15. McAdams, W. H., "Heat Transmission," 3rd ed., p. 238, McGraw-Hill Book Co., New York (1954).
16. Muhlbauer, H. G., M.Ch.E. thesis, Univ. Delaware, Newark (1950).
17. Olsen, H. L., and E. L. Gayhart, Jet Propulsion, 25, 276 (1955).
18. Petrein, R. J., J. P. Longwell, and M. A. Weiss, ibid., 26, 81 (1956).
19. Richardson, J. M., "Proceedings of the Gas Dynamics Symposium on Aerothermochemistry," p. 169, Northwestern Univ., Evanston, Illinois (1956).
20. Richmond, J. K., J. M. Singer, E. B. Cook, J. R. Oxendine, Joseph Grumer, and D. S. Burgess, "Sixth Symposium (International) on Combustion," p. 303, Reinhold, New York (1957).
21. Rosenberg, H. E., von, Ph.D. thesis, Univ. Delaware, Newark (1955).
21A. Schilly, R. A., M.Ch.E. thesis, Univ. Delaware, Newark (1953).
22. Ries, H. B., Ph.D. thesis, Univ. Delaware, Newark (1951).
23. Rossini, F. D., K. S. Pitzer, R. L. Arnett, Rita M. Braun, G. C. Pimentel, et al., Am. Petroleum Indust. Res. Proj. 44, Carnegie Press, Pittsburgh, Pennsylvania (1953).
24. Scurlock, A. C., and J. H. Grover, "Fourth Symposium (International) on Combustion," p. 645, Williams and Wilkins, Baltimore (1953). See also "Selected Combustion Problems, Fundamentals and Aeronautical Applications," p. 215, Butterworths, London (1954).
25. Scurlock, A. C., Mass. Inst. Technol. Fuels Research Laboratory, Meteor Rept. 19 (May, 1948).
26. Shelkin, K. I., J. Tech. Phys. (USSR), 13, 9, 10 (1943). English translation: Natl. Advisory Comm. Aeronaut., Tech. Mem. 1110 (1947).
27. Sherwood, T. K., and C. E. Reed, "Applied Mathematics in Chemical Engineering," 1 ed., pp. 287, 266, McGraw-Hill Book Co., New York (1939).
28. Simon, Dorothy M., and Paul Wagner, Ind. Eng. Chem., 48, 129 (1956).
29. Summerfield, Martin, S. H. Reiter, Victor Kebely, and R. W. Mascolo, Jet Propulsion, 25, 377 (1955).
30. Weil, C. W., Ph.D. thesis, Univ. Delaware, Newark (1950).
31. Westenberg, A. A., J. Chem. Phys., 22, 814 (1954).
32. Williams, D. T., and L. M. Bollinger, "Third Symposium on Combustion and Flame and Explosion Phenomena," p. 176, Williams and Wilkins, Baltimore (1949).
33. Williams, G. C., H. C. Hottel, and A. C. Scurlock, ibid., p. 21.
34. Williams, G. C., and C. W. Shipman, "Fourth Symposium (International) on Combustion," p. 733, Williams and Wilkins, Baltimore (1953).
35. Williams, G. C., P. T. Woo, and C. W. Shipman, "Sixth Symposium (International) on Combustion," p. 427, Reinhold, New York (1957).
36. Wohl, Kurt, Leon Shore, H. E. von Rosenberg, and C. W. Weil, "Fourth Symposium (International) on Combustion," p. 620, Williams and Wilkins, Baltimore (1953).
37. Wohl, Kurt, "Sixth Symposium (International) on Combustion," p. 333, Reinhold, New York (1957).
38. Wohl, Kurt, and Leon Shore, Ind. Eng. Chem., 47, 828 (1955).
39. Wright, F. H., Jet Propulsion Laboratory, Cal. Inst. Tech., Progress Rept. 3-21 (1953).
40. Zelinski, J. J., W. T. Baker, L. J. Mathews, III, and E. C. Bagnall, "Proceedings of the Gas Dynamics Symposium on Aerothermochemistry," p. 179, Northwestern Univ., Evanston, Ill. (1956).
41. Zukoski, E. E., and F. E. Marble, "Combustion Researches and Reviews 1955," p. 167, for AGARD, Butterworths, London (1955).

Low-Temperature Vapor-Liquid Equilibria in Ternary and Quaternary Systems Containing Hydrogen, Nitrogen, Methane, and Ethane

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Experimental data are presented for three ternary systems and the quaternary at pressures of 500 and 1,000 lb./sq. in. abs. and at temperatures of $-100°$ and $-200°F$. These data along with information in the literature were correlated to give charts of equilibrium ratios as a function of temperature, pressure, and composition.
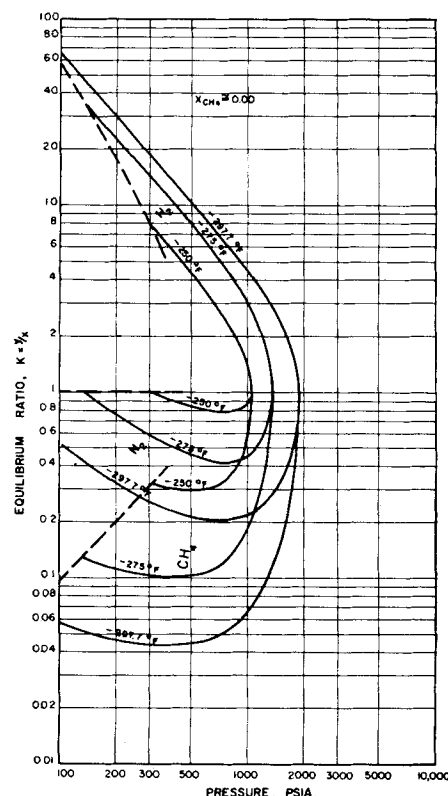
The compositions of equilibrium vapors and liquids were measured for the quaternary system hydrogen-nitrogen-methane-ethane and three of its ternaries at conditions shown in Table 1. The apparatus and procedures employed were essentially the same as those used by Aroyan, Williams, and Benham (1, 12, 2). The phase compositions were determined by mass spectrometer.

The experimental data are given in Tables 2 to 5. The binary-system data from the literature are included in the tables at the conditions of the measurements in this research. The following binary-system data were used in correlating the data for the ternary systems: hydrogen-methane (2); hydrogen-ethane (12), hydrogen-nitrogen (7, 9, 10, 11),

nitrogen-methane (5, 6), and methane-ethane (4). Ternary data for hydrogen-nitrogen-methane (10) and hydrogen-methane-ethane (8) also were used in correlating the phase behavior of these systems.

For the ternary systems the equilibrium ratios were plotted on three types of cross plots: equilibrium ratios vs. pressure, lines of constant temperature, and charts of constant percentage methane, in the liquid phase; equilibrium ratios vs. temperature, lines of constant percentage methane, and charts of constant pressure; and equilibrium ratio vs. percentage of methane in the liquid,

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Fig. 1. Equilibrium ratios for constituents in the hydrogen-nitrogen-methane system at 0 mole % methane in the liquid phase as a function of pressure for various temperatures.

TABLE 1. EXPERIMENTAL CONDITIONS CHOSEN FOR STUDY

System	Pressures, lb./sq. in. abs.	Temperatures, °F.
Hydrogen-methane-ethane	500 and 1,000	−100 and −200
Hydrogen-nitrogen-methane	500 and 1,000	−200
Nitrogen-methane-ethane	500 and 1,000	−100 and −200
Hydrogen-nitrogen-methane-ethane	1,000	−100
Hydrogen-nitrogen-methane-ethane	500	−200

TABLE 2. EXPERIMENTAL DATA FOR THE HYDROGEN-METHANE-ETHANE SYSTEM
INCLUDING BINARY SYSTEM DATA FROM THE LITERATURE

Run or reference	Liquid-phase composition			Vapor-phase composition		
	Mole % H_2	Mole % CH_4	Mole % C_2H_6	Mole % H_2	Mole % CH_4	Mole % C_2H_6

Pressure = 500 lb./sq. in. abs.
Temperature = −100°F.

(12)*	1.87	0.00	98.13	91.66	0.00	8.34
15	1.33	29.42	69.25	46.23	45.86	7.91
14	1.34	32.55	66.11	39.40	52.30	8.30
17	1.20	38.59	60.21	30.62	61.53	7.86
16	1.01	43.25	55.75	23.08	69.13	7.79
(4)*	0.00	66.00	34.00	0.00	93.00	7.00

Pressure = 1,000 lb./sq. in. abs.
Temperature = −100°F.

(12)*	3.90	0.00	96.10	94.76	0.00	5.24
29	3.82	0.00	96.18	94.83	0.00	5.17
10	3.51	4.41	92.08	93.25	3.24	3.51
11	4.00	11.53	84.47	83.72	11.02	5.26
12	3.76	49.57	46.67	45.79	48.62	5.59

Pressure = 500 lb./sq. in. abs.
Temperature = −200°F.

(12)*	1.20	0.00	98.80	99.69	0.00	0.31
24	1.67	52.24	46.09	81.54	18.19	0.272
26	1.75	76.08	22.17	74.12	25.72	0.164
22	3.27	92.03	4.70	69.15	30.80	0.051
(2)*	3.43	96.37	0.00	63.92	36.08	0.00

Pressure = 1,000 lb./sq. in. abs.
Temperature = −200°F.

(12)*	2.25	0.00	97.75	99.74	0.00	0.26
18	2.42	11.15	86.43	97.10	2.66	0.231
19	2.96	35.04	62.00	91.15	8.56	0.290
20	3.13	40.81	56.07	90.09	9.68	0.230
23	4.87	75.71	19.42	82.33	17.54	0.136
21	6.43	87.32	6.25	79.29	20.65	0.061
30	8.32	91.68	0.00	76.01	23.99	0.00
(2)*	7.81	92.19	0.00	76.18	23.82	0.00

*Data from literature.

Fig. 2. Equilibrium ratios for constituents in the hydrogen-nitrogen-methane system at 20 mole % methane in the liquid phase as a function of pressure for various temperatures.

Fig. 3. Equilibrium ratios for constituents in the hydrogen-nitrogen-methane system at 40 mole % methane in the liquid phase as a function of pressure for various temperatures.

lines of constant temperature, and pressure. Figures 1 to 6 give the smoothed results for the hydrogen-nitrogen-methane system, illustrating the first of these methods; Figure 7 is a similar plot for the hydrogen-methane-ethane system at 0.2 mole-fraction methane in the liquid. Figures 8 and 9 illustrate for this system the equilibrium ratio vs. temperature relationships, and the data for the nitrogen-methane-ethane system are given in Figures 10 and 11 as equilibrium ratios vs. composition. The full ternary behavior is not presented, since the nitrogen-ethane binary system data were not available.

A quaternary system is bounded by the four possible ternary systems. In this case the behavior of all the ternary systems is known at the conditions of the measurements on the quaternary system except that of hydrogen-nitrogen-ethane system. Interpolations among these three ternary systems were made at 500 lb./sq. in. abs. and −200°F. The equilibrium ratios are presented for hydrogen, nitrogen, ethane, and methane in Figures 12, 13, and 14, the experimental quaternary data being included in these figures. Although unintentionally, the methane concentration in the quaternary system was varied only from 0.079 to 0.088 mole fraction in the liquid, and the liquid should have fallen approximately on the 0.085 mole-fraction methane curve.

The need for four variables to describe the quaternary system is illustrated by Figures 12, 13, and 14. If three variables
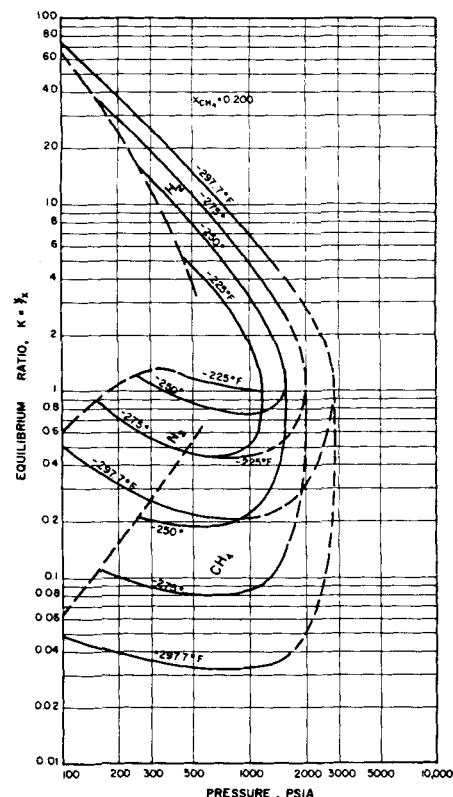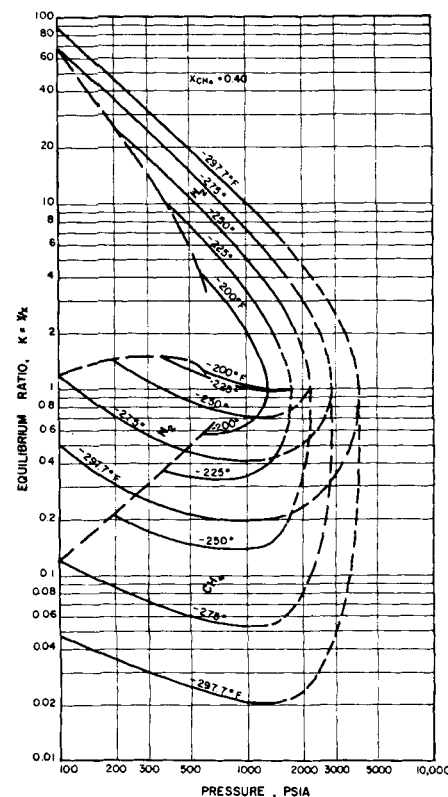
Fig. 4. Equilibrium ratios for constituents in the hydrogen-nitrogen-methane system at 60 mole % methane in the liquid phase as a function of pressure for various temperatures.
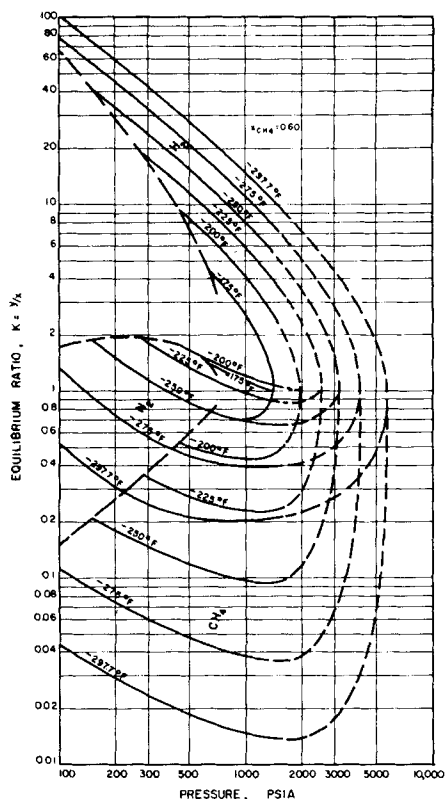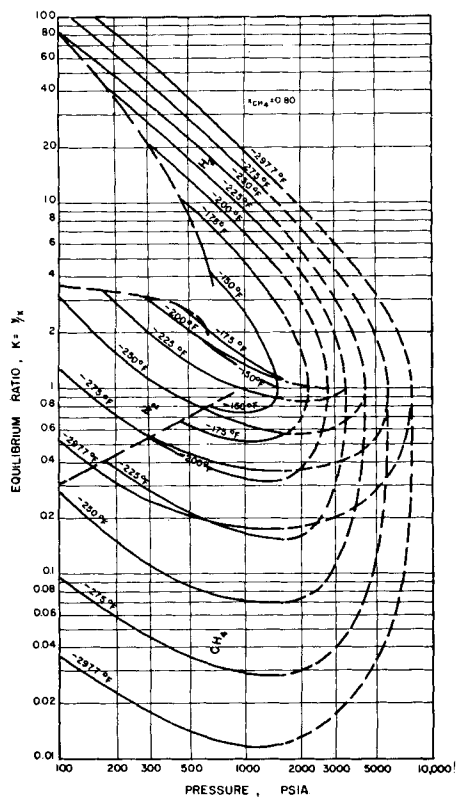

Fig. 5. Equilibrium ratios for constituents in the hydrogen-nitrogen-methane system at 80 mole % methane in the liquid phase as a function of pressure for various temperatures.

TABLE 3. EXPERIMENTAL DATA FOR THE NITROGEN-METHANE-ETHANE SYSTEM INCLUDING BINARY SYSTEM DATA FROM THE LITERATURE

Run or reference	Liquid-phase composition			Vapor-phase composition		
	Mole % N_2	Mole % CH_4	Mole % C_2H_6	Mole % N_2	Mole % CH_4	Mole % C_2H_6

Pressure = 500 lb./sq. in. abs.
Temperature = −100°F.

50	9.56	0.00	90.44	89.22	0.00	10.78
51	7.15	19.89	72.96	60.29	29.79	9.92
(4)*	0.00	66.00	34.00	0.00	93.00	7.00

Pressure = 1,000 lb./sq. in. abs.
Temperature = −100°F.

31	21.29	0.00	78.71	90.55	0.00	9.45
35	20.64	15.64	63.72	74.60	16.42	8.98
38	17.52	56.12	26.36	34.35	56.08	9.57

Pressure = 500 lb./sq. in. abs.
Temperature = −200°F.

32	18.26	0.00	81.74	99.23	0.00	0.766
33	24.03	25.25	50.72	88.10	11.31	0.593
34	35.06	44.99	19.95	79.75	19.79	0.463
(5)*	49.00	51.00	0.00	73.00	27.00	0.00
(6)*	50.90	49.10	0.00	75.20	24.80	0.00

*Data from literature.

TABLE 4. EXPERIMENTAL DATA FOR THE HYDROGEN-NITROGEN-METHANE SYSTEM INCLUDING BINARY SYSTEM DATA FROM THE LITERATURE

Run or reference	Liquid-phase composition			Vapor-phase composition		
	Mole % H_2	Mole % N_2	Mole % CH_4	Mole % H_2	Mole % N_2	Mole % CH_4

Pressure = 500 lb./sq. in. abs.
Temperature = −100°F.

(2)*	3.43	0.00	96.57	63.92	0.00	36.08
37	2.86	9.98	87.16	43.37	21.91	34.72
42	1.55	27.39	71.06	16.77	50.80	32.43
45	0.302	41.76	57.94	2.36	67.93	29.71
(5)*	0.00	49.00	51.00	0.00	73.00	27.00
(6)*	0.00	50.90	49.10	0.00	75.20	24.80

Pressure = 1,000 lb./sq. in. abs.
Temperature = −200°F.

(2)*	7.81	0.00	92.19	76.18	0.00	23.82
30	8.32	0.00	91.68	76.01	0.00	23.99
47	8.26	6.17	85.57	67.35	8.38	24.27
43	8.49	17.91	73.60	50.02	23.77	26.21
46	9.15	37.33	53.52	31.30	42.91	25.79
44	9.32	39.12	51.56	30.05	44.13	25.82
49	9.26	41.37	49.37	27.58	46.37	26.05
48	11.57	53.54	34.89	—	—	—

*Data from literature.

TABLE 5. EXPERIMENTAL DATA FOR THE HYDROGEN-NITROGEN-METHANE-ETHANE SYSTEM

| Run	52	53	54	55	56	57	58
Pressure, lb./sq. in. abs.	1000	1000	500	500	500	500	500
Temperature, °F.	−100	−100	−200	−200	−200	−200	−200
Liquid-phase H_2	0.296	1.46	0.462	0.626	0.698	0.743	0.882
N_2	18.80	14.10	12.15	9.73	7.95	7.05	6.33
composition, CH_4	8.52	7.91	8.80	8.73	8.41	8.44	8.48
mole % C_2H_6	72.39	76.53	78.59	80.91	82.95	83.77	84.31
Vapor-phase H_2	4.10	20.73	24.54	34.48	44.76	50.44	56.76
N_2	61.96	62.82	70.87	61.01	50.96	45.32	39.32
composition, CH_4	8.66	8.14	3.98	3.91	3.74	3.71	3.46
mole % C_2H_6	25.28	8.31	0.606	0.608	0.549	0.525	0.456
Equilibrium H_2	13.9	14.2	53.1	55.1	64.1	67.9	64.4
ratios N_2	3.30	4.46	5.83	6.27	6.41	6.43	6.21
CH_4	1.02	1.03	0.452	0.448	0.445	0.440	0.408
$K = y/x$ C_2H_6	0.349	0.109	0.00771	0.00751	0.00662	0.00627	0.00541
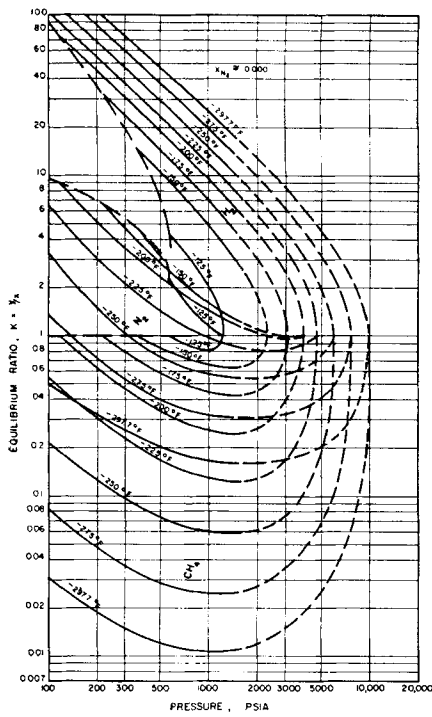
Fig. 6. Equilibrium ratios for constituents in the hydrogen-nitrogen-methane system at 0 mole % nitrogen in the liquid phase as a function of pressure for various temperatures.
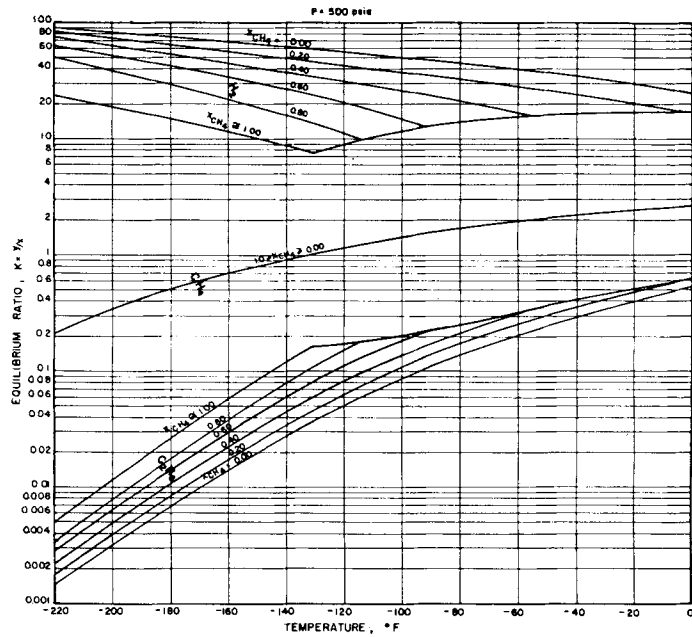
had been sufficient, these charts at constant temperature and pressure would have been a single curve of equilibrium ratio vs. composition. In this case the full number of variables indicated by the phase rule is required to correlate the phase behavior. Benham, Katz, and Williams (3) found a similar situation for a six-component system involving hydrogen and light hydrocarbons.

Fig. 8. Equilibrium ratios for constituents in the hydrogen-methane-ethane system at 500 lb./sq. in. abs. as a function of temperature with varying amounts of methane in the liquid phase.
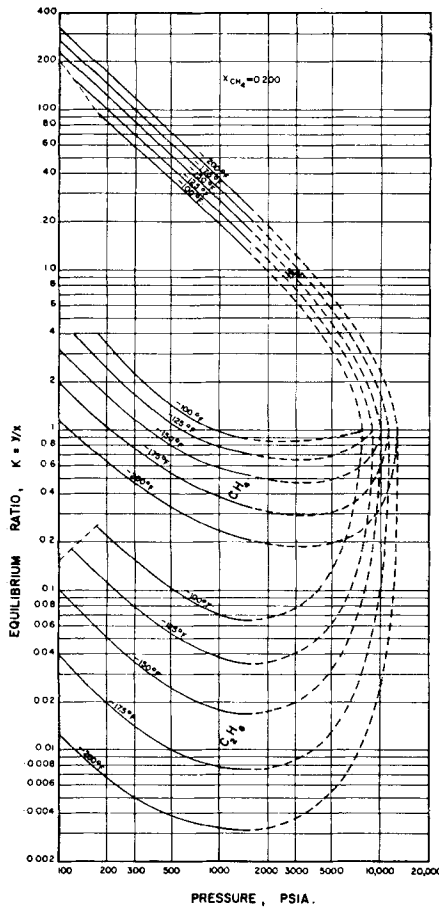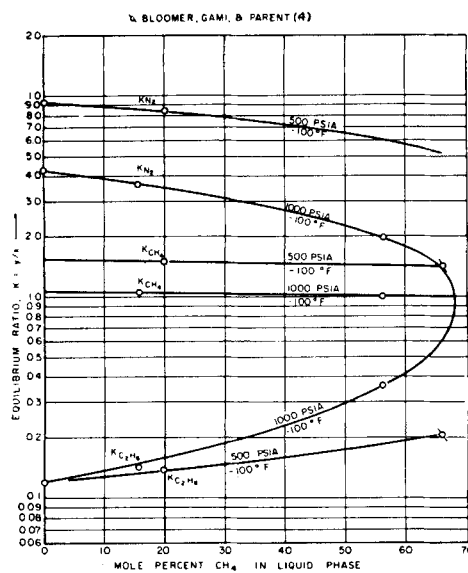

Fig. 7. Equilibrium ratios for constituents in the hydrogen-methane-ethane system at 20 mole % methane in the liquid phase as a function of pressure for various temperatures.
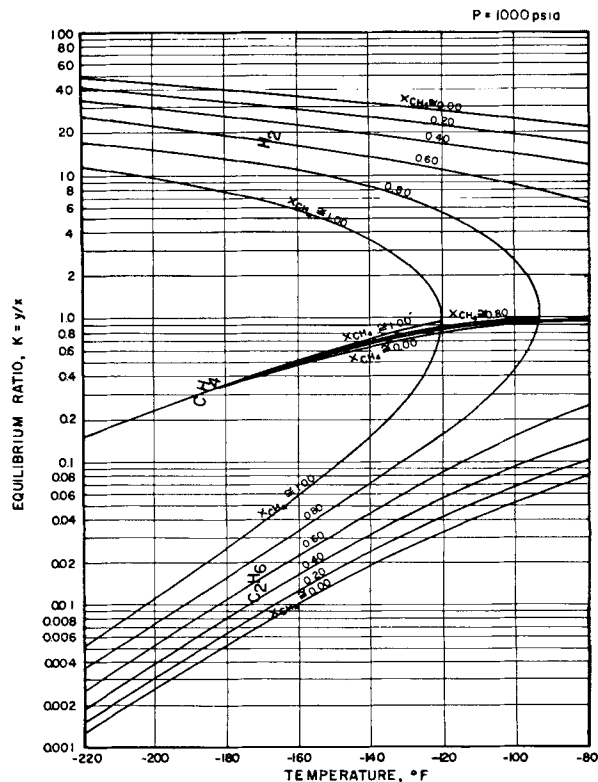
Fig. 9. Equilibrium ratios for constituents in the hydrogen-methane-ethane system at 1,000 lb./sq. in. abs. as a function of temperature with varying amounts of methane in the liquid phase.

Fig. 10. Equilibrium ratios for constituents in the nitrogen-methane-ethane system at −100°F. as a function of the mole percentage of methane in the liquid phase.

ACKNOWLEDGMENT
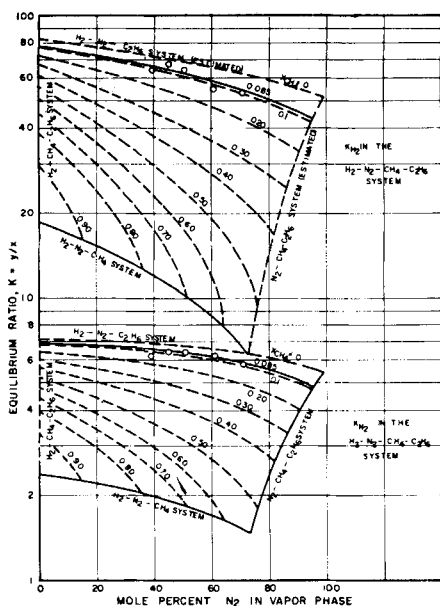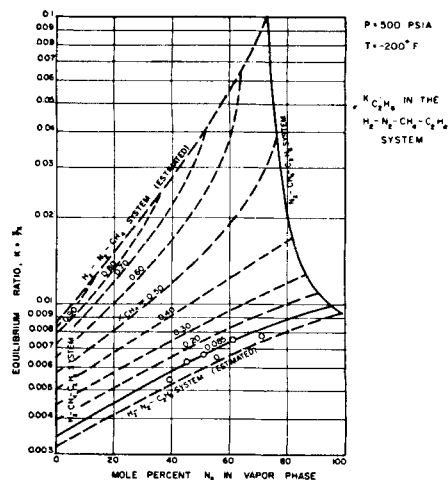
Fig. 12. Equilibrium ratios for hydrogen and nitrogen in the hydrogen-nitrogen-methane-ethane quaternary system at 500 lb./sq. in. abs. and −200°F. as a function of the mole percentage of nitrogen in the vapor phase with varying amounts of methane in the liquid phase.

LITERATURE CITED
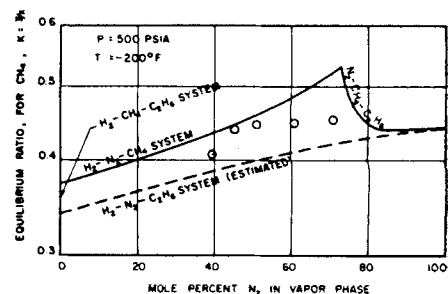
1. Aroyan, H. J., and D. L. Katz, *Ind. Eng. Chem.*, **43**, 185 (1951).

Fig. 13. Equilibrium ratios for ethane in the hydrogen-nitrogen-methane-ethane quaternary system at 500 lb./sq. in. abs. and −200°F. as a function of the mole percentage of nitrogen in the vapor phase with varying amounts of methane in the liquid phase.

Fig. 14. Equilibrium ratios for methane in the hydrogen-nitrogen-methane-ethane quaternary system at 500 lb./sq. in. abs. and −200°F. as a function of the mole percentage of nitrogen in the vapor phase.
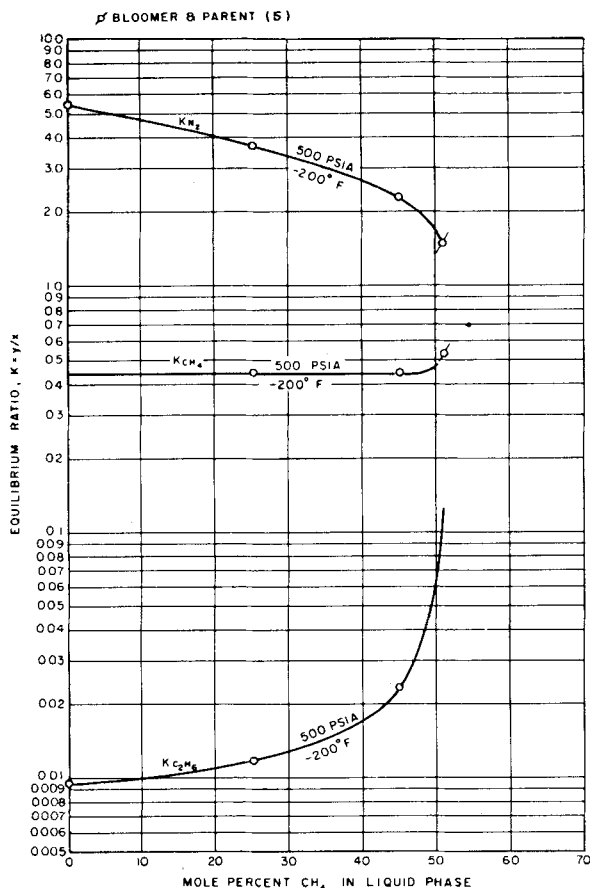
2. Benham, A. L., and D. L. Katz, *A.I.Ch.E. Journal*, **3**, 33 (1957).
3. ———, and R. B. Williams, *ibid.*, p. 236.
4. Bloomer, O. T., D. C. Gami, and J. D. Parent, *Inst. Gas. Tech. Res. Bull.* **22**, p. 1 (1953).
5. Bloomer, O. T., and J. D. Parent, *Chem. Eng. Progr. Symposium Ser.* No. 6, **49**, p. 11 (1953).
6. Cines, M. R., J. T. Roach, R. J. Hogan, and C. H. Roland, *ibid.*, p. 1.
7. Gonikberg, M. G., V. G. Fastowsky, and I. G. Gurwitsch, *Acta Physicochim. U.S.S.R.*, **11**, 865 (1939).
8. Levitskaya, E. P., *J. Tech. Phys. (U.S.S.R.)*, **11**, 197 (1941).
9. Ruhemann, M., and N. M. Zinn, *Physik. Z. Sowjetunion*, **12**, 389 (1937).
10. Steckel, F. A., and N. M. Zinn, *J. Chem. Ind. (U.S.S.R.)*, **16**, 24 (1939).
11. Verschoyle, T. T. H., *Trans. Roy. Soc. (London)*, **230A**, 189 (1931).
12. Williams, R. B., and D. L. Katz, *Ind. Eng. Chem.*, **46**, 2512 (1954).

Fig. 11. Equilibrium ratios for constituents in the nitrogen-methane-ethane system at −200°F. as a function of the mole percentage of methane in the liquid phase.