Vapor-Liquid Equilibrium of Methane–Ethane–Propane System at Low Temperatures and High Pressures

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Measurements of 49 ternary equilibrium phase concentrations from 0.00001–0.99999 mol fraction were made at −75° to −175°F in 25° intervals for various fixed pressures from 32–875 psia. These data with previous binary methane–ethane and methane–propane data completely define the ternary from −75° to −225°F. A simple linear relationship describes the system, except at the highest (800, 700) pressures at the highest (−75°F, −100°F) temperatures.

Current low-temperature operation of chemical industrial processes led to this study, which showed that the older data (*4*) on this system were valid at 0° and −50°F but were erroneous at lower temperatures. Improvements in sampling and analytical methods have made possible a more precise evaluation of this region of very low to very high mole fractions.

EXPERIMENTAL

The vapor recycle equilibrium cell has been described (*3*), with modifications for this study given in detail elsewhere (*6*, *7*). Individual components were charged in order of increasing vapor pressure, and the final pressure was set by addition of the most volatile component (methane) to the equilibrium cell.

Sampling and analytical improvements (*7*) have made possible measurement of mole fractions from 0.00001–0.99999 mol fraction. The error analysis given for a binary system (*6*, *7*) can be applied also to the ternary mixtures. An exact determination of the error due to the concentration is not possible because of complexity, but the total error in the *K*-values is estimated as twice that for the binary systems, which gives a mean 2% deviation in the *K*-values.

Material Used. "Ultra high purity" methane, purchased from Matheson Gas Products Co., was reported to analyze at least 99.97% methane, with the total amount of major impurities as 105 ppm. The gas was purified by a molecular

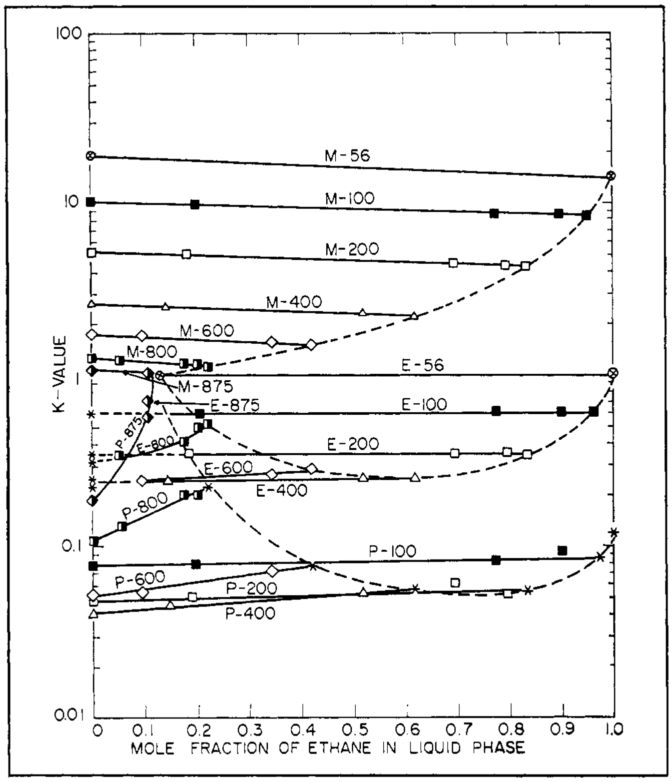

Figure 1. *K*-value vs. composition for the methane–ethane–propane system at −75°F

Symbols for Figures 1 through 7

⊗ = saturated vapor pressure of ethane
◓ = 10 psia
● = 32 psia
○ = 40 psia
◑ = 70 psia
■ = 100 psia

□ = 200 psia
▲ = 300 psia
△ = 400 psia
◆ = 550 psia
◇ = 600 psia

▲ = 725 psia
◨ = 800 psia
⬖ = 875 psia
* = extrapolated
- - = K^{∞} locus

M = methane
E = ethane
P propane
designates component

Number following letter (M, E, P) designates pressure, psia

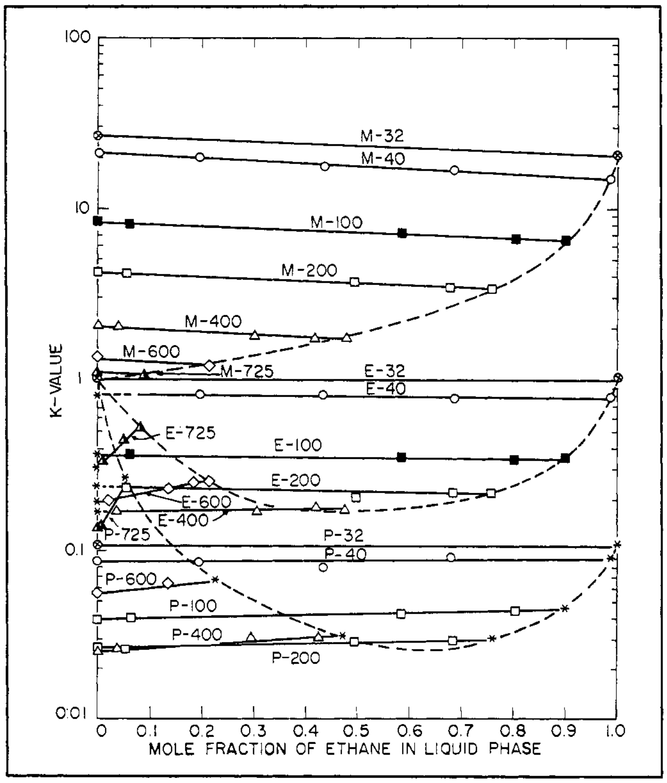

Figure 2. *K*-value vs. composition for the methane–ethane–propane system at −100°F

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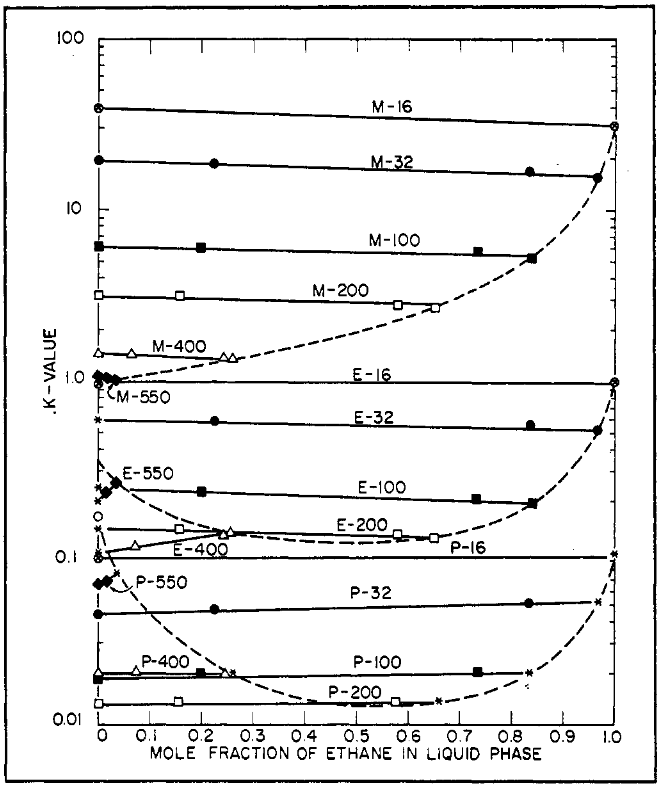

Figure 3. K-value vs. composition for the methane–ethane–propane system at −125°F

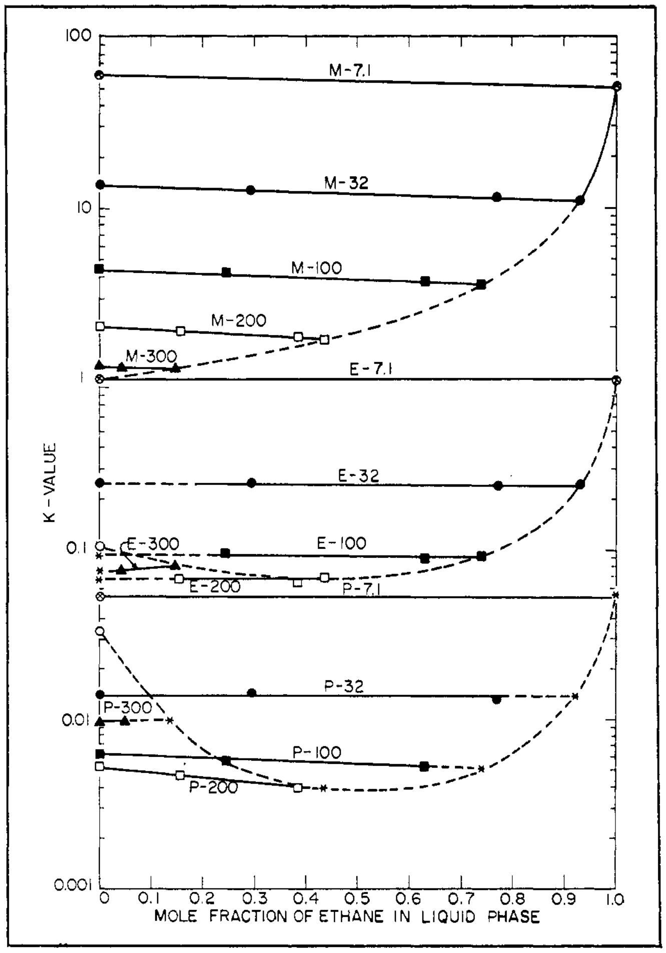

Figure 4. K-value vs. composition for the methane–ethane–propane system at −150°F

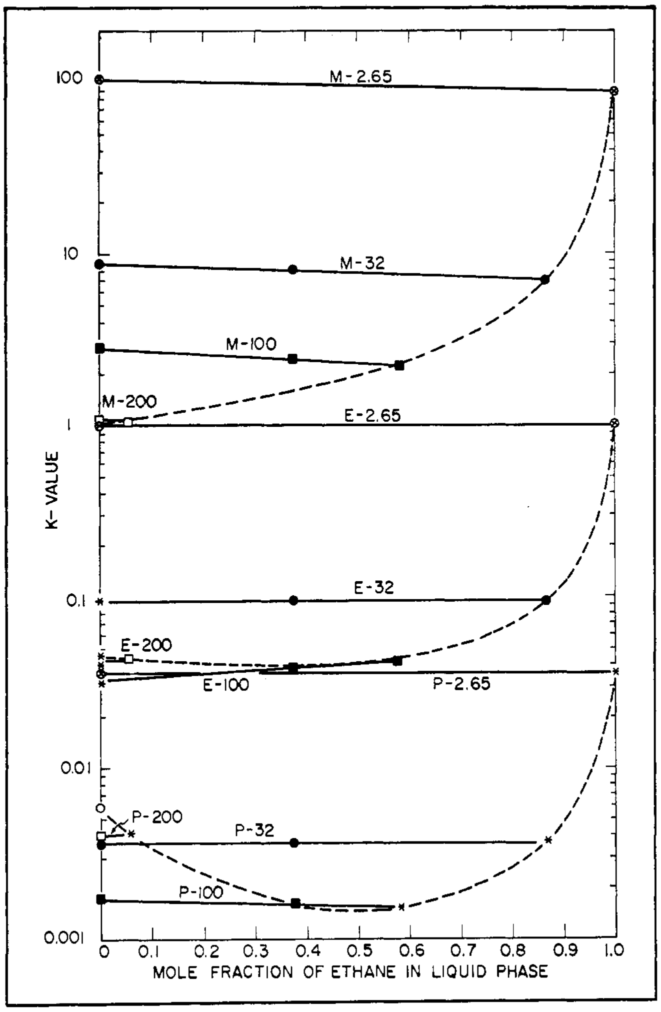

Figure 5. K-value vs. composition for the methane–ethane–propane system at −175°F

sieve purifier to remove water, oil, and particles down to approximately 12 μ in size.

Research-grade ethane was donated by Phillips Petroleum Co. It was used without further purification. Research-grade 99.99% propane was also donated by Phillips Petroleum Co. and was used without additional purification.

No impurities in the three gases were detected by the investigator's gas chromatograph. The gases were from the same samples used in the earlier studies of binary systems (*7*, *8*).

RESULTS

Starting mixtures were prepared at near-infinite dilution concentrations, since these are important for extrapolation. The earlier methane binary data, interpolated where necessary, determined four end points of the ternary at each temperature and pressure. Mixtures in the midconcentration range were measured to cover the entire range.

Pressure and temperature are sufficient to define a binary system; but, as governed by the Phase Rule, a ternary system has an additional degree of freedom. Triangular composition diagrams are not suitable for this system, since the components have a wide range of relative volatilities. Thus, one of the phase compositions must be selected which will give a reasonable representation of the results. The mole fraction of the ethane in the liquid phase was selected, for the work of Price and Kobayashi (*4*) had shown this to be a suitable variable. This was also useful for comparison purposes and to establish experimental conditions for this investigation.

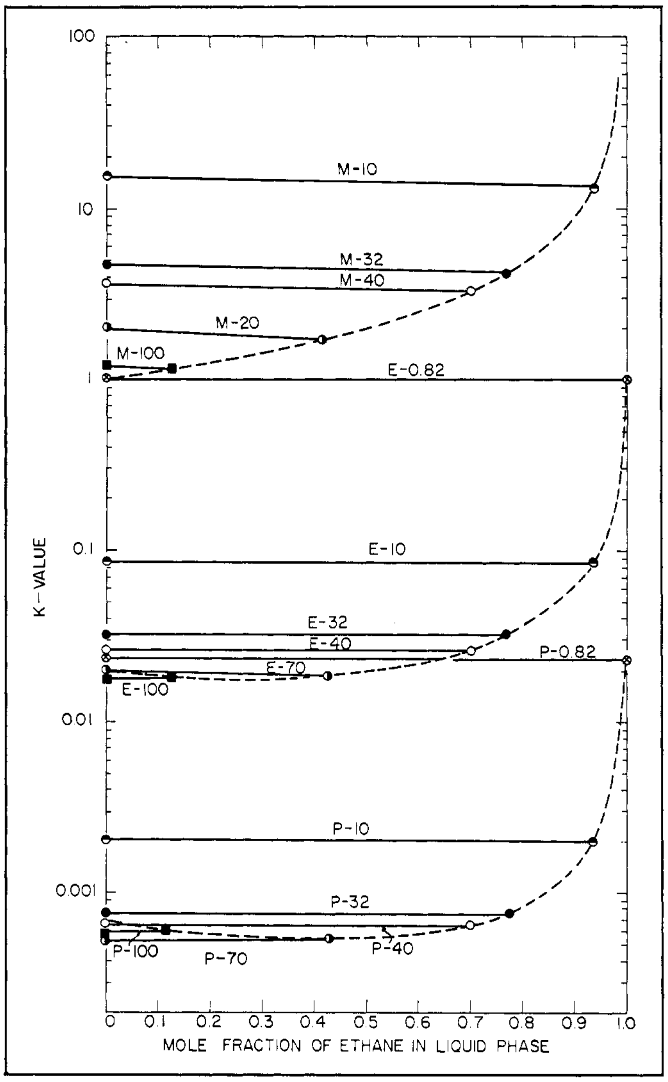

Figure 6. ***K*-value vs. composition for the methane–ethane–propane system at −200°F based only on binary system data**

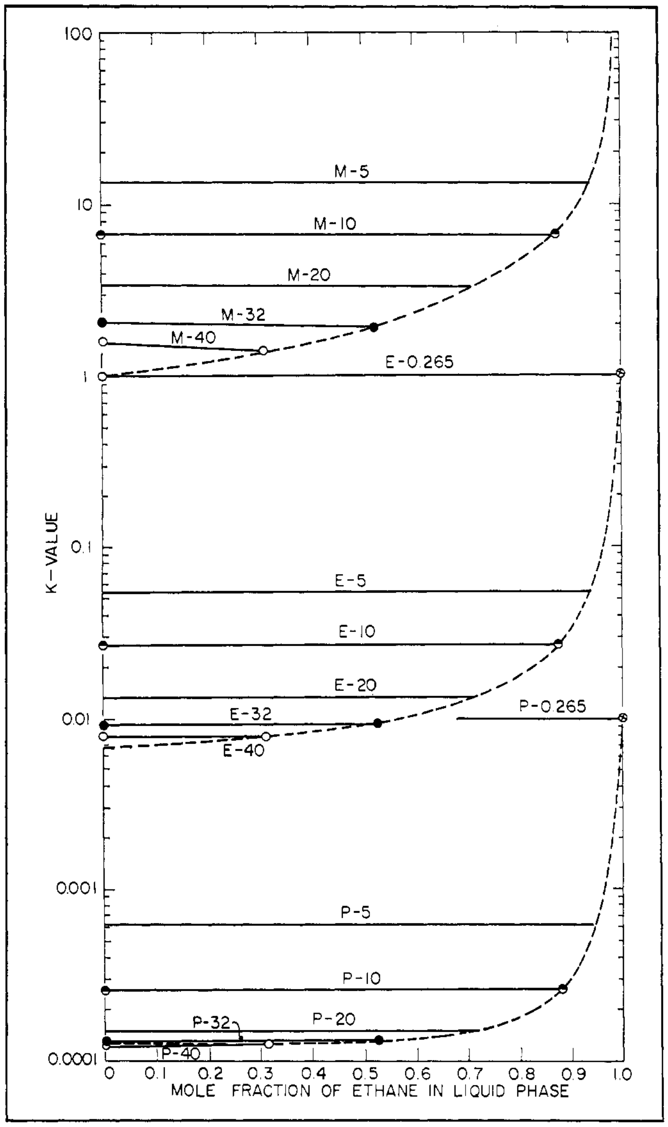

Figure 7. ***K*-value vs. composition for the methane–ethane–propane system at −225°F based only on binary system data**

Results of this study are presented as *K*-values vs. mole fraction of ethane in the liquid phase in Figures 1 through 5. The lines in these Figures are identified by a combination of a letter and number corresponding to the component and the pressure in psia, respectively (M = methane, E = ethane, P = propane). Dashed lines represent (a) the limiting binary *K*-value loci for the methane and ethane system, and (b) a locus of the *K*-values of propane at infinite dilution in the methane–ethane mixtures.

Only the results at 800 and 875 psia at −75°F and 725 psia at −100°F, exhibit nonlinear behavior of log *K* vs. the mole fraction of ethane in the liquid phase. All other data show that the dependence of logarithm of all three *K*-values vs. the mole fraction of ethane in the liquid phase is linear. In addition, for most cases (especially for lower pressures) the *K*-value is essentially independent of the mole fraction of ethane in the liquid phase. These observations made possible the construction of similar diagrams, Figures 6 and 7, for the temperatures of −200° and −225°F based only on binary data. At these low temperatures only methane deviates from ideal behavior.

Table I gives the 49 experimental data sets of this investiga-

Table I. Vapor-Liquid Equilibrium for Methane–Ethane–Propane System

Liquid mole fraction			Vapor mole fraction			Pressure		*K*-Value			
CH_4	C_2H_6	C_3H_8	CH_4	C_2H_6	C_3H_8	Psia	Atm	CH_4	C_2H_6	C_3H_8	Notes
				Temp = 213.71°K = −59.49°C = −75.0°F							
. . .	>0.0000	. . .	. . .	>0.0000	. . .	56.2	3.82	19.0	1.000	0.12	a,b,c
. . .	<1.0000	. . .	. . .	<1.0000	. . .	56.2	3.82	15.0	1.000	0.12	a,b,d
0.0899	0.0000	0.9101	0.9288	0.0000	0.0712	100.0	6.80	10.3	0.62[e]	0.0782	a
0.0813	0.2052	0.7135	0.8176	0.1261	0.0563	100.0	6.80	10.05	0.615	0.0789	f
0.0580	0.7770	0.1650	0.5005	0.4861	0.0134	100.0	6.80	8.63	0.626	0.0812	f
									0.61		g
0.0533	0.9008	0.0459	0.4483	0.5474	0.00431	100.0	6.80	8.41	0.608	0.0939	f
								8.6		0.085	g
0.0506	0.9494	0.0000	0.4304	0.5696	0.0000	100.0	6.80	8.5	0.60	0.0860[e]	a,b

(*Continued on next page*)

Table I. *(Continued)*

Liquid mole fraction			Vapor mole fraction			Pressure		*K*-Value			
CH_4	C_2H_6	C_3H_8	CH_4	C_2H_6	C_3H_8	Psia	Atm	CH_4	C_2H_6	C_3H_8	Notes
Temp = 213.71°K = −54.49°C = −75.0°F											
0.1743	0.0000	0.8257	0.9587	0.0000	0.0413	200.0	13.60	5.5	0.360^e	0.050	^{a,b}
0.1777	0.1834	0.6389	0.9036	0.0645	0.0319	200.0	13.60	5.08	0.352	0.0499	^{f}
0.1667	0.6943	0.1390	0.7470	0.2444	0.00852	200.0	13.60	4.48	0.352	0.0613	^{f}
								4.4		0.052	^{g}
0.1624	0.7963	0.0413	0.7142	0.2836	0.00216	200.0	13.60	4.40	0.356	0.0523	^{f}
								4.3			^{g}
0.1688	0.8312	0.0000	0.7090	0.2910	0.0000	200.0	13.60	4.20	0.35	0.054^e	^{a,b}
0.3656	0.0000	0.6344	0.9741	0.0000	0.0259	400.0	27.20	2.66	0.250^e	0.0408	^{a}
0.3720	0.1412	0.4868	0.9440	0.0345	0.0215	400.0	27.20	2.54	0.244	0.0442	^{f}
0.3725	0.5193	0.1082	0.8673	0.1270	0.00573	400.0	27.20	2.33	0.245	0.0530	^{f}
								2.25	0.241		^{g}
0.3878	0.6122	0.0000	0.8532	0.1468	0.0000	400.0	27.20	2.20	0.240	0.058^e	^{a,b}
0.5563	0.0000	0.4437	0.9767	0.0000	0.0233	600.0	40.85	1.76	0.23^e	0.0525	^{a}
0.5453	0.0971	0.3576	0.9576	0.0234	0.0190	600.0	40.85	1.76	0.241	0.0531	^{f}
								1.70	0.25	0.058	^{g}
0.5826	0.3427	0.0747	0.9042	0.0903	0.00553	600.0	40.85	1.55	0.263	0.0740	^{f}
									0.28	0.072	^{g}
0.5833	0.4167	0.0000	0.8750	0.1250	0.0000	600.0	40.85	1.50	0.30	0.077^e	^{a,b}
0.7573	0.0000	0.2427	0.9726	0.0000	0.0274	800.0	54.45	1.28	0.340^e	0.113	^{a}
0.7711	0.0512	0.1777	0.9586	0.0178	0.0236	800.0	54.45	1.24	0.348	0.133	^{f}
0.7796	0.1795	0.0409	0.9173	0.0742	0.00844	800.0	54.45	1.18	0.413	0.206	^{f}
0.7840	0.2037	0.0123	0.9060	0.0914	0.00254	800.0	54.45	1.16	0.449	0.207	^{f}
								1.12	0.48		^{g}
0.8196	0.1804	0.0000	0.9098	0.0902	0.0000	800.0	54.45	1.11	0.50	0.230^e	^{a,b}
0.8636	0.1093	0.0271	0.9045	0.0799	0.0156	875.0	59.55	1.05	0.731	0.576	^{f}
Temp = 199.82°K = −73.33°C = 100.0°F											
...	>0.0000	...	...	>0.0000	...	32.0	2.18	27.0	1.000	0.11	^{a,b,c}
...	<1.0000	...	...	<1.0000	...	32.0	2.18	20.5	1.000	0.11	^{a,b,d}
0.0427	0.0000	0.9573	0.9197	0.0000	0.0803	40.0	2.72	21.5	0.82^e	0.084	^{a,b}
0.0390	0.1999	0.7611	0.7713	0.1640	0.0647	40.0	2.72	19.8	0.82	0.085	^{f}
0.0342	0.4313	0.5345	0.6067	0.3509	0.0424	40.0	2.72	17.7	0.814	0.0793	^{f}
										0.088	^{g}
0.0255	0.6771	0.2974	0.4382	0.5350	0.0268	40.0	2.72	17.1	0.790	0.0901	^{f}
									0.81	0.090	^{g}
0.0129	0.9871	0.0000	0.2062	0.7938	0.0000	40.0	2.72	16.0	0.804	0.092^e	^{a,b}
0.1149	0.0000	0.8851	0.9652	0.0000	0.0348	100.0	6.80	8.40	0.36^e	0.039	^{a,b}
0.1169	0.0610	0.8221	0.9454	0.0244	0.0302	100.0	6.80	8.09	0.400	0.0367	^{f}
									0.36	0.040	^{g}
0.1058	0.5843	0.3099	0.7819	0.2051	0.0131	100.0	6.80	7.39	0.351	0.0422	^{f}
								7.1			^{g}
0.1037	0.8045	0.0918	0.7091	0.2868	0.0041	100.0	6.80	6.84	0.339	0.0447	^{f}
									0.35		^{g}
0.1039	0.8961	0.0000	0.6800	0.3200	0.0000	100.0	6.80	6.54	0.357	0.046^e	^{a}
0.2335	0.0000	0.7665	0.9807	0.0000	0.0193	200.0	13.60	4.20	0.235^e	0.025	^{a,b}
0.2332	0.0528	0.7140	0.9691	0.0123	0.0186	200.0	13.60	4.15	0.233	0.0261	^{f}
										0.028	^{g}
0.2366	0.4960	0.2674	0.8905	0.1017	0.00776	200.0	13.60	3.76	0.205	0.0290	^{f}
									0.225		^{g}
0.2501	0.6823	0.0675	0.8502	0.1477	0.00202	200.0	13.60	3.52	0.220	0.0299	^{f}
								3.60			^{g}
0.2453	0.7547	0.0000	0.8340	0.1660	0.0000	200.0	13.60	3.40	0.220	0.0300^e	^{a,b}
0.4937	0.0000	0.5063	0.9874	0.0000	0.0126	400.0	27.20	2.00	0.17^e	0.025	^{a,b}
0.4877	0.0373	0.4750	0.98125	0.00625	0.0125	400.0	27.20	2.01	0.168	0.0263	^{f}
									0.17		^{g}
0.5206	0.3083	0.1711	0.9438	0.0511	0.00512	400.0	27.20	1.81	0.166	0.0299	^{f}
									0.17		^{g}
0.5510	0.4173	0.0316	0.9268	0.0722	0.000992	400.0	27.20	1.68	0.185	0.0310	^{f}
								1.75	0.17		^{g}
0.5410	0.4590	0.0000	0.9197	0.0803	0.0000	400.0	27.20	1.70	0.175	0.032^e	^{a,b}
0.7472	0.0000	0.2528	0.9863	0.0000	0.0137	600.0	40.85	1.32	0.19^e	0.054	^{a,b}
0.7668	0.0179	0.2153	0.98425	0.00355	0.0122	600.0	40.85	1.28	0.198	0.0567	^{f}
								1.30			^{g}
0.7795	0.1364	0.0841	0.9631	0.0313	0.00557	600.0	40.85	1.24	0.229	0.0662	^{f}
0.8000	0.1815	0.0185	0.9526	0.0462	0.00119	600.0	40.85	1.19	0.255	0.0643	^{f}
								1.22			^{g}
0.7852	0.2148	0.0000	0.9461	0.0539	0.0000	600.0	40.85	1.20	0.251	0.066^e	^{a}
0.8979	0.0000	0.1021	0.9879	0.0000	0.0121	725.0	49.35	1.10	0.32^e	0.12	^{a,b}
0.9194	0.00562	0.0750	0.9856	0.00184	0.01256	725.0	49.35	1.07	0.327	0.167	^{f}

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Table I. *(Continued)*

Liquid mole fraction			Vapor mole fraction			Pressure		K-Value			
CH_4	C_2H_6	C_3H_8	CH_4	C_2H_6	C_3H_8	Psia	Atm	CH_4	C_2H_6	C_3H_8	Notes
Temp = 199.82°K = −73.33°C = 100.0°F (*Contd.*)											
0.9201	0.0501	0.0298	0.9707	0.0221	0.00723	725.0	49.35	1.055	0.441	0.243	f
0.9600	0.0400	0.0000	0.9792	0.0208	0.0000	725.0	49.35	1.02	0.520	0.26[e]	a,b
Temp = 185.93°K = −87.22°C = −125.0°F											
...	>0.0000	...	...	>0.0000	...	16.0	1.09	38	1.000	0.076	a,b,c
...	<1.0000	...	...	<1.0000	...	16.0	1.09	31	1.000	0.1[h]	a,b,d
0.0493	0.0000	0.9507	0.9619	0.0000	0.0381	32.0	2.18	19.5	0.55[e]	0.040	a,b
0.0451	0.2274	0.7275	0.8337	0.1320	0.0343	32.0	2.18	18.5	0.580	0.0471	f
									0.56	0.041	g
0.0304	0.8378	0.1318	0.5124	0.4809	0.00671	32.0	2.18	16.9	0.574	0.0509	f
0.0264	0.9736	0.0000	0.4353	0.5647	0.0000	32.0	2.18	16.5	0.58	0.050[e]	a,b
0.1516	0.0000	0.8484	0.9854	0.0000	0.0146	100.0	6.80	6.5	0.195[e]	0.0170	a,b
0.1553	0.2000	0.6467	0.9430	0.0444	0.0126	100.0	6.80	6.07	0.222	0.0194	f
								6.3	0.195	0.0185	g
0.1479	0.7354	0.1167	0.8491	0.1486	0.00233	100.0	6.80	5.74	0.202	0.0200	f
								5.5	0.195	0.0190	g
0.1608	0.8392	0.0000	0.8362	0.1638	0.0000	100.0	6.80	5.2	0.195	0.0190[e]	a,b
0.3198	0.0000	0.6802	0.9914	0.0000	0.0086	200.0	13.60	3.10	0.130[e]	0.0125	a,b
0.3142	0.1579	0.5279	0.97156	0.0214	0.00704	200.0	13.60	3.09	0.136	0.0133	f
								3.0		0.0127	g
0.3332	0.5735	0.0933	0.9252	0.0735	0.00127	200.0	13.60	2.78	0.128	0.0136	f
								2.7	0.138	0.0129	g
0.3568	0.6432	0.0000	0.9098	0.0902	0.0000	200.0	13.60	2.55	0.140	0.0130[e]	a,b
0.7082	0.0000	0.2918	0.9915	0.0000	0.0085	400.0	27.20	1.40	0.10[e]	0.019	a,b
0.6828	0.0729	0.2443	0.98713	0.00784	0.00502	400.0	27.20	1.45	0.108	0.0205	f
								1.38		0.0195	g
0.6954	0.2539	0.0507	0.9675	0.0315	0.00099	400.0	27.20	1.39	0.124	0.0196	f
								1.32	0.130		g
0.7432	0.2568	0.0000	0.9662	0.0338	0.0000	400.0	27.20	1.30	0.132	0.020[e]	a,b
0.8000	0.0000	0.2000	0.8800	0.0000	0.1200	550.0	37.45	1.10	0.20[e]	0.060	a,b
0.9357	0.0141	0.0502	0.99345	0.00311	0.00344	550.0	37.45	1.06	0.221	0.0685	f
0.9615	0.0385	0.0000	0.9903	0.0097	0.0000	550.0	37.45	1.03	0.250	0.08[e]	a,b
Temp = 172.04°K = −101.11°C = −150.0°F											
...	>0.0000	...	...	>0.0000	...	7.1	0.483	61	1.000	0.054	a,b,c
...	<1.0000	...	...	<1.0000	...	7.1	0.483	50	1.000	0.054	a,b,d
0.0720	0.0000	0.9280	0.9870	0.0000	0.0130	32.0	2.18	13.7	0.245[e]	0.0140	a,b
0.0721	0.2933	0.6346	0.9188	0.0720	0.00918	32.0	2.18	12.7	0.245	0.0145	f
									0.242	0.0140	g
0.0715	0.7701	0.1584	0.8180	0.1799	0.00207	32.0	2.18	11.4	0.234	0.0131	f
									0.241	0.0140	g
0.0700	0.9300	0.0000	0.7768	0.2232	0.0000	32.0	2.18	11.1	0.240	0.0139[e]	a,b
0.2262	0.0000	0.7738	0.9951	0.0000	0.0049	100.0	6.80	4.40	0.095[e]	0.00633	a,b
0.2359	0.2416	0.5225	0.9739	0.0232	0.00294	100.0	6.80	4.13	0.0960	0.00563	f
								4.10	0.094	0.0059	g
0.2541	0.6305	0.1154	0.9433	0.0561	0.000607	100.0	6.80	3.71	0.0890	0.00526	f
									0.093	0.0053	g
0.2626	0.7374	0.0000	0.9322	0.0678	0.0000	100.0	6.80	3.55	0.0920	0.00510[e]	a,b
0.4865	0.0000	0.5135	0.99728	0.0000	0.00272	200.0	13.60	2.05	0.068[e]	0.00530	a,b
0.5162	0.1554	0.3284	0.9877	0.01078	0.00154	200.0	13.60	1.91	0.0694	0.00469	f
									0.068		g
0.5487	0.3826	0.0687	0.97508	0.0246	0.000272	200.0	13.60	1.78	0.0644	0.00395	f
									0.068		g
0.5708	0.4292	0.0000	0.9704	0.0296	0.0000	200.0	13.60	1.70	0.0690	0.0039[e]	a,b
0.8319	0.0000	0.1681	0.99832	0.0000	0.00168	300.0	20.40	1.20	0.074[e]	0.0100	a,b
0.8565	0.0462	0.0973	0.99554	0.00350	0.000960	300.0	20.40	1.16	0.0758	0.00987	f
0.8673	0.1327	0.0000	0.9887	0.0113	0.0000	300.0	20.40	1.14	0.085	0.0098[e]	a,b
Temp = 158.15°K = −115.00°C = −175.0°F											
...	>0.0000	...	...	>0.0000	...	2.65	0.180	100	1.000	0.0036	a,b,c
...	<1.0000	...	...	<1.0000	...	2.65	0.180	88	1.000	0.0036	a,b,d
0.1133	0.0000	0.8867	0.99678	0.0000	0.00322	32.0	2.18	8.80	0.098[e]	0.00365	a,b
0.1174	0.3770	0.5056	0.96181	0.03637	0.00182	32.0	2.18	8.19	0.0965	0.00360	f
								7.90			g
0.1331	0.8669	0.0000	0.9185	0.0815	0.0000	32.0	2.18	6.90	0.0940	0.005[e]	a,b
0.3996	0.0000	0.6004	0.99896	0.0000	0.00104	100.0	6.80	2.50	0.040[e]	0.00173	a,b
0.4190	0.3783	0.2027	0.98520	0.01449	0.000312	100.0	6.80	2.35	0.0383	0.00154	f
									0.041		g
0.4439	0.5561	0.0000	0.97665	0.0233	0.0000	100.0	6.80	2.20	0.0420	0.0015[e]	a,b

[a] Binary system values. [b] Interpolated. [c] Infinite dilution of ethane in methane-propane mixture. [d] Infinite dilution of methane-propane mixture in ethane. [e] Infinite dilution value. [f] Experimental. [g] Smoothed. [h] Extrapolated.

tion and the necessary limiting binary and infinite dilution values, interpolated when necessary, which define the ternary system from −75° to − 175°F. The system is defined at lower temperatures by the binary data (*7*, *8*). Simple expressions for the linear region, which represents almost all of the data, are

$$\log K_{\mathrm{M}} = \log K_{\mathrm{M(P)}} - (x_{\mathrm{E}}/x_{\mathrm{E}}') \log [K_{\mathrm{M(P)}}/K_{\mathrm{M(E)}}] \qquad (1)$$

$$\log K_{\mathrm{E}} = \log K_{\mathrm{E(MP)}}^{\infty} - (x_{\mathrm{E}}/x_{\mathrm{E}}') \log [K_{\mathrm{E(MP)}}^{\infty}/K_{\mathrm{E(M)}}] \qquad (2)$$

$$\log K_{\mathrm{P}} = \log K_{\mathrm{P(M)}} - (x_{\mathrm{E}}/x_{\mathrm{E}}') \log [K_{\mathrm{P(M)}}/K_{\mathrm{P(ME)}}^{\infty}] \qquad (3)$$

$$\text{for } 0 \leq x_{\mathrm{E}} \leq x_{\mathrm{E}}'$$

Values for $K_{\mathrm{M(P)}}$, $K_{\mathrm{P(M)}}$, $K_{\mathrm{M(E)}}$, and $K_{\mathrm{E(M)}}$ can be easily found from the pressure temperature cross-plots of the binary data (*7*, *8*); x_{E}' has to be determined from the methane–ethane data (*8*); values for $K_{\mathrm{E(MP)}}^{\infty}$ and $K_{\mathrm{P(ME)}}^{\infty}$ are found from cross-plots of ternary data extrapolated to boundary concentrations. The extrapolation is justified because it is not extensive. These plots must be carefully constructed on large-scale engineering paper to retain the accuracy of the data.

The linearity of the *K*-values in the low temperature region was not evident in the data of Price and Kobayashi (*4*). Significant deviations from this investigation were found at temperatures below −50°F, especially for the methane–propane system. The most probable explanations are improper sampling and lack of analytical sensitivity. At the time of the older work, analysis could only be made to a mole fraction of ±0.001; now, with the improvements that have been made in chromatographic analysis, it is possible to determine amounts less than 0.001% with a good accuracy and reproducibility. Improvements in the sampling system (*7*, *8*) are also highly significant. The effect of a small amount of the less volatile component in the vapor phase becomes more pronounced as the temperature and pressure decrease.

The construction of pressure temperature cross-plots is helped by using data of other investigators (*1*, *2*, *4*, *5*) at higher temperatures than this investigation.

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NOMENCLATURE

All values are determined at the same temperature and pressure.

K_{M}, K_{E}, K_{P} = *K*-values of methane, ethane, and propane, respectively, in the ternary system
$K_{\mathrm{A(B)}}$ = *K*-value of A in the A-B binary system
$K_{\mathrm{A(BC)}}^{\infty}$ = *K*-value of A at infinite dilution in the B-C binary
x_{E}' = ethane mole fraction in the liquid phase in the methane–ethane system
x_{E} = ethane mole fraction in the liquid phase in the ternary system

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Thermal Decomposition of Alkali Metal Hexafluorophosphates

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The thermal decomposition of $NaPF_6$, KPF_6, $RbPF_6$, and $CsPF_6$ has been studied using mass spectrometric–effusion cell and differential thermal analysis techniques. All evolve PF_5 when heated under effusion conditions. The PF_5 decomposition pressure equations and first values for the formation enthalpies have been determined.

The hexafluorophosphates of the alkali metals present an interesting study of the variation in stability with cation size and are commercially important as well. Because stability data were not available, we conducted mass spectrometric and thermal analysis studies of the decomposition of these compounds.

EXPERIMENTAL

All compounds were used as received without further purification. According to the manufacturer the fluorine contents were 99.6, 97.1, and 101.0% of theoretical for the Na, Rb, and Cs salts, respectively. The PF_6^- content was 100.2 and 96.7 of theoretical for the Na and K salts, respectively (*13*). For our experiments, volatile impurities would contribute to the total weight loss measurements upon which the decomposition pressure calibrations are based while nonvolatile substances would be troublesome only if they altered the sample's activity.

The extent of both problems can be evaluated from our data since volatiles would be mass spectrometrically observed while activity variations would be seen as variations in the sample's vapor/decomposition pressure with time at a constant temperature. The compounds are stable enough not to require unusual precautions for handling. Differential thermal analyses were performed under vacuum with a Du Pont 900 DTA in-

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