.392	0.793
685	0.700	0.259	0.0413	0.461	0.429	0.110	1.518	0.604	0.375	0.796
758	0.712	0.246	0.042	0.520	0.389	0.091	1.369	0.632	0.462	0.810
822 ^a				0.575	0.348	0.0765				
817 ^b	0.696	0.258	0.046							

^a Liquid sample only. ^b Vapor sample only.

Table II. Experimental Vapor-Liquid Equilibrium Data at 250° F.

Pressure, P.s.i.a.	Vapor Mole Fraction			Liquid Mole Fraction			$K = y/x$			C
	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	
Charge I										
451	0.564	0.148	0.288	0.204	0.178	0.618	2.765	0.831	0.466	0.224
547	0.595	0.144	0.261	0.272	0.186	0.542	2.188	0.774	0.482	0.255
658	0.623	0.137	0.240	0.353	0.180	0.467	1.765	0.761	0.514	0.278
718	0.636	0.133	0.231	0.397	0.179	0.424	1.602	0.743	0.545	0.297
805	0.630	0.132	0.238	0.452	0.166	0.382	1.394	0.795	0.623	0.303
826	0.593	0.137	0.270	0.466	0.164	0.370	1.273	0.835	0.730	0.307
Charge II										
467	0.518	0.245	0.237	0.201	0.309	0.490	2.577	0.793	0.484	0.387
525	0.541	0.244	0.215	0.246	0.316	0.438	2.199	0.772	0.491	0.419
603	0.555	0.236	0.209	0.294	0.309	0.397	1.888	0.764	0.526	0.438
690	0.584	0.222	0.194	0.352	0.298	0.350	1.659	0.745	0.554	0.460
755 ^a	0.598	0.215	0.187		0.398	0.285	0.317			
757 ^a					0.431	0.267	0.302			
792 ^a	0.594	0.216	0.190							
Charge III										
489	0.440	0.384	0.176	0.185	0.474	0.341	2.378	0.810	0.499	0.582
537	0.475	0.362	0.163	0.215	0.464	0.321	2.209	0.780	0.508	0.591
602	0.505	0.344	0.151	0.264	0.455	0.281	1.913	0.756	0.537	0.618
667	0.526	0.340	0.134	0.317	0.435	0.248	1.659	0.782	0.540	0.637
718 ^a				0.352	0.417	0.231				
737 ^b	0.543	0.316	0.141		0.367	0.414	0.219			
738 ^a					0.375	0.409	0.216			
753 ^a	0.544	0.315	0.141							
Charge IV										
484	0.377	0.519	0.104	0.158	0.638	0.204	2.386	0.813	0.510	0.758
534	0.403	0.501	0.0962	0.191	0.627	0.182	2.110	0.799	0.529	0.775
595	0.433	0.476	0.0905	0.234	0.610	0.156	1.850	0.780	0.580	0.796
658 ^b	0.469	0.449	0.082		0.293	0.574	0.133			
674 ^b										

Table I. Experimental Vapor-Liquid Equilibrium Data at 200° F. (Continued).

Pressure, P.s.i.a.	Vapor Mole Fraction			Liquid Mole Fraction			K = y/x			C
	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	
Charge V										
609	0.462	0.442	0.096	0.250	0.574	0.176	1.848	0.770	0.545	0.765
645	0.476	0.433	0.091	0.274	0.566	0.160	1.737	0.765	0.569	0.780
699	0.500	0.414	0.086	0.322	0.533	0.145	1.553	0.777	0.593	0.786
742	0.514	0.401	0.085	0.353	0.514	0.133	1.456	0.780	0.639	0.794
755 ^a				0.370	0.504	0.126				
759 ^b	0.506	0.408	0.086							

^a Liquid sample only. ^b Vapor sample only.

Table III. Experimental Vapor-Liquid Equilibrium Data at 300° F.

Pressure, P.S.I.A.	Vapor Mole Fraction			Liquid Mole Fraction			K = y/x			C
	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	Ethane	n-Butane	n-Pentane	
Charge I										
600	0.477	0.105	0.418	0.210	0.155	0.635	2.271	0.677	0.658	0.196
659	0.475	0.104	0.421	0.239	0.136	0.625	1.987	0.765	0.674	0.179
742	0.492	0.104	0.404	0.296	0.114	0.590	1.662	0.912	0.685	0.162
744	0.489	0.105	0.406	0.272	0.120	0.608	1.798	0.875	0.668	0.165
807	0.481	0.104	0.415	0.322	0.112	0.566	1.494	0.929	0.733	0.165
833 ^a				0.339	0.110	0.551				
836 ^b	0.473	0.105	0.422							
Charge II										
621	0.402	0.236	0.362	0.207	0.262	0.531	1.942	0.901	0.682	0.330
700	0.414	0.234	0.352	0.226	0.255	0.519	1.832	0.918	0.678	0.329
747	0.418	0.234	0.348	0.244	0.252	0.504	1.713	0.929	0.690	0.333
793 ^b	0.408	0.236	0.356		0.272	0.250	0.478			
Charge III										
598	0.322	0.400	0.278	0.169	0.419	0.412	1.905	0.955	0.675	0.504
605	0.323	0.400	0.277	0.171	0.423	0.406	1.888	0.946	0.682	0.510
632	0.329	0.400	0.271	0.188	0.425	0.387	1.750	0.941	0.700	0.523
672	0.334	0.398	0.268	0.199	0.420	0.381	1.678	0.948	0.703	0.524
715 ^b	0.337	0.396	0.267		0.230	0.419	0.351			
716 ^a				0.240	0.418	0.342				
Charge IV										
462	0.355	0.127	0.518	0.134	0.119	0.747	2.649	1.067	0.693	0.137
515	0.390	0.127	0.483	0.158	0.126	0.716	2.468	1.008	0.675	0.150
566	0.413	0.125	0.462	0.191	0.129	0.680	2.162	0.969	0.679	0.159
633 ^b	0.441	0.124	0.435		0.448	0.123	0.429			
650 ^a				0.185	0.292	0.523				
Charge V										
464	0.289	0.290	0.421	0.114	0.275	0.611	2.535	1.055	0.689	0.310
515	0.322	0.283	0.395	0.142	0.282	0.576	2.268	1.003	0.686	0.329
572	0.355	0.279	0.366	0.172	0.288	0.540	2.064	0.969	0.678	0.351
593 ^b	0.367	0.273	0.360		0.185	0.292	0.523			
595 ^a				0.183	0.464	0.353				
Charge VI										
508	0.228	0.463	0.309	0.128	0.450	0.422	1.781	1.029	0.732	0.516
535	0.250	0.459	0.291	0.119	0.460	0.421	2.100	0.998	0.691	0.522
563	0.263	0.455	0.282	0.135	0.462	0.403	1.948	0.985	0.700	0.534
605	0.286	0.449	0.265	0.160	0.470	0.370	1.788	0.955	0.716	0.560
633 ^a				0.183	0.464	0.353				
634 ^b	0.298	0.443	0.259							
Charge VII										
500	0.156	0.633	0.211	0.067	0.612	0.321	2.328	1.034	0.657	0.656
526	0.167	0.624	0.209	0.080	0.620	0.300	2.088	1.006	0.697	0.674
575	0.200	0.613	0.187	0.115	0.628	0.257	1.739	0.976	0.728	0.710
600 ^a				0.133	0.629	0.238				
600 ^b	0.212	0.607	0.181							

^a Liquid sample only. ^b Vapor sample only.

corresponding composition values reported by Reamer, Sage, and Lacey. However, for pressure approaching the critical point, this deviation increased to a maximum value of 3.4% c. These results were considered acceptable.

For a ternary system, the vapor-liquid equilibrium constant, $K = y/x$, is a function of temperature, pressure, and composition. 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):

$$C = \frac{x_i}{x_i + x_h} \quad (1)$$

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

Table IV. Critical Pressures and Compositions for each Temperature Investigated

	Critical Pressure, P.S.I.A.	Compn. at Critical Point, Mole Fraction			C
		Ethane	n-Butane	n-Pentane	
Critical Temperature, 200° F.					
Ethane-n-pentane (5)	980	0.764	0.000	0.236	0.000
Charge I	975	0.750	0.038	0.212	0.152
Charge II	960	0.739	0.070	0.191	0.268
Charge III	925	0.723	0.112	0.165	0.404
Charge V	888	0.692	0.188	0.120	0.610
Charge VI	855	0.661	0.277	0.062	0.817
Ethane-n-butane (4)	837	0.625	0.375	0.000	1.000
Critical Temperature, 250° F.					
Ethane-n-pentane (5)	984	0.652	0.000	0.348	0.000
Charge I	930	0.582	0.148	0.270	0.354
Charge II	885	0.545	0.235	0.220	0.516
Charge III	827	0.504	0.333	0.163	0.671
Charge V	790	0.460	0.438	0.102	0.811
Ethane-n-butane (4)	750	0.382	0.618	0.000	1.000
Critical Temperature, 300° F.					
Ethane-n-pentane (5)	904	0.481	0.000	0.519	0.000
Charge I	880	0.430	0.110	0.460	0.193
Charge II	833	0.366	0.240	0.394	0.379
Charge III	753	0.298	0.410	0.292	0.584
Charge VII	675	0.215	0.610	0.175	0.777
Ethane-n-butane (4)	578	0.050	0.950	0.000	1.000

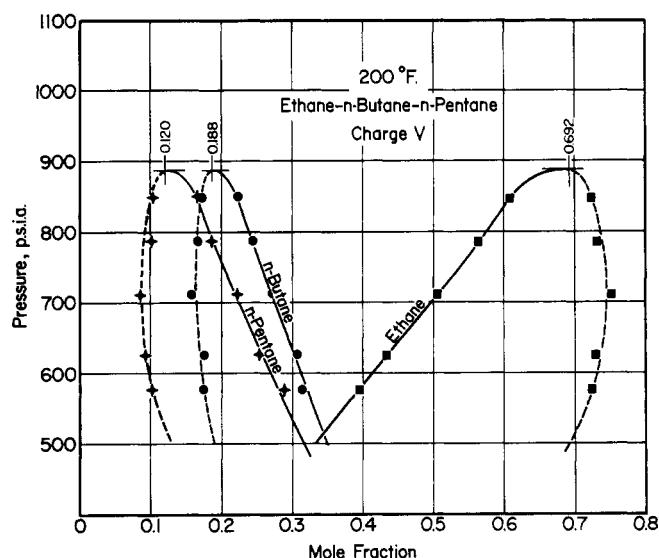


Figure 1. Vapor-liquid equilibrium composition and pressure relationships for a mixture of ethane, n-butane, and n-pentane at 200° F. (Charge V)

For temperatures of 200°, 250°, and 300° F., charges were prepared with composition parameters ranging from zero to unity. These parameters were chosen so that each charge was at its critical temperature, and therefore the vapor and liquid phases would be present as the critical pressure was approached. These compositions were determined by the method described by Grieves and Thodos (2). For each charge the compositions of the vapor and liquid phases in equilibrium were determined at several pressures

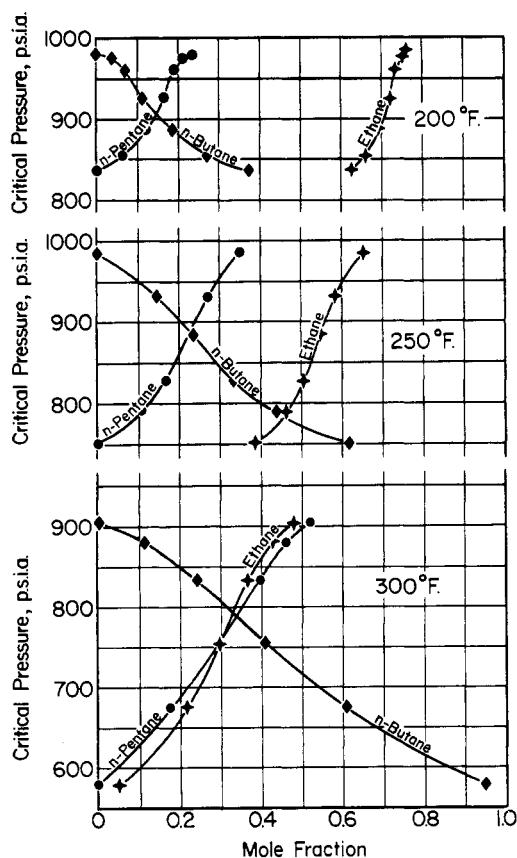


Figure 2. Relationships between the critical pressure and composition at 200°, 250°, and 300° F.

Table V. Final K Values at 200° F.

	Pressure, P.s.i.a.	Vapor-Liquid Equilibrium Constant, $K = y/x$		
		Ethane	<i>n</i> -Butane	<i>n</i> -Pentane
$C = 0.000$	500	2.111	0.299	
	550	1.960	0.300	
	600	1.806	0.305	
	650	1.693	0.318	
	700	1.567	0.336	
	750	1.480	0.361	
	800	1.386	0.395	
	850	1.305	0.442	
	900	1.231	0.512	
	920	1.198	0.556	
	940	1.159	0.617	
	960	1.110	0.720	
Critical	980	1.000	1.000	
$C = 0.200$	500	2.099	0.532	0.310
	550	1.938	0.529	0.313
	600	1.793	0.527	0.320
	650	1.668	0.535	0.333
	700	1.558	0.545	0.345
	750	1.456	0.560	0.381
	800	1.364	0.585	0.412
	850	1.283	0.628	0.460
	900	1.203	0.690	0.540
	920	1.168	0.725	0.597
	940	1.122	0.772	0.678
	960	1.068	0.857	0.832
Critical	968	1.000	1.000	1.000
$C = 0.400$	500	2.078	0.544	0.321
	550	1.912	0.542	0.325
	600	1.769	0.544	0.331
	650	1.641	0.550	0.347
	700	1.530	0.560	0.370
	750	1.430	0.582	0.399
	800	1.339	0.620	0.439
	840	1.272	0.666	0.495
	880	1.200	0.741	0.591
	900	1.152	0.796	0.675
	920	1.080	0.887	0.820
Critical	928	1.000	1.000	1.000
$C = 0.600$	500	2.055	0.569	0.330
	550	1.888	0.566	0.336
	600	1.740	0.567	0.345
	650	1.618	0.573	0.365
	700	1.500	0.585	0.391
	750	1.399	0.614	0.431
	800	1.301	0.661	0.495
	840	1.218	0.735	0.590
	860	1.166	0.795	0.670
	880	1.082	0.885	0.820
Critical	888	1.000	1.000	1.000
$C = 0.800$	500	2.015	0.589	0.338
	550	1.852	0.587	0.346
	600	1.705	0.589	0.361
	650	1.581	0.590	0.385
	700	1.467	0.606	0.420
	750	1.367	0.640	0.477
	800	1.259	0.705	0.574
	820	1.210	0.749	0.645
	840	1.150	0.810	0.745
Critical	858	1.000	1.000	1.000
$C = 0.900$	500	1.980		
	550	1.810		
	600	1.666		
	650	1.548		
	700	1.440		
	750	1.332		
	800	1.225		
	820	1.170		
	840	1.065		
Critical	846	1.000		
$C = 1.000$	500	1.938	0.610	
	550	1.771	0.605	
	600	1.630	0.605	
	650	1.520	0.609	
	700	1.410	0.628	
	750	1.303	0.666	
	800	1.197	0.741	
	820	1.129	0.796	
Critical	837	1.000	1.000	

Table VI. Final K Values at 250° F.

	Pressure, P.s.i.a.	Vapor-Liquid Equilibrium Constant, $K = y/x$		
		Ethane	<i>n</i> -Butane	<i>n</i> -Pentane
$C = 0.000$	450	2.632		0.475
	500	2.393		0.463
	550	2.191		0.460
	600	2.012		0.464
	650	1.870		0.477
	700	1.750		0.498
	750	1.630		0.531
	800	1.522		0.573
	850	1.416		0.628
	900	1.305		0.658
	920	1.263		0.699
	940	1.218		0.763
Critical	960	1.159		1.000
$C = 0.200$	450	2.602	0.810	0.491
	500	2.368	0.776	0.477
	550	2.161	0.757	0.475
	600	1.980	0.745	0.480
	650	1.826	0.737	0.490
	700	1.697	0.735	0.510
	750	1.575	0.737	0.535
	800	1.470	0.750	0.567
	850	1.363	0.775	0.617
	900	1.252	0.810	0.690
	920	1.202	0.834	0.737
	940	1.148	0.874	0.805
Critical	958	1.000	1.000	1.000
$C = 0.400$	450	2.570	0.816	0.503
	500	2.340	0.783	0.495
	550	2.130	0.765	0.496
	600	1.944	0.751	0.503
	650	1.780	0.744	0.518
	700	1.647	0.742	0.542
	750	1.520	0.750	0.572
	800	1.410	0.770	0.612
	840	1.310	0.800	0.663
	860	1.260	0.820	0.698
	880	1.210	0.843	0.744
	900	1.150	0.878	0.806
Critical	919	1.000	1.000	1.000
$C = 0.600$	450	2.550	0.825	0.512
	500	2.312	0.792	0.510
	550	2.098	0.773	0.515
	600	1.905	0.760	0.527
	650	1.719	0.753	0.548
	700	1.597	0.750	0.578
	750	1.458	0.769	0.622
	800	1.306	0.807	0.700
	820	1.242	0.833	0.755
	840	1.155	0.877	0.847
Critical	853	1.000	1.000	1.000
$C = 0.800$	450	2.480	0.836	0.525
	500	2.240	0.805	0.525
	550	2.020	0.788	0.533
	600	1.839	0.777	0.555
	650	1.678	0.773	0.583
	700	1.530	0.780	0.632
	740	1.400	0.812	0.688
	760	1.323	0.846	0.735
	780	1.220	0.905	0.816
Critical	793	1.000	1.000	1.000
$C = 0.900$	450	2.405		
	500	2.170		
	550	1.949		
	600	1.760		
	650	1.600		
	700	1.448		
	720	1.380		
	740	1.305		
	760	1.185		
Critical	770	1.000		
$C = 1.000$	450	2.255	0.860	
	500	2.040	0.830	
	550	1.841	0.815	
	600	1.657	0.809	
	650	1.482	0.818	
	700	1.320	0.851	
	720	1.250	0.880	
	740	1.155	0.938	
Critical	750	1.000	1.000	

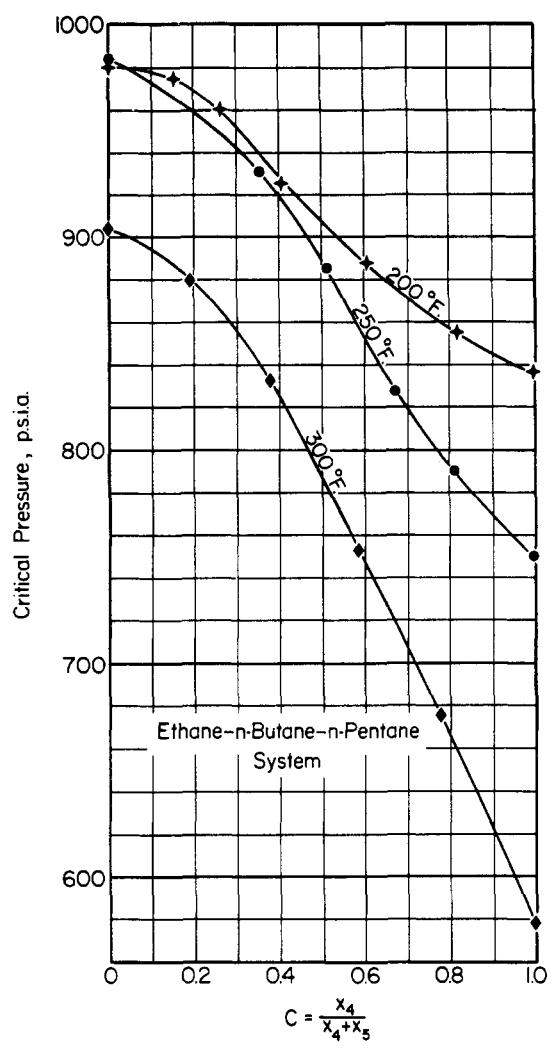


Figure 3. Relationships between critical pressure and composition parameter

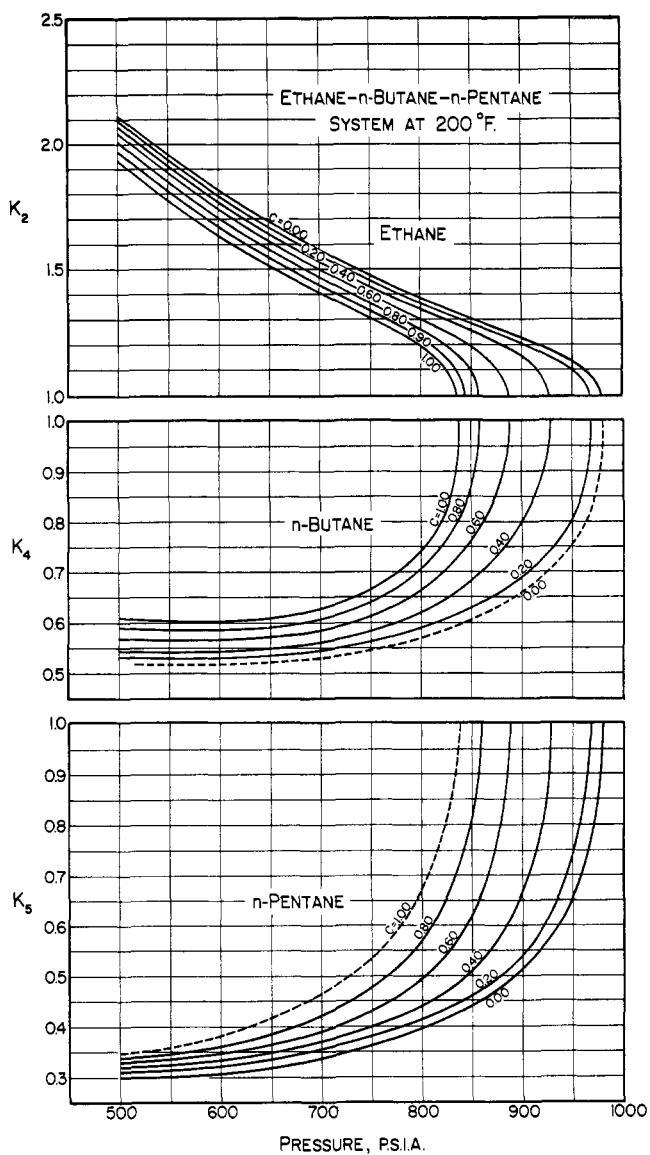


Figure 4. Vapor-liquid equilibrium constants at 200° F.

Table VII. Final K Values at 300° F.

Vapor-Liquid Equilibrium Constant, $K = y/x$				Vapor-Liquid Equilibrium Constant, $K = y/x$			
Pressure, P.S.I.A.	Ethane	n-Butane	n-Pentane	Pressure, P.S.I.A.	Ethane	n-Butane	n-Pentane
$C = 0.000$	500	2.500	0.666	$C = 0.400$	500	2.350	1.020
	550	2.289	0.652		550	2.132	0.970
	600	2.100	0.649		600	1.946	0.930
	650	1.925	0.653		650	1.778	0.910
	700	1.775	0.665		700	1.624	0.909
	750	1.632	0.688		740	1.501	0.919
	800	1.498	0.726		760	1.440	0.928
	820	1.445	0.751		780	1.372	0.939
	840	1.390	0.781		800	1.295	0.954
	860	1.328	0.820		820	1.140	0.984
$C = 0.200$	880	1.248	0.873		825	1.000	1.000
	900	1.110	0.958	$C = 0.600$	500	2.240	1.030
	Critical	903	1.000		550	2.020	0.987
	500	2.440	1.010		600	1.812	0.955
	550	2.220	0.956		640	1.655	0.941
	600	2.032	0.916		660	1.570	0.940
	650	1.870	0.891		680	1.452	0.942
	700	1.728	0.885		700	1.410	0.950
	750	1.586	0.891		720	1.310	0.960
	800	1.448	0.905		740	1.160	0.983
$C = 0.400$	820	1.385	0.915		746	1.000	1.000
	840	1.305	0.928	$C = 0.600$	500	2.240	1.030
	860	1.205	0.950		550	2.020	0.987
	Critical	877	1.000		600	1.812	0.955

(Continued on page 7)

Table VII. Final K Values at 300° F. (Continued)

		Vapor-Liquid Equilibrium Constant, $K = y/x$		
Pressure, P.s.i.a.		Ethane	<i>n</i> -Butane	<i>n</i> -Pentane
$C = 0.700$	500	2.143		
	550	1.908		
	600	1.670		
	640	1.475		
	660	1.375		
	680	1.272		
	700	1.142		
Critical	707	1.000		
$C = 0.800$	500	2.023	1.040	0.705
	550	1.768	1.000	0.724
	600	1.502	0.972	0.768
	620	1.382	0.972	0.800
	640	1.252	0.976	0.845
	650	1.185	0.980	0.875
	660	1.060	0.988	0.922
Critical	667	1.000	1.000	1.000

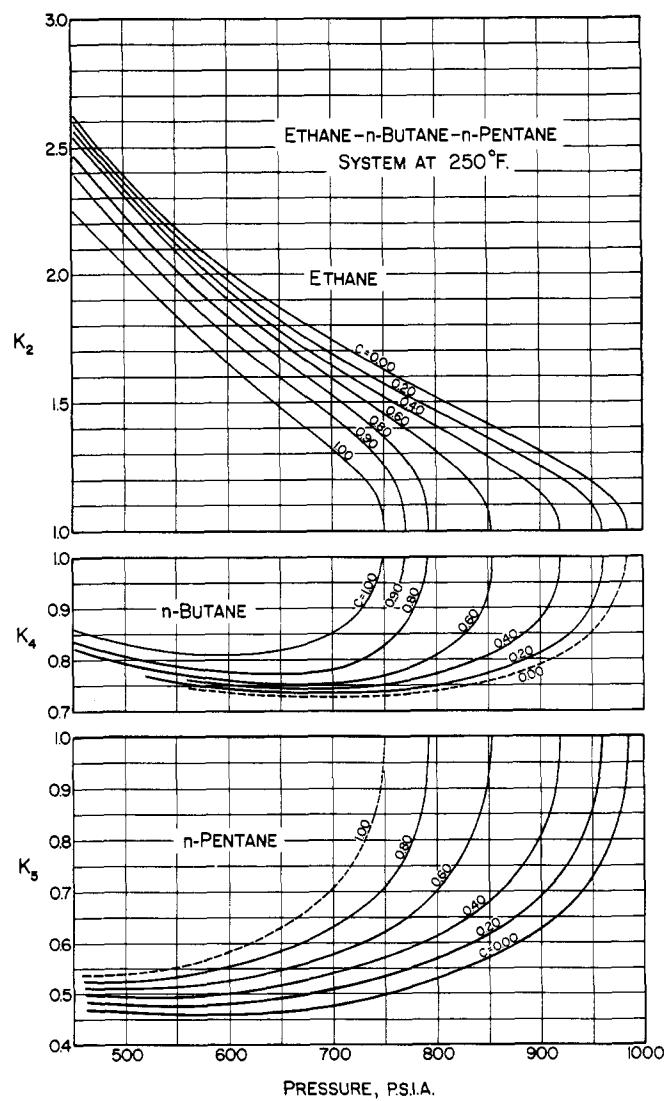


Figure 5. Vapor-liquid equilibrium constants at 250° F.

above 500 p.s.i.a. The experimentally determined compositions for the different charges are presented in Table I, II, and III for temperatures of 200°, 250°, and 300° 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

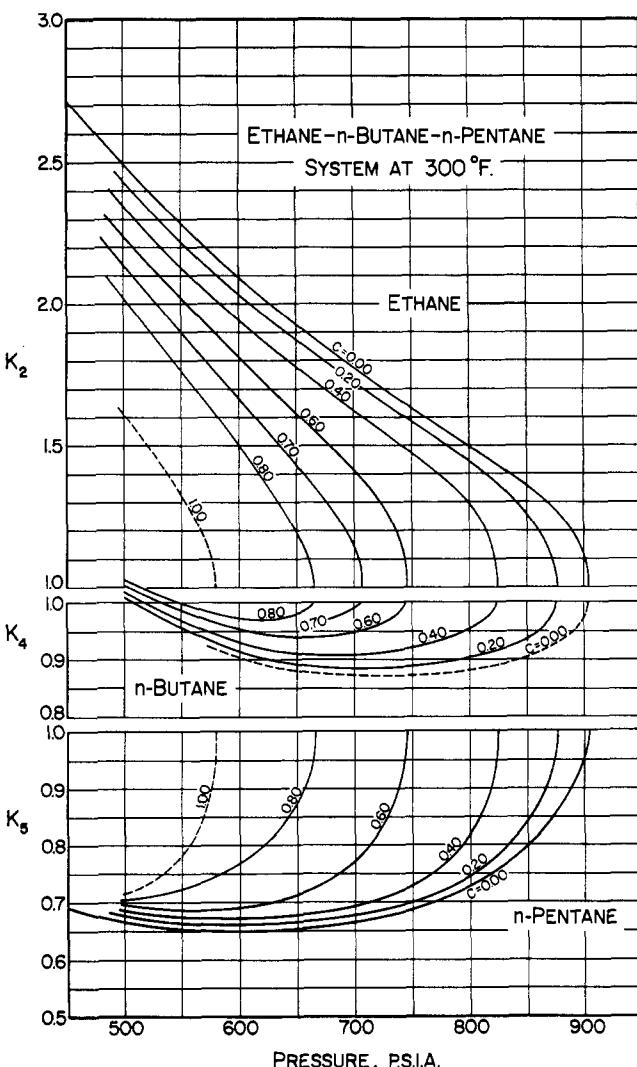


Figure 6. Vapor-liquid equilibrium constants at 300° F.

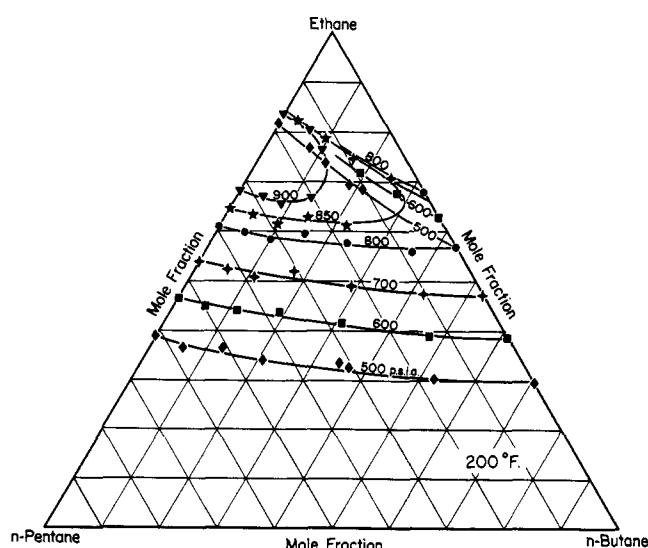


Figure 7. Vapor-liquid equilibrium behavior at 200° F.

before withdrawing the liquid sample. This was done in order to eliminate the possible contamination of vapor phase with liquid, caused by the similarity between the densities of the two phases at these conditions. Data for each charge were smoothed by plotting them against pressure (Figure 1). Solid lines represent the liquid phase; dashed lines,

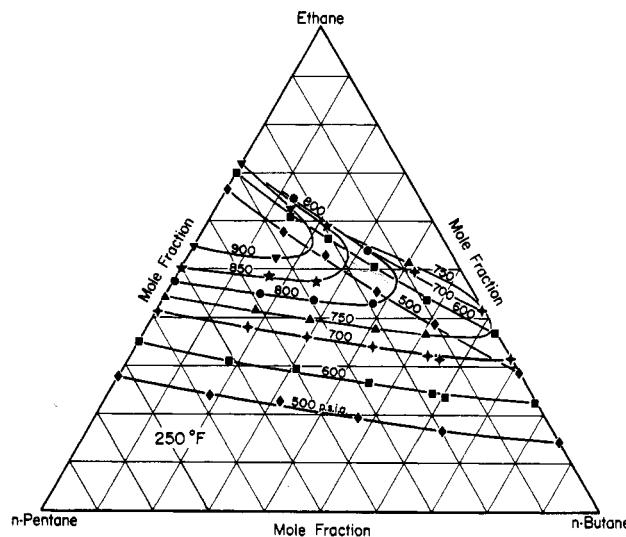


Figure 8. Vapor-liquid equilibrium behavior at 250° F.

the vapor phase. For Charge V, vapor and liquid compositions were obtained for pressures up to 848 p.s.i.a., and the resulting bubble point and dew point curves of each component were extended to their point of convergence, the critical pressure. For the charge of Figure 1, the critical pressure was found to be 888 p.s.i.a. for mole fraction compositions of 0.692 ethane, 0.188 *n*-butane, and 0.120 *n*-pentane. For the remaining charges, plots similar to Figure 1 were prepared to estimate the critical pressures and compositions. Equilibrium constants were determined from the smoothed curves for 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 the equilibrium constant for the charge *vs.* pressure. Resulting values of the critical pressure are presented in Table IV, along with corresponding critical temperatures and compositions and critical values for the related binaries.

These critical pressures (Figure 2) are plotted against the corresponding compositions to produce similar relationships for each temperature. Critical pressures for the charges and related binaries were also plotted against the composition parameter to obtain a single relationship for each temperature (Figure 3).

Vapor-liquid equilibrium constants obtained from the smoothed curves for each charge of the form of Figure 1 were plotted against the composition parameter for convenient pressures and were cross plotted as K against pressures for constant composition parameters, as shown in Figure 4, 5, and 6 for 200°, 250°, and 300° F., respectively. In general, the equilibrium constants resulting from the experimental data are in close agreement with the smoothed values presented in these figures. Over 100 randomly selected experimental values at these temperatures were compared with corresponding values obtained from Figures 4, 5, and 6 to produce an average deviation of 1.56% for ethane, 1.58% for *n*-butane, and 2.23% for *n*-heptane. Final K values for this ternary system obtained from Figures 4, 5, and 6 are presented in Tables V, VI, and VII, respectively.

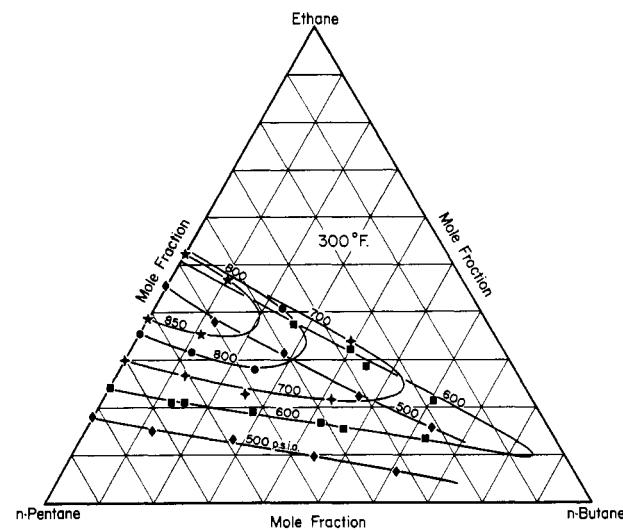


Figure 9. Vapor-liquid equilibrium behavior at 300° F.

The vapor-liquid equilibrium behavior of this system is presented in the form of triangular plots for the three temperatures as shown in Figures 7, 8, and 9. In these figures the tie line for each charge was found to be independent of the pressure.

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NOMENCLATURE

- C = composition parameter, $x_i/(x_i + x_h)$
- K = vapor-liquid equilibrium constant, y/x
- P_c = critical pressure, p.s.i.a.
- 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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