

Vapor-liquid Equilibria for Hydrogen-light-Hydrocarbon Systems at Low Temperatures

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Experimental equilibrium vapor and liquid compositions are reported for the hydrogen-methane system at -150° , -200° , and -250°F . and at pressures of 500 to 4,000 lb./sq. in. The ternary system hydrogen-methane-propane was studied at 0° , -100° , and -200°F . at 500 and 1,000 lb./sq. in. Phase compositions were determined for a limited number of similar conditions for the hydrogen-methane-propylene and hydrogen-methane-ethylene-ethane-propylene-propane systems.

It has been noted that although low-temperature processing of hydrogen-containing light-hydrocarbon systems is becoming increasingly important, there is a deficiency in our knowledge of the behavior of these systems. Aroyan and Katz (1) and later Williams and Katz (10) have reviewed the available binary data for hydrogen-light hydrocarbon systems. Data are available for hydrogen with methane (4, 5, and 7), ethylene (10), ethane (10), propylene (10), propane (2 and 10), isobutane (3), and *n*-butane (1 and 9) and also for the hydrogen-

methane-ethylene (8) - and hydrogen-methane-ethane (7) systems.

Since a study of the available hydrogen-methane data revealed internal scatter and inconsistency, new data were obtained for this system. Ternary-system data were obtained for the hydrogen-methane-propylene and the hydrogen-methane-propane systems. As an indica-

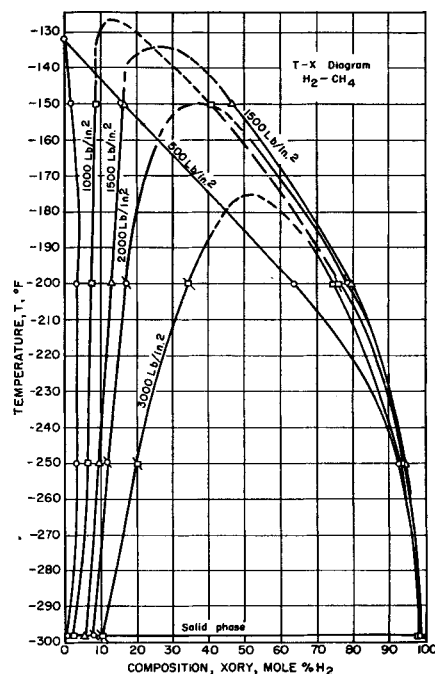
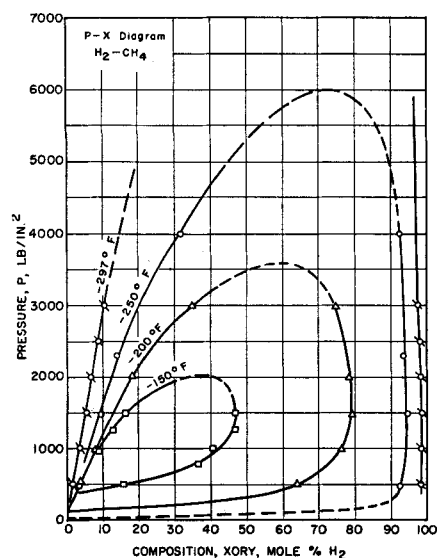


Fig. 2. ↑ Temperature-composition diagram for hydrogen-methane binary system.

Fig. 1. ← Pressure-composition diagram for hydrogen-methane binary system.

TABLE 1. ORIGINAL DATA FOR HYDROGEN-METHANE SYSTEM

Run	Temperature, °F.	Pressure,* lb./sq. in.	Phase compositions	
			Vapor mole % H ₂	Liquid mole % H ₂
3	-150	500	15.83	1.70
4	-150	1,000	40.60	8.77
8	-150	1,280	46.31	12.55
9	-150	1,500	46.78	16.22
2A	-200	500	63.92	3.43
5	-200	1,000	76.18	7.81
11	-200	1,490	79.31	13.10
2B	-200	1,990	78.23	18.05
15	-200	3,000	74.57	34.99
12	-250	490	92.79	3.18
13	-250	1,490	94.66	9.50
14	-250	2,300	93.83	13.94
16	-250	4,000	92.89	31.70

*All pressures are absolute pressures.

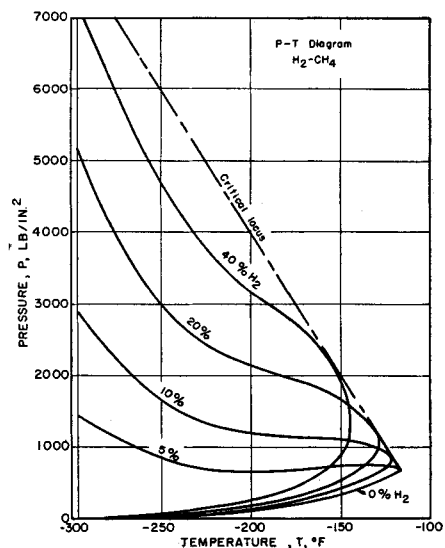


Fig. 3. Pressure-temperature diagram for hydrogen-methane binary system.

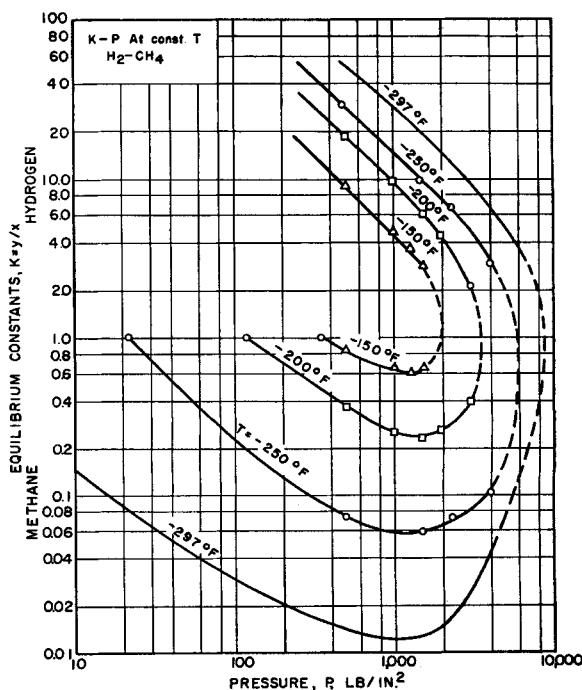


Fig. 4. Equilibrium constants vs. pressure for the hydrogen-methane system.

tion of the behavior of hydrogen in complex systems, some data were obtained for the hydrogen-methane-ethylene-ethane-propylene-propane system.

EQUIPMENT AND PROCEDURES

The equipment used for obtaining the experimental data was the same as previously described (1 and 10). Essentially it consisted of a high-pressure stainless steel cell in a constant-temperature air bath. An external circulating system took vapor from the top of the cell and returned it to the bottom of the cell.

The temperature in the cell was measured by a three-junction copper-constantan thermopile. The error in temperature measurement is believed to be within $\pm 1.0^\circ\text{F.}$ at -300°F. and $\pm 0.1^\circ\text{F.}$ at room temperature. Pressures are believed to be within $\pm 0.5\%$ of the true pressure. During measurements temperatures and pressures were held constant from 2 to 8 hr. within these limits. Samples of liquid phases were analyzed at intervals until two successive samples gave a constant composition. A thermal-conductivity cell was used to indicate the constancy of composition for the hydrogen-methane system.

Analyses of vapor and liquid phases, made with a CEC 21-103B mass spectrometer, are generally accurate to within $\pm \frac{1}{2}\%$ of the component composition except at low concentrations, where the error may be somewhat larger. Many of the analyses for the hydrogen-methane binary system were made by means of the gas-density method described by Williams and Katz (10) and are also believed to be accurate to within $\pm \frac{1}{2}\%$.

The gases used in this investigation as they existed in their containers were shown by the mass spectrometer to have a minimum purity of 99.0% (H_2 99.5%). Hydrogen and methane were both purified further by passing them through a train containing silica gel, Ascarite, and activated charcoal. The ethylene, ethane, propylene, and propane were purified further by a partial-differential vaporization.

HYDROGEN-METHANE SYSTEM

The hydrogen-methane system was studied at temperatures of -150° , -200° , and -250°F. and at pressures from 500 to 4,000 lb./sq. in. as given in Table 1. The pressure-composition diagram is given in Figure 1, in which the data of Freeth (5) at -297°F. have been included. The critical regions of the envelopes as shown in the illustrations are extrapolations. The reverse-order solubility of hydrogen is shown in the temperature-composition diagram, Figure 2. The envelopes terminate with the formation of a solid phase at about -300°F. The pressure-temperature plot of the data in Figure 3 shows that at low concentrations of hydrogen the phase envelopes contain a minimum and that at higher concentrations the slope of the bubble-point curve is always negative. The phenomenon was first noted by Kay (6) for the hydrogen-petroleum-

naphtha system. The equilibrium constants for hydrogen and methane have been plotted as a function of pressure in Figure 4.

HYDROGEN-METHANE-PROPANE SYSTEM

The hydrogen-methane-propane system was studied at temperatures of 0° , -100° , and -200°F. , Table 2, and at pressures of 500 and 1,000 lb./sq. in. Selected triangular plots of the phase compositions are given in Figures 5, 6, and 7. At -100°F. and 1,000 lb./sq. in., Figure 6, liberty was taken to extrapolate the phase-composition curves since a three-component critical point is known to lie on a curve connecting the liquid and vapor lines.

The equilibrium constants for hydrogen in the hydrogen-methane-propane system taken from smoothed triangular diagrams are plotted in Figure 8 as a function of the mole percentage of propane in the liquid phase. As shown, composition does have an effect upon the equilibrium constant for hydrogen, the effect being that addition of methane to the hydrogen-propane system results in decreasing the hydrogen equilibrium constant. Figure 9 contains the methane equilibrium constants taken from smoothed triangular diagrams and plotted as a function of the mole percentage of propane in the liquid phase. Figure 10 contains a similar plot of the propane equilibrium constants as a function of the mole percentage of propane in the liquid

TABLE 2. ORIGINAL DATA FOR HYDROGEN-METHANE-PROPANE SYSTEM

Run	Liquid composition			Vapor composition		
	Mole % H_2	Mole % CH_4	Mole % C_3H_8	Mole % H_2	Mole % CH_4	Mole % C_3H_8
Temperature = 0°F. Pressure = 500 lb./sq. in.						
25	0.15	25.83	74.02	3.98	84.08	11.94
26	0.329	23.57	76.10	8.31	80.26	11.43
27	0.717	20.98	78.30	13.96	73.29	12.75
28	0.907	16.13	82.96	27.90	60.70	11.40
29	1.13	13.67	85.20	37.26	52.08	10.66
30	1.31	11.72	86.98	45.76	43.37	10.87
31	1.00	7.97	91.03	58.75	31.66	9.59
(46)	2.30	0.00	97.70	90.70	0.00	9.30
Temperature = -100°F. Pressure = 500 lb./sq. in.						
(1)	0.00	62.0	38.0	0.0	98.70	1.30
20	0.452	49.58	49.97	14.36	84.43	1.21
21	0.645	44.99	54.36	22.13	76.73	1.14
22	0.683	42.38	56.94	24.57	74.21	1.22
19	1.09	24.93	73.98	59.80	39.25	0.95
18	1.22	21.40	77.38	68.72	30.46	0.82
24	1.16	16.07	82.77	67.83	31.04	1.13
(46)	1.55	0.00	98.45	99.02	0.00	0.976
Temperature = -200°F. Pressure = 500 lb./sq. in.						
(46)	0.86	0.0	99.14	99.9+	0.00	
46	0.789	8.59	90.62	95.73	3.79	0.48
44	1.79	43.67	54.54	83.40	15.92	0.68
48	2.85	87.07	10.08	—	—	
2A	3.43	96.57	0.00	63.92	36.08	0.00
Temperature = 0°F. Pressure = 1,000 lb./sq. in.						
(1)	0.00	53.00	47.0	0.00	90.30	9.70
32	2.02	32.77	65.21	25.54	66.09	8.37
33	2.67	25.70	71.63	45.49	47.77	6.74
34	2.75	24.30	72.95	46.89	45.78	7.33
35	3.09	17.90	79.01	58.95	34.57	6.48
36	3.79	13.03	83.18	66.57	26.57	6.86
(46)	4.75	0.00	95.25	94.08	0.00	5.92
Temperature = -100°F. Pressure = 1,000 lb./sq. in.						
(46)	3.02	0.00	96.98	99.31	0.00	0.69
37	2.76	14.70	82.54	85.62	13.39	0.99
38	3.27	34.28	62.45	61.82	36.81	1.37
39	3.27	46.37	50.36	—	—	
40	3.66	58.44	37.90	43.23	53.01	3.76
Temperature = -200°F. Pressure = 1,000 lb./sq. in.						
(46)	1.63	0.00	98.37	99.9+	0.00	
45	1.79	10.14	88.07	99.00	0.37	0.63
43	3.00	55.93	41.07	87.70	12.04	0.26
42	2.96	57.84	39.20	87.70	12.04	0.26
41	3.12	59.14	37.74	86.66	13.07	0.27
47	5.97	81.22	12.81	80.08	19.61	0.31
5	7.81	92.19	0.00	76.18	23.82	0.00

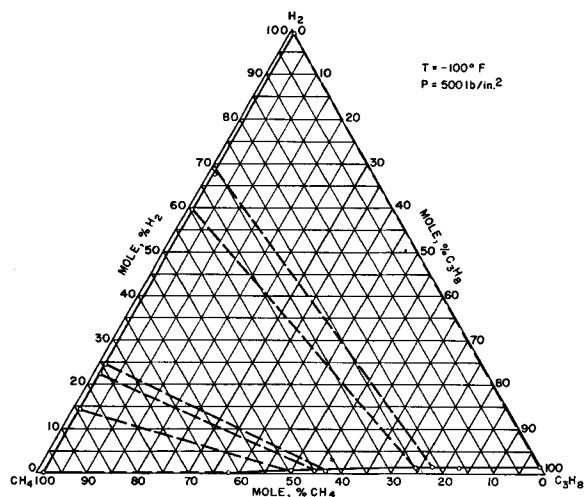


Fig. 5. Triangular composition diagram for hydrogen-methane-propane system at -100°F . and 500 lb./sq. in.

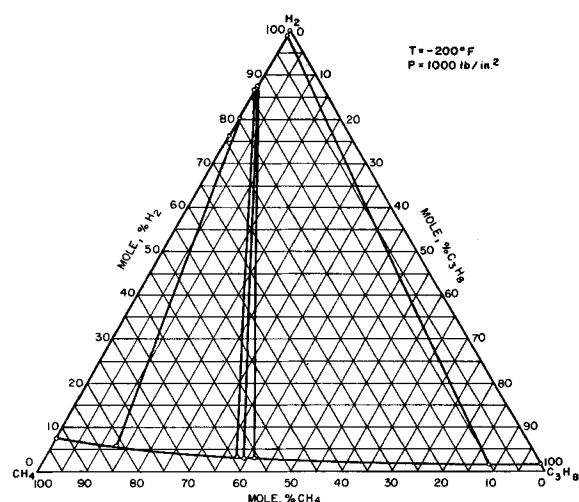


Fig. 7. Triangular composition diagram for hydrogen-methane-propane system at -200°F . and 1,000 lb./sq. in.

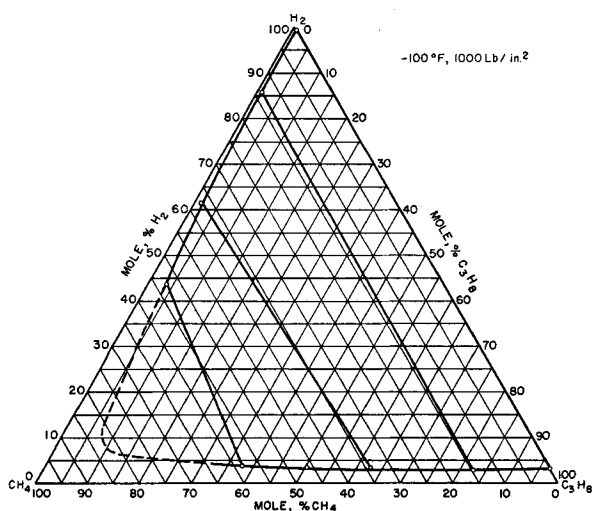


Fig. 6. Triangular composition diagram for hydrogen-methane-propane system at -100°F . and 1,000 lb./sq. in.

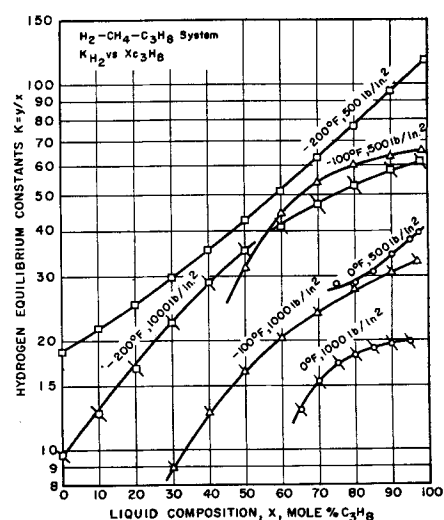


Fig. 8. Equilibrium constants for hydrogen in the hydrogen-methane-propane system as a function of mole percentage of propane in the liquid phase—cross plots.

TABLE 3. ORIGINAL DATA FOR HYDROGEN-METHANE-PROPYLENE SYSTEM

-100°F ., 500 lb./sq. in.

Run	Liquid composition			Vapor composition		
	x_{H_2}	x_{CH_4}	$x_{\text{C}_3\text{H}_6}$	y_{H_2}	y_{CH_4}	$y_{\text{C}_3\text{H}_6}$
49	0.728	51.26	48.01	14.93	83.37	1.70
50	0.986	41.15	57.86	29.33	69.09	1.58
(46)	1.36	0.00	98.64	98.72	0.00	1.28

TABLE 4

ORIGINAL DATA FOR COMPLEX SYSTEM CONTAINING HYDROGEN, METHANE, ETHYLENE, ETHANE, PROPYLENE, AND PROPANE

Run		52	53	54	55	56	
Temperature, °F.		0	-100	-100	0	-100	
Pressure, lb./sq. in.		500	500	500	1,000	1,000	
Liquid phase compositions, mole %	}	H ₂	1.04	1.34	1.48	2.36	1.97
		H ₄	7.67	14.84	12.77	16.45	17.82
		C ₂ H ₄	9.42	9.06	18.23	17.32	17.97
		C ₂ H ₆	5.07	4.66	4.21	4.02	3.74
		C ₃ H ₆	8.39	7.77	7.07	6.67	6.00
		C ₃ H ₈	68.41	62.33	56.24	53.18	52.50
Vapor- phase compositions, mole %	}	H ₂	38.28	65.79	68.60	46.93	77.26
		CH ₄	31.37	30.45	25.45	35.18	19.66
		C ₂ H ₄	8.56	2.00	4.06	9.64	2.09
		C ₂ H ₆	3.44	0.65	0.60	1.73	0.38
		C ₃ H ₆	2.63	0.26	0.24	0.86	0.10
		C ₃ H ₈	15.72	0.85	1.05	5.66	0.51

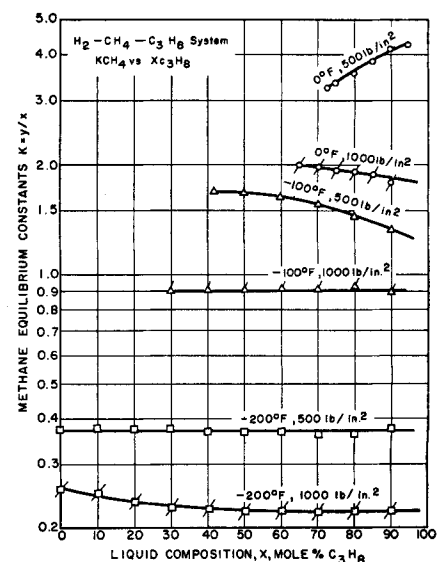


Fig. 9. Equilibrium constants for methane in the hydrogen-methane-propane system as a function of mole percentage of propane in the liquid phase—cross plots.

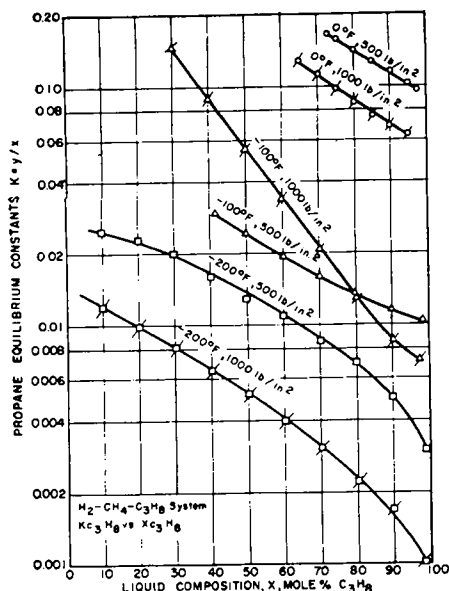


Fig. 10. ← Equilibrium constants for propane in the hydrogen-methane-propane system as a function of mole percentage of propane in the liquid phase—cross plots.

Fig. 12. → Constituent equilibrium constants in the hydrogen-methane-ethylene-ethane-propylene-propane system as a function of the normal boiling point.

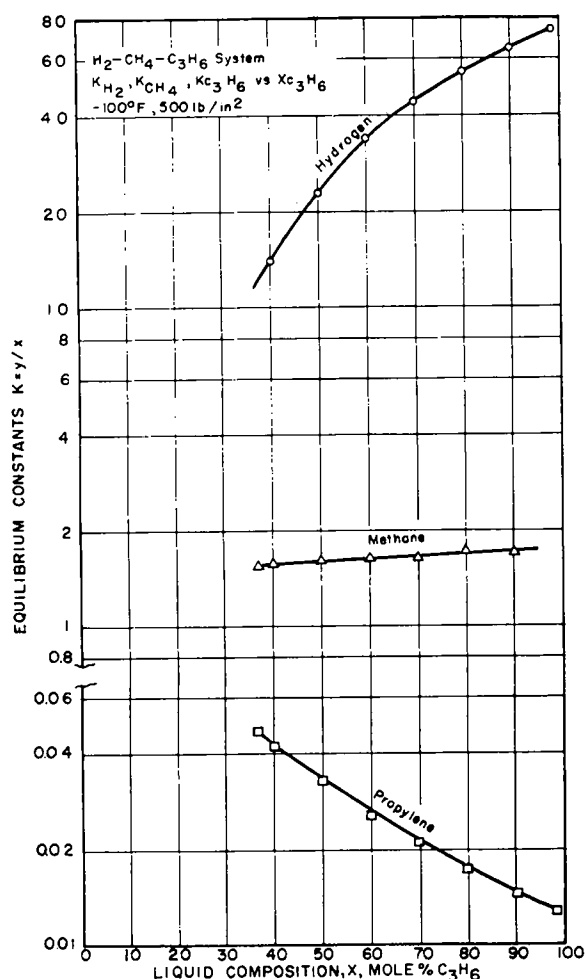


Fig. 11. ← Hydrogen, methane, and propylene equilibrium constants in the hydrogen-methane-propylene system as a function of the mole percentage of propylene in the liquid phase—cross plots.

phase. The effect of adding methane to the hydrogen-propane system is to increase the equilibrium constant for propane.

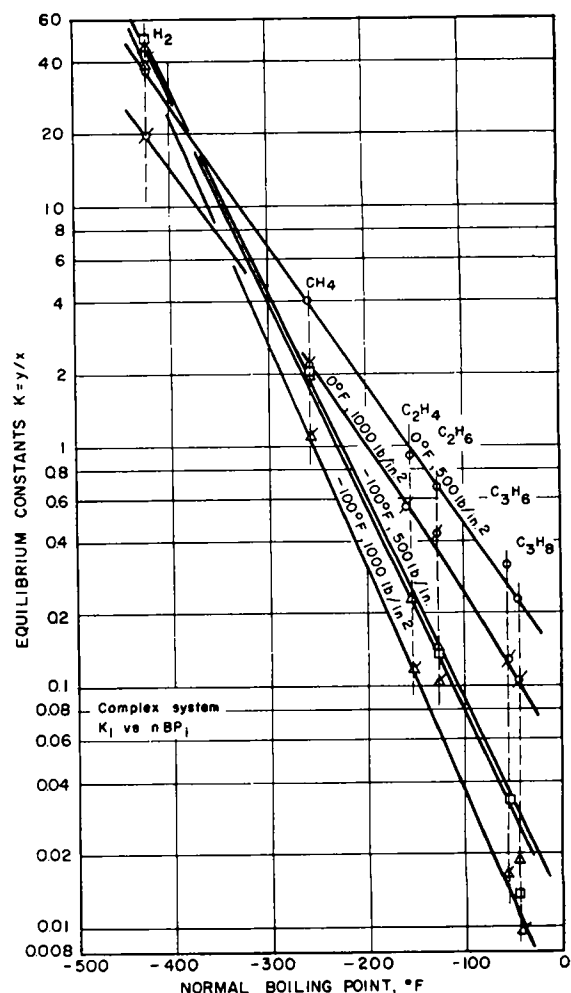
HYDROGEN-METHANE-PROPYLENE SYSTEM

Table 3 contains the phase compositions for two equilibria of the hydrogen-methane-propylene system at -100°F. and 500 lb./sq. in. These two equilibria along with the binary systems were

sufficient to establish the ternary diagram. Figure 11 shows equilibrium constants for the ternary system taken from this triangular diagram.

HYDROGEN-METHANE-ETHYLENE-ETHANE-PROPYLENE-PROPANE SYSTEM

Six equilibria were determined for the six-component system. Data were obtained at temperatures of 0°F. and -100°F. and at 500 and 1,000 lb./sq. in. (Table 4).



A plot of the equilibrium constants for the constituents as a function of their normal boiling points, Figure 12, indicates the consistency of the results.

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LITERATURE CITED

1. Aroyan, H. J., and D. L. Katz, *Ind. Eng. Chem.*, **43**, 185 (1951).
2. Burris, W. L., N. T. Hsu, H. H. Reamer, and B. H. Sage, *Ind. Eng. Chem.*, **45**, 210 (1953).
3. Dean, M. R., and J. W. Tooke, *Ind. Eng. Chem.*, **38**, 389 (1946).
4. Fastowsky, M. G., and V. G. Gonikberg, *J. Phys. Chem. (U.S.S.R.)*, **14**, 427 (1940).
5. Freeth, F. A., and T. T. H. Verschoyle, *Proc. Roy. Soc. (London)*, **130A**, 453 (1931).
6. Kay, W. B., *Chem. Revs.*, **29**, 501 (1941).
7. Levitskaya, E. P., *J. Tech. Phys. (U.S.S.R.)*, **11**, 197 (1941).
8. Likhter, A. I., and N. P. Tikhonovich, *ibid.*, **10**, 1201 (1940).
9. Nelson, E. E., and W. S. Bonnell, *Ind. Eng. Chem.*, **35**, 204 (1943).
10. Williams, R. B., and D. L. Katz, *ibid.*, **46**, 2512 (1954).