Isothermal equilibrium constants for helium are shown as functions of pressure in Figure 6. For a given pressure, the *K* value for helium is greatest at the lowest temperature. For any given isotherm, the *K* values increase with decreasing pressure.

This study represents a more thorough investigation than previously reported (*3, 5, 7, 8, 10*) on the helium-nitrogen system at temperatures from 76.5° to 120° K. and pressures up to 2000 p.s.i.a. The average reproducibility of all vapor phase data was within ±0.13 mole %. The corresponding value for the liquid phase was within ±0.07 mole %.

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RECEIVED for review December 18, 1962. Accepted May 13, 1963.

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# Vapor-Liquid Equilibria in a Natural Gas-Condensate-Nitrogen System

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**This paper describes an experimental investigation on the effect of nitrogen on the vapor-liquid equilibrium ratios of hydrocarbons in the natural gas-condensate system. Experimental work was carried out under constant temperature conditions at 100° F. and 220° F. At each temperature, experiments were conducted at pressures of 500, 1000, 1500, 2000, and 3000 p.s.i.a. Nitrogen concentration in the vapor phase was varied from 10% to 50% at each percentage. The equilibrium constants for hydrocarbons and for nitrogen are shown.**

THIS PAPER describes an experimental investigation on the effect of nitrogen on the vapor-liquid equilibrium ratios of the hydrocarbons in a natural gas-condensate system. Nitrogen is often found in appreciable concentrations in petroleum fluids, either as a natural occurrence or as a result of the application of secondary recovery techniques.

*K*-values for complex hydrocarbon systems have been reported in the literature (*7, 16*). Poettman (*11*), and Poettman and Katz (*12*) have reported *K*-values for $CO_2$ in similar hydrocarbon systems. Jacoby and Rzasa (*6*) list *K*-values for nitrogen, methane, $CO_2$, ethane and hydrogen sulfide in mixtures of all these components in heavier hydrocarbons. Eilerts and coworkers (*3*) have published a report on the effect of nitrogen and other gases and light hydrocarbons on the phase-boundary pressures of complex systems. In addition several binary systems of various hydrocarbons with nitrogen have been investigated (*1, 2, 14*) as well as the ternary system *n*-butane-methane-nitrogen (*15*).

## EXPERIMENTAL

The experimental work was carried out under constant temperature conditions at 100° F. and at 220° F. At each temperature, experiments were conducted at pressures of 500, 1000, 1500, 2000 and 3000 p.s.i.a. The nitrogen concentration in the vapor phase was varied from 10% to 50% at each pressure.

The fluids were brought to equilibrium in a 35-ml. windowed stainless steel cell. In order to attain equilibrium the vapor was circulated from the top of the cell through a magnetic-piston pump and into the bottom of the cell so that it bubbled up through the liquid layer.

The equilibrium phases at each different set of conditions of temperature, pressure and composition were sampled and analyzed in a Beckman Thermotrac temperature programmer. The samples were withdrawn from the equilibrium cell into stainless steel high pressure tubing which was connected to the cell. Pressure in the equilibrium cell was maintained constant by injecting mercury into the bottom of the cell during the sampling procedure.

Finally each sample was allowed to expand into a glass flask. The size of each sample was regulated so that the pressure in the flask was 10 to 20 cm. of Hg. In addition

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the entire sampling apparatus was maintained at elevated temperatures. The sample introduction system of the temperature programmer was also kept at elevated temperatures. The chromatographic columns were 12 foot lenghts of ¼-inch aluminum tubing packed with Silicone SE-30 impregnated fire brick.

A detailed description of the equilibrium, sampling and analytical apparatus, the experimental procedures and the analytical calculations are available (*13*).

## RESULTS

The experimental and analytical data are shown in Tables I and II. The *K*-values calculated directly from the analytical data are presented in Table III.

Figures 1 and 2 show the variation of the equilibrium ratio of methane with pressure and increasing concentration of nitrogen for the different temperatures. Figures 3, 4, 5, and 6 show the *K*-values for *iso*- and *n*-butane plotted *vs.*

Table I. Experimental Data for the Complex System at 100° F.

| Sample No. | Pressure, P.S.I.A. | Mole Per Cent of Components | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $N_2$ | $C_1$ | $C_2$ | $C_3$ | *iso*-$C_4$ | *n*-$C_4$ | *iso*-$C_5$ | *n*-$C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$+ |
| 37V | 539 | 63.30 | 32.11 | 3.41 | 0.72 | 0.16 | 0.17 | 0.08 | 0.05 | ... | ... | ... | ... |
| 37L | | 13.31 | 5.07 | 1.87 | 2.25 | 0.70 | 1.48 | 1.45 | 1.73 | 4.45 | 10.06 | 14.27 | 43.36 |
| 38V | 507 | 47.04 | 47.31 | 4.38 | 0.81 | 0.16 | 0.14 | 0.10 | 0.06 | ... | ... | ... | ... |
| 38L | | 8.15 | 9.74 | 2.48 | 2.35 | 0.68 | 1.45 | 1.57 | 1.61 | 4.46 | 10.41 | 14.09 | 42.83 |
| 39V | 1040 | 40.13 | 54.30 | 4.36 | 0.80 | 0.11 | 0.15 | 0.08 | 0.07 | ... | ... | ... | ... |
| 39L | | 22.30 | 16.39 | 3.32 | 2.82 | 0.71 | 1.50 | 1.02 | 1.22 | 3.39 | 7.11 | 10.02 | 30.47 |
| 40V | 509 | 14.40 | 81.21 | 2.66 | 1.17 | 0.21 | 0.26 | 0.09 | ... | ... | ... | ... | ... |
| 40L | | 5.72 | 13.74 | 2.89 | 2.65 | 0.88 | 1.53 | 1.58 | 1.59 | 4.59 | 9.59 | 13.68 | 41.56 |
| 41V | 1038 | 13.94 | 79.89 | 4.73 | 0.98 | 0.18 | 0.15 | 0.06 | 0.07 | ... | ... | ... | ... |
| 41L | | 16.32 | 24.02 | 4.38 | 3.24 | 0.76 | 1.56 | 1.20 | 1.39 | 3.34 | 6.93 | 9.12 | 27.74 |
| 43V | 1555 | 19.09 | 74.10 | 5.23 | 0.95 | 0.22 | 0.23 | 0.11 | 0.06 | ... | ... | ... | ... |
| 43L | | 19.06 | 29.78 | 4.60 | 3.34 | 0.74 | 1.44 | 1.12 | 1.21 | 2.85 | 5.60 | 7.49 | 22.77 |
| 45V | 1487 | 24.66 | 69.19 | 4.53 | 1.04 | 0.17 | 0.26 | 0.05 | 0.10 | ... | ... | ... | ... |
| 45L | | 19.16 | 21.15 | 4.58 | 4.15 | 0.66 | 2.23 | 1.11 | 1.39 | 3.03 | 6.39 | 8.95 | 27.20 |
| 46V | 1050 | 24.15 | 69.54 | 4.86 | 0.94 | 0.19 | 0.21 | 0.08 | 0.03 | ... | ... | ... | ... |
| 46L | | 16.66 | 18.46 | 4.09 | 3.13 | 0.74 | 1.66 | 0.95 | 1.11 | 3.16 | 7.00 | 10.65 | 32.39 |
| 48V | 1507 | 48.03 | 46.69 | 4.30 | 0.77 | 0.11 | 0.06 | 0.03 | 0.01 | ... | ... | ... | ... |
| 48L | | 7.64 | 16.66 | 4.22 | 2.63 | 0.88 | 1.74 | 1.66 | 1.44 | 4.46 | 9.01 | 12.29 | 37.36 |
| 49V | 1996 | 16.62 | 76.88 | 5.05 | 0.89 | 0.20 | 0.23 | 0.09 | 0.04 | ... | ... | ... | ... |
| 49L | | 2.76 | 34.11 | 4.46 | 2.33 | 0.72 | 1.05 | 1.02 | 1.03 | 2.63 | 6.57 | 10.72 | 32.60 |
| 50V | 2055 | 31.80 | 62.43 | 4.53 | 0.84 | 0.11 | 0.16 | 0.08 | 0.05 | ... | ... | ... | ... |
| 50L | | 4.95 | 30.95 | 4.87 | 2.60 | 0.90 | 1.26 | 1.19 | 1.17 | 3.37 | 6.60 | 10.43 | 31.71 |
| 51V | 2027 | 41.16 | 53.25 | 4.36 | 0.81 | 0.14 | 0.14 | 0.07 | 0.04 | 0.03 | ... | ... | ... |
| 51L | | 15.62 | 25.00 | 5.90 | 3.13 | 0.75 | 1.63 | 1.28 | 1.49 | 2.84 | 6.09 | 8.98 | 27.29 |
| 52V | 2542 | 22.51 | 70.36 | 4.81 | 1.01 | 0.21 | 0.21 | 0.11 | 0.09 | 0.16 | 0.19 | 0.08 | 0.26 |
| 52L | | 31.81 | 30.65 | 6.38 | 3.18 | 0.44 | 1.60 | 0.60 | 1.02 | 1.25 | 3.28 | 4.90 | 14.89 |
| 53V | 2910 | 44.98 | 48.76 | 4.68 | 0.99 | 0.16 | 0.17 | 0.11 | 0.15 | ... | ... | ... | ... |
| 53L | | 10.14 | 26.12 | 4.68 | 2.37 | 0.76 | 1.12 | 0.92 | 0.95 | 1.95 | 5.95 | 11.14 | 33.90 |

Table II. Experimental Data for the Complex System at 220° F.

| Sample No. | Pressure, P.S.I.A. | Mole Per Cent Components | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $N_2$ | $C_1$ | $C_2$ | $C_3$ | *iso*-$C_4$ | *n*-$C_4$ | *iso*-$C_5$ | *n*-$C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$+ |
| 18V | 2516 | 11.50 | 79.14 | 4.92 | 0.96 | 0.18 | 0.27 | 0.22 | 0.12 | 0.45 | 0.47 | 0.44 | 1.33 |
| 18L | | 28.27 | 35.26 | 6.95 | 3.10 | 0.30 | 1.56 | 0.46 | 0.78 | 1.55 | 3.34 | 4.56 | 13.87 |
| 19V | 1993 | 10.81 | 81.00 | 4.25 | 1.05 | 0.19 | 0.23 | 0.22 | 0.20 | 0.12 | 0.35 | 0.39 | 1.19 |
| 19L | | 34.29 | 31.39 | 6.24 | 2.95 | 0.41 | 1.35 | 0.51 | 0.77 | 1.31 | 3.24 | 4.34 | 13.19 |
| 21V | 1023 | 18.86 | 73.11 | 4.40 | 1.12 | 0.22 | 0.39 | 0.27 | 0.16 | 0.18 | 0.21 | 0.27 | 0.81 |
| 21L | | 8.07 | 23.32 | 3.54 | 2.36 | 0.59 | 1.32 | 1.22 | 1.34 | 3.54 | 7.99 | 11.56 | 35.15 |
| 22V | 505 | 9.09 | 80.06 | 4.98 | 1.22 | 0.28 | 0.44 | 0.29 | 0.27 | 0.54 | 0.72 | 0.52 | 1.59 |
| 22L | | 3.14 | 14.35 | 2.79 | 1.51 | 0.50 | 1.22 | 1.36 | 1.42 | 3.89 | 9.46 | 14.94 | 45.42 |
| 24V | 985 | 8.07 | 84.80 | 3.90 | 1.03 | 0.29 | 0.45 | 0.24 | 0.10 | 0.12 | 0.20 | 0.20 | 0.60 |
| 24L | | 13.77 | 27.60 | 4.61 | 2.45 | 0.61 | 1.56 | 1.25 | 1.31 | 3.32 | 6.83 | 9.08 | 27.61 |
| 26V | 1033 | 48.89 | 43.88 | 4.20 | 0.73 | 0.12 | 0.21 | 0.17 | 0.14 | 0.16 | 0.35 | 0.28 | 0.87 |
| 26L | | 54.34 | 11.69 | 3.80 | 2.69 | 0.23 | 1.62 | 0.41 | 0.89 | 1.30 | 3.04 | 4.95 | 15.04 |
| 27V | 1532 | 32.98 | 58.67 | 4.15 | 0.89 | 0.21 | 0.26 | 0.21 | 0.13 | 0.26 | 0.52 | 0.43 | 1.29 |
| 27L | | 5.99 | 25.51 | 2.78 | 1.93 | 0.73 | 1.45 | 1.60 | 1.47 | 3.92 | 8.32 | 11.46 | 34.84 |
| 28V | 1527 | 49.68 | 43.80 | 3.85 | 0.62 | 0.14 | 0.19 | 0.16 | 0.14 | 0.16 | 0.36 | 0.22 | 0.68 |
| 28L | | 8.02 | 17.14 | 1.79 | 1.40 | 0.53 | 1.04 | 1.37 | 1.37 | 4.07 | 9.31 | 13.36 | 40.60 |
| 29V | 1510 | 11.07 | 79.26 | 4.70 | 0.95 | 0.09 | 0.18 | 0.20 | 0.16 | 0.39 | 0.70 | 0.57 | 1.73 |
| 29L | | 13.81 | 29.60 | 4.88 | 2.17 | 0.48 | 1.09 | 0.99 | 1.05 | 3.02 | 6.42 | 9.03 | 27.46 |
| 30V | 2016 | 23.40 | 67.27 | 4.65 | 0.87 | 0.11 | 0.17 | 0.19 | 0.12 | 0.32 | 0.54 | 0.58 | 1.78 |
| 30L | | 6.37 | 33.54 | 3.29 | 1.90 | 0.47 | 0.92 | 0.96 | 0.97 | 2.90 | 7.10 | 10.29 | 31.29 |
| 31V | 2062 | 46.17 | 44.80 | 4.23 | 0.75 | 0.16 | 0.26 | 0.18 | 0.11 | 0.31 | 0.55 | 0.61 | 1.87 |
| 31L | | 43.79 | 18.99 | 4.53 | 2.77 | 0.25 | 1.46 | 0.46 | 0.83 | 1.68 | 3.24 | 5.45 | 16.55 |
| 32V | 3079 | 31.71 | 57.63 | 4.38 | 0.77 | 0.07 | 0.13 | 0.25 | 0.18 | 0.34 | 0.73 | 0.94 | 2.87 |
| 32L | | 12.41 | 41.27 | 5.11 | 1.80 | 0.44 | 0.81 | 0.85 | 0.80 | 2.38 | 5.32 | 7.13 | 21.68 |
| 33V | 3015 | 12.04 | 75.46 | 5.08 | 1.01 | 0.14 | 0.20 | 0.16 | 0.10 | 0.39 | 0.81 | 1.14 | 3.47 |
| 33L | | 4.19 | 54.55 | 4.67 | 2.13 | 0.39 | 0.56 | 0.75 | 0.60 | 1.64 | 4.38 | 6.47 | 19.37 |
| 35V | 499 | 32.41 | 55.44 | 5.81 | 1.39 | 0.32 | 0.41 | 0.22 | 0.19 | 0.36 | 0.64 | 0.68 | 2.05 |
| 35L | | 1.87 | 8.06 | 1.38 | 1.15 | 0.34 | 0.74 | 0.98 | 0.88 | 3.33 | 9.88 | 17.67 | 53.72 |
| 36V | 503 | 61.32 | 28.62 | 3.60 | 0.09 | 0.23 | 0.22 | 0.24 | 0.19 | 0.46 | 0.78 | 0.83 | 2.25 |
| 36L | | 5.47 | 6.48 | 1.55 | 1.42 | 0.54 | 0.75 | 1.19 | 1.19 | 4.60 | 11.36 | 16.20 | 49.25 |

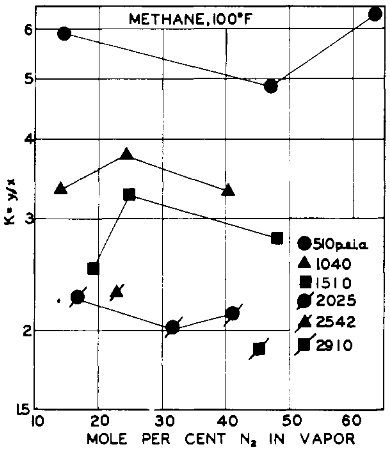

Figure 1. Effect of $N_2$ on $K$-values

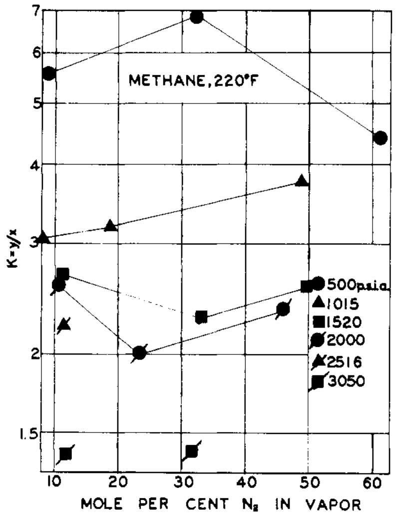

Figure 2. Effect of $N_2$ on $K$-values

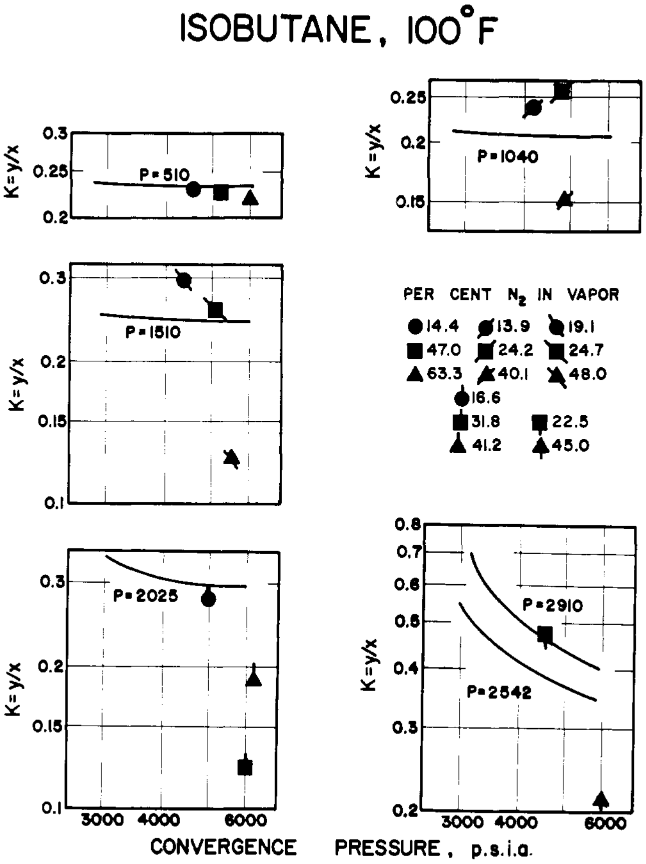

Figure 3. Experimental $K$-values compared to NGAA charts

Table III. Experimental Equilibrium Ratios for the Complex System

| Sample No. | E.P. P.S.I.A.[a] | $K$-Values at 220° F. | | | | | | | | | | | C.P. P.S.I.A.[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $N_2$ | $C_1$ | $C_2$ | $C_3$ | iso-$C_4$ | n-$C_4$ | iso-$C_5$ | n-$C_5$ | $C_6$ | $C_7$ | $C_8$ | |
| 18 | 2516 | 0.407 | 2.24 | 0.708 | 0.310 | 0.600 | 0.173 | 0.478 | 0.154 | 0.290 | 0.141 | 0.096 | 3510 |
| 19 | 1993 | 0.315 | 2.58 | 0.681 | 0.356 | 0.463 | 0.170 | 0.431 | 0.260 | 0.092 | 0.108 | 0.090 | 3260 |
| 21 | 1023 | 2.34 | 3.14 | 1.24 | 0.475 | 0.373 | 0.295 | 0.221 | 0.119 | 0.051 | 0.026 | 0.023 | 4170 |
| 22 | 505 | 2.89 | 5.58 | 1.78 | 0.808 | 0.560 | 0.360 | 0.213 | 0.190 | 0.139 | 0.076 | 0.035 | 3920 |
| 24 | 985 | 0.586 | 3.07 | 0.846 | 0.420 | 0.475 | 0.288 | 0.192 | 0.076 | 0.036 | 0.029 | 0.022 | 3950 |
| 26 | 1033 | 0.900 | 3.75 | 1.11 | 0.271 | 0.522 | 0.130 | 0.415 | 0.157 | 0.123 | 0.115 | 0.057 | 3700 |
| 27 | 1532 | 5.51 | 2.30 | 1.49 | 0.461 | 0.288 | 0.179 | 0.131 | 0.088 | 0.066 | 0.063 | 0.038 | 4550 |
| 28 | 1527 | 6.19 | 2.56 | 2.15 | 0.443 | 0.264 | 0.183 | 0.117 | 0.102 | 0.039 | 0.039 | 0.016 | 5900 |
| 29 | 1510 | 0.802 | 2.68 | 0.963 | 0.438 | 0.188 | 0.165 | 0.202 | 0.152 | 0.129 | 0.109 | 0.063 | 3570 |
| 30 | 2016 | 3.67 | 2.01 | 1.41 | 0.458 | 0.234 | 0.185 | 0.198 | 0.124 | 0.110 | 0.076 | 0.056 | 4075 |
| 31 | 2062 | 1.05 | 2.36 | 0.934 | 0.271 | 0.640 | 0.178 | 0.391 | 0.133 | 0.185 | 0.170 | 0.112 | 4400 |
| 32 | 3079 | 2.56 | 1.40 | 0.857 | 0.428 | 0.160 | 0.160 | 0.294 | 0.225 | 0.143 | 0.137 | 0.132 | 4175 |
| 33 | 3015 | 2.87 | 1.38 | 1.09 | 0.474 | 0.359 | 0.357 | 0.213 | 0.167 | 0.238 | 0.185 | 0.176 | 3825 |
| 35 | 499 | 17.33 | 6.88 | 4.21 | 1.21 | 0.941 | 0.554 | 0.224 | 0.216 | 0.108 | 0.065 | 0.038 | 4200 |
| 36 | 503 | 11.21 | 4.42 | 2.32 | 0.697 | 0.426 | 0.293 | 0.202 | 0.160 | 0.100 | 0.069 | 0.051 | 4950 |
| | | $K$-Values at 100° F. | | | | | | | | | | | |
| 37 | 539 | 4.76 | 6.33 | 1.82 | 0.320 | 0.229 | 0.115 | 0.055 | 0.029 | ... | ... | ... | 6000 |
| 38 | 507 | 5.77 | 4.86 | 1.77 | 0.345 | 0.235 | 0.097 | 0.064 | 0.037 | ... | ... | ... | 5170 |
| 39 | 1040 | 1.82 | 3.31 | 1.31 | 0.284 | 0.151 | 0.100 | 0.078 | 0.057 | ... | ... | ... | 4850 |
| 40 | 509 | 2.52 | 5.91 | 0.920 | 0.442 | 0.239 | 0.170 | 0.057 | ... | ... | ... | ... | 4530 |
| 41 | 1038 | 0.854 | 3.33 | 1.08 | 0.302 | 0.237 | 0.096 | 0.050 | 0.050 | ... | ... | ... | 4190 |
| 43 | 1555 | 1.00 | 2.49 | 1.14 | 0.284 | 0.297 | 0.160 | 0.098 | 0.050 | ... | ... | ... | 4340 |
| 45 | 1487 | 1.29 | 3.27 | 0.989 | 0.251 | 0.258 | 0.117 | 0.045 | 0.072 | ... | ... | ... | 5070 |
| 46 | 1050 | 1.45 | 3.77 | 1.19 | 0.300 | 0.257 | 0.127 | 0.084 | 0.027 | ... | ... | ... | 4775 |
| 48 | 1507 | 6.29 | 2.80 | 1.02 | 0.293 | 0.125 | 0.034 | 0.018 | 0.007 | ... | ... | ... | 5500 |
| 49 | 1996 | 6.02 | 2.25 | 1.13 | 0.382 | 0.278 | 0.219 | 0.088 | 0.039 | ... | ... | ... | 4965 |
| 50 | 2055 | 6.42 | 2.02 | 0.930 | 0.323 | 0.122 | 0.127 | 0.067 | 0.043 | ... | ... | ... | 5960 |
| 51 | 2027 | 2.64 | 2.13 | 0.739 | 0.259 | 0.187 | 0.086 | 0.055 | 0.027 | 0.011 | ... | ... | 6200 |
| 52 | 2542 | 0.708 | 2.30 | 0.754 | 0.318 | 0.477 | 0.131 | 0.183 | 0.088 | 0.128 | 0.058 | 0.016 | 4500 |
| 53 | 2910 | 4.44 | 1.87 | 1.00 | 0.418 | 0.211 | 0.152 | 0.120 | 0.158 | ... | ... | ... | 6000 |

[a] Equilibrium Pressure, P.S.I.A. [b] Convergence Pressure, P.S.I.A.

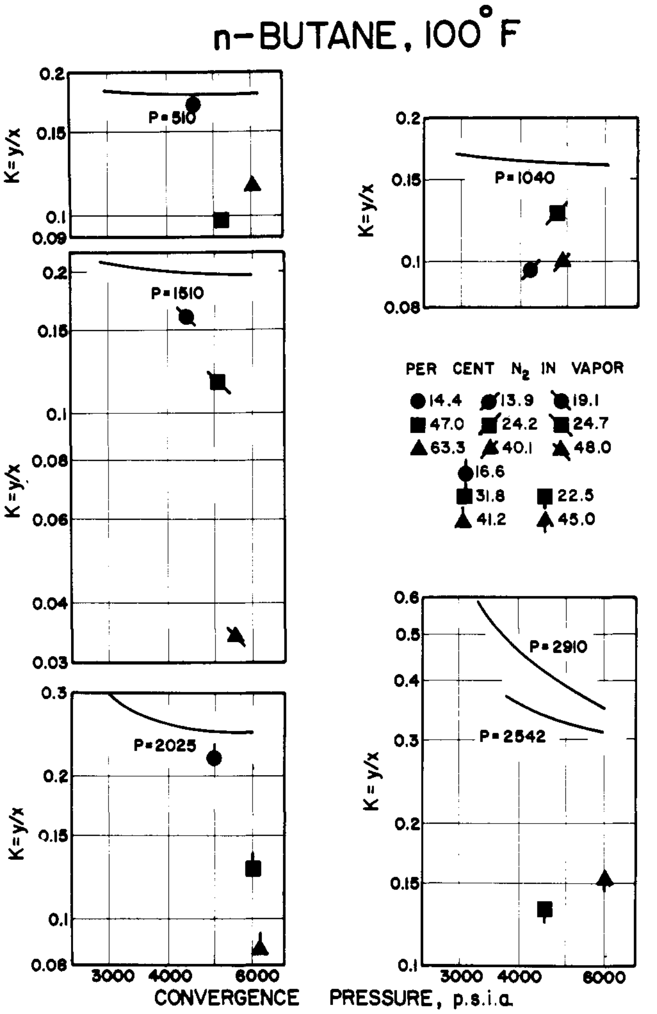

Figure 4. Experimental *K*-values compared to NGAA charts

convergence pressure at the varying pressure and temperature levels. Figures 7, 8, and 9 represent still another method, after Katz and Rzasa (*8*), for presenting *K*-value data of this type. Figure 7 and 8 show the effect of temperature upon the *K*-values of the hydrocarbon components, and Figure 9 shows the effect of increasing nitrogen concentration. Figures 10 and 11 are included to show the effect of pressure at constant nitrogen content.

## DISCUSSION

At the outset of the investigation it was necessary to establish a basis for comparison in order to demonstrate the effect of the different variables upon the *K*-values. The NGAA Charts (*4*) were a logical choice for this basis. Equilibrium data of the nitrogen-free hydrocarbon system were obtained in order to establish that the experimental data could be compared logically to the NGAA Charts. These experimental *K*-values are given in Table IV along with the values taken from the NGAA Charts. With the exception of two or three isolated discrepancies in the *K*-values of the hydrocarbons the comparisons were considered satisfactory.

The use of the NGAA Charts necessitated calculating the convergence pressure for every set of equilibrium fluids. These calculations imposed a problem, since the convergence pressure of a system containing large amounts

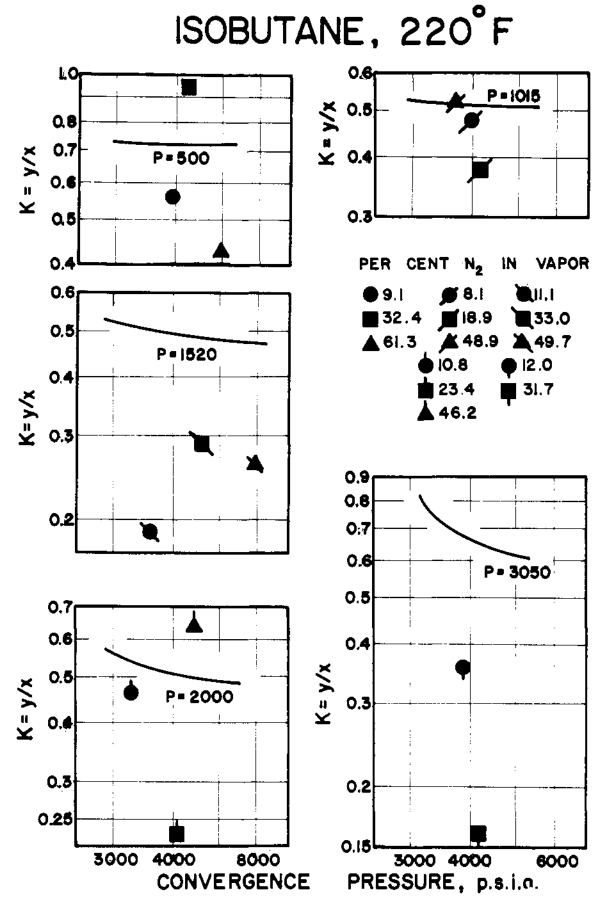

Figure 5. Experimental *K*-values compared to NGAA charts

Table IV. Comparison of Experimental and NGAA Data

| | *K*-Values at 100° F. | | *K*-Values at 220° F. | |
|---|---|---|---|---|
| Component | NGAA | Experimental | NGAA | Experimental |
| $C_1$ | 3.45 | 3.36 | 4.17 | 2.16 |
| $C_2$ | 0.875 | 1.49 | 1.61 | 1.58 |
| $C_3$ | 0.364 | 0.369 | 0.840 | 0.712 |
| *iso*-$C_4$ | 0.208 | 0.194 | 0.535 | 0.612 |
| *n*-$C_4$ | 0.165 | 0.167 | 0.443 | 0.511 |
| *iso*-$C_5$ | 0.088 | 0.042 | 0.277 | 0.275 |
| *n*-$C_5$ | 0.070 | 0.070 | 0.240 | 0.144 |
| $C_6$ | ... | ... | 0.126 | 0.087 |
| $C_7$ | ... | ... | 0.066 | 0.052 |
| $C_8$ | ... | ... | 0.033 | 0.024 |
| C.P.[a] | | 3500 | | 3695 |

[a] Convergence pressure.

Table V. Analyses of Natural Gas and Condensate

| Component | Gas Sample Mole % | Liquid Sample Mole % |
|---|---|---|
| $N_2$ | 0.08 | |
| $CO_2$ | 0.61 | |
| $C_1$ | 91.26 | 8.79 |
| $C_2$ | 4.88 | 3.43 |
| $C_3$ | 2.21 | 3.97 |
| *iso*-$C_4$ | 0.36 | 1.68 |
| *n*-$C_4$ | 0.42 | 2.39 |
| $C_5$+ | 0.18 | 79.74 |
| $C_5$ | ... | 5.20 |
| $C_6$ | ... | 7.10 |
| $C_7$+[a] | ... | 67.40 |

[a] Molecular weight, heptanes and heavier = 130, specific gravity, heptanes and heavies = 0.723.

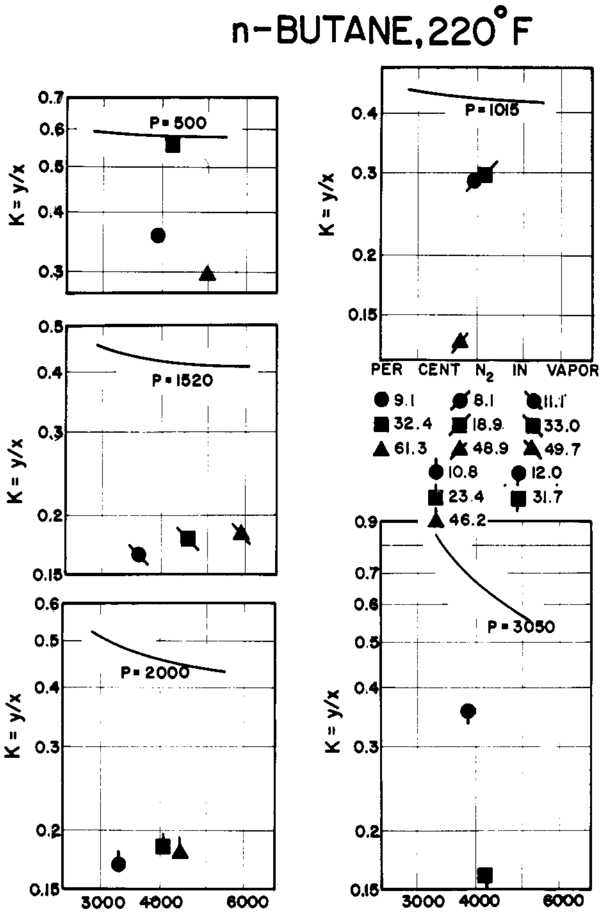

Figure 6. Experimental *K*-values compared to NGAA charts

of nitrogen and also large amounts of hydrocarbons heavier than decane is difficult to determine. The method of Organick and Brown (*10*) was used, although its use was not recommended for systems such as these. However, other methods which have been proposed (*5, 9*) did not seem to offer any advantages. Fortunately the NGAA *K*-values were relatively constant with respect to the convergence pressure for most of the samples.

Although the puzzling discrepancies present a disappointing feature of the data, several very interesting phenomena were observed. Generally speaking, the *K*-values of the hydrocarbons were lowered by the addition of nitrogen. This effect is more pronounced at 220° F. than at 100° F. Indeed it can be said in general that the effect upon the *K*-values of the other variables is more pronounced at the higher temperature. This effect can be observed in Figures 7 and 8. A nitrogen concentration of 8 mole per cent in the vapor at 220° F. causes a greater shift in the *K*-values than 40 per cent nitrogen does at 100° F.

Figure 9 shows the effect of increasing nitrogen concentration at constant temperature and pressure. The effect is much more pronounced for the heavier components. This difference of behavior of the different components is probably the same effect as observed in the ternary *n*-butane–methane–nitrogen system (*15*). The interactions, however, are without doubt much more complicated in the complex system.

Figure 10 shows the effect of pressure,and reflects the familiar pattern of the log *K vs.* log *P* graphs. The *K*-values for methane decreases steadily with pressure until it reaches unity at the convergence pressure. *K*-values for the other hydrocarbons decrease at the lower pressure levels but reverse this trend and also approach unity as the convergence pressure is approached. The actual behavior in the convergence pressure region is outside the scope of this work. Figure 11 presents this familiar method of plotting equilibrium ratio data.

In considering the data as shown in Figure 11, it must be kept in mind that each sample was from a system of a different composition. Thus each system had a different convergence pressure. Although many samples were from systems having similar convergence pressures, it is certain that some of the samples represent systems having widely different total compositions.

One very interesting phenomenon observed is that the addition of the nitrogen causes the butane isomers, and to a lesser extent the pentane isomers, to be preferentially separated between the two phases. It can be noticed in Figures 3, 4, 5, 6, and 9 and also in Table III that the *K*-values for the normal isomers decrease much more sharply in the presence of nitrogen than do the *K*-values of the *iso*-isomers. This effect seems to be influenced by temperature and pressure.

In conclusion it must be pointed out that these data should be regarded as preliminary. The general agreement

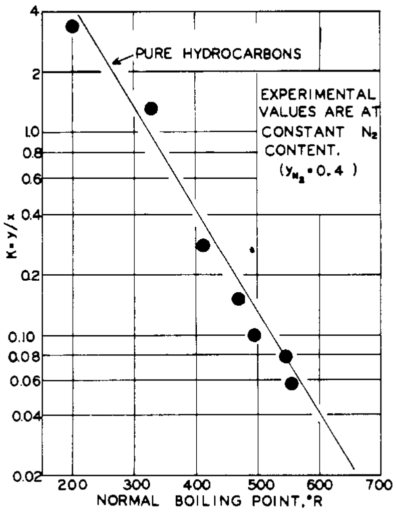

Figure 7. *K*-values at 100° F., 1030 p.s.i.a.

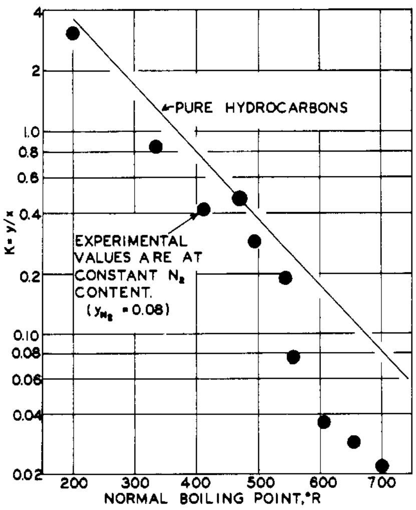

Figure 8. *K*-values at 220° F., 975 p.s.i.a.

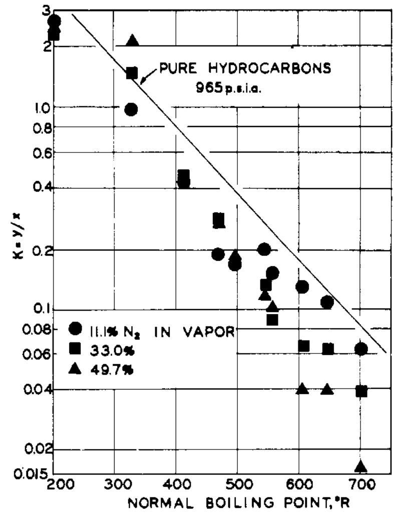

Figure 9. *K*-values at 220° F., 1520 p.s.i.a.

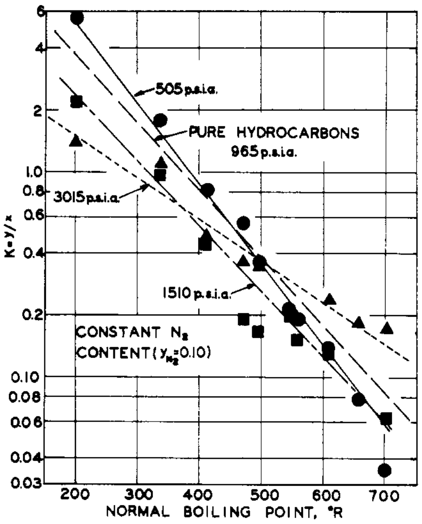

Figure 10. *K*-values at 220° F.

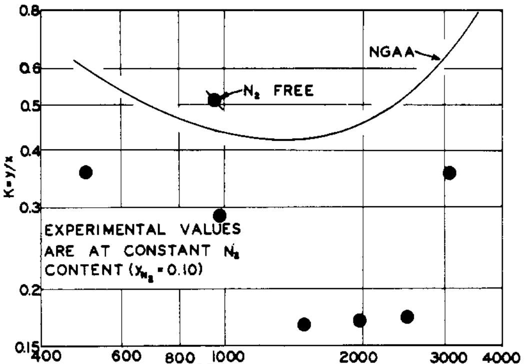

Figure 11. *n*-Butane *K*-values at 220° F.

with published data for the hydrocarbons is encouraging. The *K*-values for the nitrogen are the ones most puzzling. Although this work indicates that nitrogen *K*-values are not predictable, one does not expect these *K*-values to be lower than those for methane.

## MATERIALS USED

The natural gas and the condensate used in these experiments were supplied by the Marathon Oil Company. These were taken from a field separator at a gas condensate well from the League City Field, Texas. The materials were obtained at 390 p.s.i.g. and 86° F. at an estimated liquid-vapor ratio of 8 bbls./MMCF. The analysis furnished by the donor of the materials is shown in Table V. The vapor analysis was obtained by gas chromography and the liquid analysis by low-temperature fractionation. The molecular weight and specific gravity of the heptane and heavier fraction were 130 and 0.723 respectively.

The nitrogen used in the experiments was OP grade, which had a purity of 99.9 mole per cent.

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Received for review December 11, 1962. Accepted July 8, 1963. This project is sponsored by the National Science Foundation.