

Low-Temperature Vapor-Liquid Equilibria of Nitrogen-Methane System

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The vapor-recycle method was used to analyze equilibrium vapor and liquid samples for the nitrogen-methane system beginning at 5–47 psi above the methane saturation pressure up to the system critical pressure at nine temperatures: -130.00° , -140.00° , -150.00° , -170.00° , -190.00° , -210.45° , -230.00° , -240.00° , and -255.00°F . From nine to sixteen pressures were measured at each isotherm. In addition, two isotherms near the critical condition of nitrogen were measured at -232.42° and -235.50°F , with eight and seven points each within 43–65 psi of the system critical pressure. Analysis of the two isotherms taken near the critical of nitrogen gave a value of $\frac{1}{3}$ for the critical exponent β . An extrapolation of the K -values to -270°F is presented.

This investigation is part of a continuing program to provide basic data needed for gas processing. The nitrogen content plays an important role, for example, in the determination of the compression horsepower for LNG operation. The data presented here and in the companion paper (20) on the nitrogen-ethane system provide a basis for precise calculations.

The complete system includes nitrogen, methane, and ethane. The binary systems need to be known before the ternary systems are studied. The previous low-temperature investigation in this laboratory by Wichterle et al. (24, 28) on the CH_4 , C_2H_6 , C_3H_8 systems combined with Price and Kobayashi (15) and Bloomer et al. (7) defines the methane-ethane system from -225° up to 50°F .

Previous work N_2 - CH_4 . Several reports on this system are listed in Table I; however, the four earliest investigations up to 1939 were limited by the analytical technique of the time. The six most recent investigations covered only limited pressure regions of one or two isotherms each. This leaves only two investigations which covered the full pressure (above 1 atm) and temperature ranges below -125°F . The investigation of Bloomer and Parent (2, 3) at IGT was made with a bubble point-dew point apparatus. Such data are not best suited for extensive isothermal-isobaric evaluations. The second investigation by Cines et al. (8) used a vapor recycle apparatus; however, their data differ from those of Bloomer and Parent, especially at high pressure. There was also considerable high-pressure scatter in the data of Cines et al. The two isotherms at -150° and -240°F of Chang and Lu (6) both disagreed seriously with that of Cines et al.

Cheung and Wang (7) reported 20 equilibrium values (four points each at five temperatures) at low temperatures below -235°F . These scattered data, with mole fraction reported, for example, as 0.009, were not sufficiently accurate to define the systems.

Two recent reports from the Boulder laboratory of the National Bureau of Standards (13, 14) covered the region between the triple point of methane and the critical point

of nitrogen. Both studies were used to evaluate excess Gibbs free energy.

Experimental Equipment

The experimental apparatus was essentially the same as used in earlier studies at this laboratory (5, 24, 27). Only the minor, but significant, modifications made to adapt the apparatus for the present study will be reported here.

A complete description of the vapor-recycle apparatus is available (19), although most of the information is available in a recent article (27).

There was a problem of condensation in the sample lines in the bath fluid. Sample lines were $\frac{1}{16}$ -in. o.d. stainless-steel capillary lines. A system of fiberglass sleeves, resistance wire, thermocouples, and $\frac{3}{4}$ -in. o.d. Teflon tubes filled with powdered calcium silicate was installed to heat the sample lines as close as possible to the sample valves.

Gas chromatography was used for analysis because of its simplicity and accuracy. Briefly, the analytical unit consisted of a gas chromatograph with a thermal conductivity cell for the detector. Both liquid and vapor sample lines were connected to the sample valve of the chromatography unit. Helium was used as carrier gas, with optimal flow rates set by two micro metering valves. Parallel analytical and reference columns were used to give a more stable base line and a lower noise level (no more than 2–5 μV). The columns were made from 0.125-in. o.d. 316 stainless steel filled with 120–150 mesh Porapak-Q. A 14-in. column was used for the nitrogen-methane system.

A digital integrator recorded retention time and peak area. Visual observation of the peak shapes, separation, and base lines was made by a 1-mV pen recorder connected to the integrator. Occasionally, for checking purposes, base line and noise were recorded directly from the TC cell output.

The analytical system of sampling valve, columns, and TC cell was mounted in an air bath at ambient temperature. Room variation around 1 – 2°C in 24 hr did not influence the analytical accuracy, especially since the digital integrator included an automatic base line correction.

The wiring circuit was made according to the recommendations of the manufacturer of the TC cell with a small but important modification. The zero adjustment was changed from a 100- Ω ten-turn resistor to a 10- Ω ten-turn resistor with two fixed resistors. This gave a very stable base line, especially at an attenuation of 1.

The optimal helium flow rate was 16.8 cc/min for this investigation.

Procedure

The equilibrium cell was purged with nitrogen, the lightest component, and evacuated several times during the initial cooling down period.

The cell was charged with the components in order of decreasing normal boiling temperature. The recycle magnetic pump was used continuously during the charging procedure. The amount of the hydrocarbon was visually

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observed by the liquid level in the cell. The final addition of nitrogen was made by the vapor sample valve with the pressure monitored. Final fine pressure adjustment was made by adding nitrogen (occasionally methane) through the proportioning pump. The bath temperature was controlled at 0.01°C. After the initial 30-min mixing period, the rate of the magnetic pump was reduced to a minimum. The vapor-phase sample line was opened to a flow rate about 1 drop in 5 sec on the soap bubbler. After bleeding a small amount to eliminate the dead volume, multiple vapor-phase analyses were made. Typically, six analyses were made, but at times up to 10 were taken to obtain a better statistically averaged concentration.

The magnetic pump was then stopped for the liquid-phase analysis. A larger gas volume of the liquid phase had to be bled to purge the dead volume in the sample line and the mixer. The flow rate was 2 drops/sec on the soap flow meter. The liquid sample was manually mixed with a magnet to homogenize the evaporated sample. Four to six analyses were generally made; occasionally more.

Periodically, the vapor analysis was repeated after the liquid analysis. No change in vapor composition was observed. The pressure was recorded at the beginning of the analytical procedure. Total pressure drop during analysis was generally a few tenths of a psi.

In general, the average of the multiple analyses was taken as the measurement. Rarely, one analysis would be significantly high or low, and additional analyses would be made. After the analyses were made at the equilibrium pressure, more nitrogen was charged to the cell to reach the next higher pressure.

Procedure in critical region. An estimate was made of the critical pressure and critical composition. A slight excess of the heavier component was charged; then the lighter component was charged slowly while observing the liquid level in the cell. As the critical point was approached, to minimize gravitational effects, the liquid-vapor volume ratio was kept at 1:1 by withdrawal of small amounts of the liquid phase through the liquid sample line.

Materials used. The methane used in this investigation had a specified purity of 99.99%. The nitrogen was supplied by Matheson with a specified purity of 99.99% minimum. No further checks for purity over these supplier's specifications were made.

Error Analysis

In an investigation of vapor-liquid equilibria, the possible sources of error arise in the fundamental measurements for the K -value of pressure, temperature, and composition. The total absolute error is given by

$$\epsilon_K = \left| \left(\frac{\partial K}{\partial P} \right)_{T,x,y} \Delta P \right| + \left| \left(\frac{\partial K}{\partial T} \right)_{P,x,y} \Delta T \right| + \left| \left(\frac{\partial K}{\partial x} \right)_{T,P,y} \Delta x \right| + \left| \left(\frac{\partial K}{\partial y} \right)_{T,P,x} \Delta y \right| \quad (1)$$

Pressure error. The accuracy of the Heise gages is 0.1% of full scale. For pressures up to 400 psia, the error (ΔP) would be 0.4 psi; for the higher pressures the 2000-psi gage was used to give an error of 2 psi. At the lowest experimental pressures (40 psi), the relative error is 1%.

Examination of the log K -log P plots (Figures 1-3) shows that the slope is 45° for about 60-70% of the measurements. About 30% of the data occur at the minima where $(\partial K/\partial P) \approx 0$; the remaining 10% of the data are in the region of rapidly changing K with P ; i.e., P close to $P_{C_{mix}}$ and T above T_{CN_2} .

The error in the first region is approximately the error in reading the pressure; in the second region the error is close to zero; and in the third region the possible error can become quite large and even indeterminate.

Temperature error. The accuracy of the temperature measurement, T , was 0.01°C or 0.01%. From Figure 4, the sensitivity $(\partial K/\partial T)$ can be estimated. The slope of log K vs. $1/T$ is 45° or less for about 60% of the data and for the remainder the slope is about zero. The total error contribution from the temperature is less than 0.02% for the vast majority of the measurements, and the maximum error is estimated as 0.1%.

Table I. Previous Vapor-Liquid Investigations of Nitrogen-Methane System

Investigators	Year reported	Temperatures	Pressures	Method
McTaggart & Edwards (12)	1919	-306° to -268°F	1 atm	
Rysakov et al. (16)	1934	72.63 to 149.5K	0.5-10 atm	Isobaric
Torochesnikov & Levis (21)	1939	-295° to -220°F	Full isotherms	Vapor recycle
Vellinger & Pons (22)	1943	-183°C	Solubility study	
Bloomer & Parent (2, 3)	1952	-290° to -125°F	14.7-7000 psia	Dew-bubble point
Cines et al. (8)	1953	-280° to -150°F	Full isotherms	
Fastovskii & Petrovskii (10)	1957	-312° to -189°F	Below 16 atm	
Brandt & Stroud (4)	1958	-213° to -145°F	500 psia	
Sprow & Prausnitz (18)	1960	-284°F	Full isotherm	
Cheung & Wang (7)	1964	-296° to -236°F	Below 5 atm	
Chang & Lu (6)	1967	-151° & -240°F	Full isotherms	
Skripka et al. (17)	1970	-256°F	Full isotherm	
Miller et al. (13)	1973	112K	One isotherm	
Parrish & Hiza (14)	1973	95 to 120K	Six isotherms	

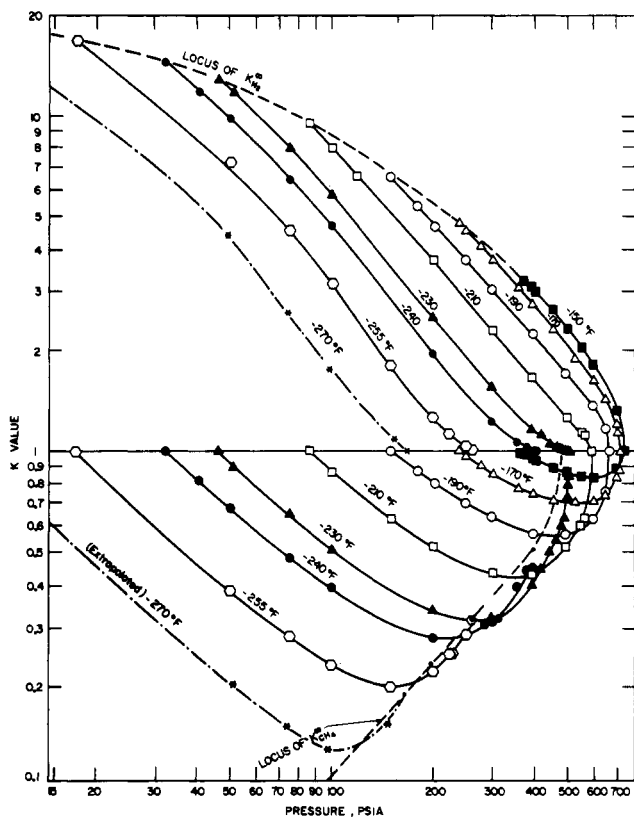


Figure 1. Isothermal equilibrium $K = y/x$ vs. pressure data for nitrogen-methane system

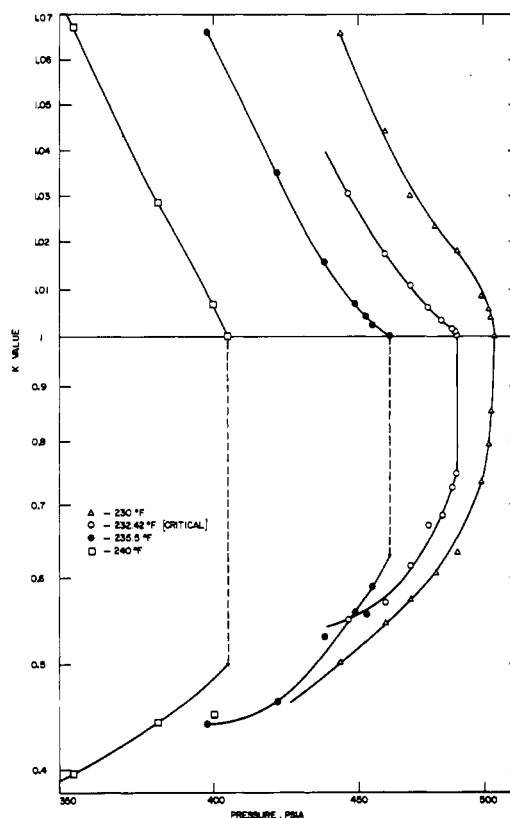


Figure 3. K -value vs. pressure for nitrogen-methane system near critical temperature of nitrogen on expanded scale

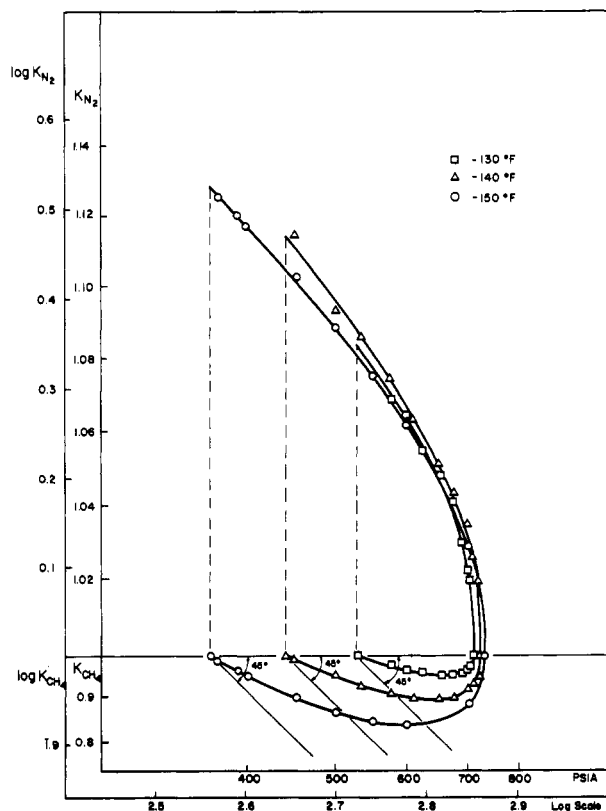


Figure 2. K -value vs. pressure for nitrogen-methane system near critical temperature of methane on expanded scale

Concentration error. The last two terms of Equation 1 gave the error owing to the measurement of the liquid and vapor concentrations, x and y . The reproducibility of the chromatographic analysis was 0.1–0.2% for mole fractions from 0.01 to 0.99.

The calibration of the chromatograph was made with samples prepared by weight. About 15 mixtures between 0.01 and 0.99 mole fraction were analyzed; the calculated rms was 0.6% in the f_{ij} factors. The f_{ij} is defined as the ratio of mole fractions to ratios of chromatograph areas. This error was minimized by repeated analyses (3–6) and by using average values in the calculations.

The total concentration error is estimated from 0.2 to 1% at the lowest concentrations. The total error is summarized in Table II.

The probability that all errors contribute in the same direction is small; statistically, the errors should tend to cancel since the probability of negative and positive error is equal. Therefore, the average total error in the K -values is probably less than 0.5%.

No evaluation could be made on any manual error from the manipulations of the experimenter.

Table II. Error Analysis

Due to	Av, %	Range, %
Pressure	0.5	0–1
Temperature	0.1	0–0.1
Concentration	0.5	0–1

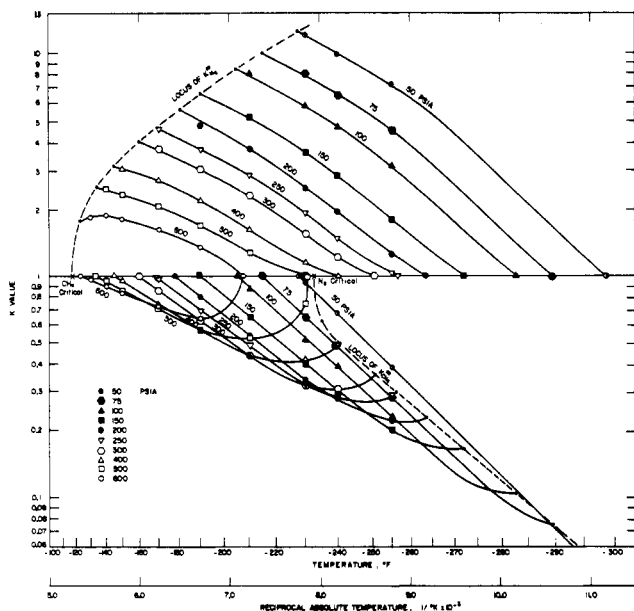


Figure 4. Isobaric K -values vs. temperature for nitrogen-methane system

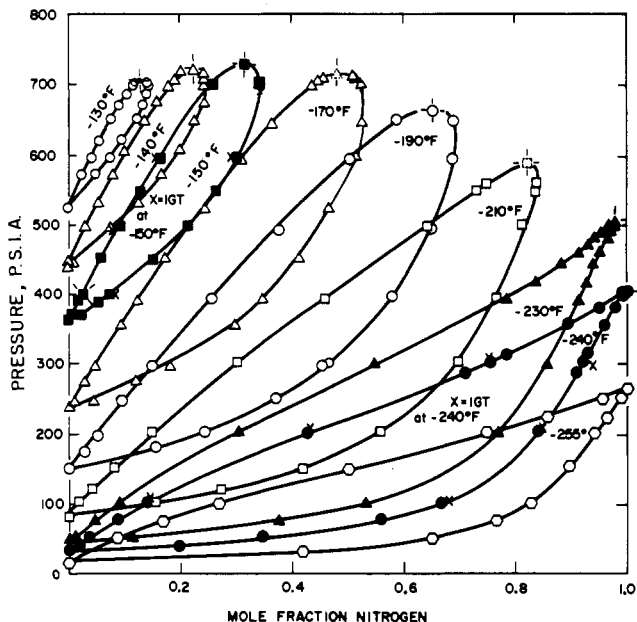


Figure 5. Pressure vs. composition (P - x,y) plot for nitrogen-methane system

Results

The experimental data are tabulated in Table III along with limiting extrapolated conditions and saturation conditions.

The experimental compositions were used to calculate the equilibrium K -values for each component where

$$K = y/x$$

These data were plotted on an extremely expanded scale (about 50 in. square) as $\log K$ vs. $\log P$ along isotherms. The vapor pressure of methane (23) provided the low-pressure limits of the system, where the methane K -value was 1.0000 and the nitrogen K^∞ was obtained by extrapolation.

The majority of the data are shown in Figure 1 as $\log K$ vs. $\log P$ along isotherms -150° , -170° , -190° , -210° , -230° , -240° , and -255°F . The -150°F isotherm is repeated with the data at -140° and -130°F on a larger scale in Figure 2. The increased deviation from a 45° line as the temperature increases toward the critical temperature of methane is evident. The data closely spaced about the critical of nitrogen are shown in Figure 3. These data exhibit the same qualitative features of the critical region as observed by Wichterle et al. (24-29).

The nitrogen K -value at each isotherm corresponding to the vapor pressure of methane at that temperature is obtained by extrapolation. These data are termed the K -values of nitrogen at infinite dilution in methane, $K(\text{N}_2(\text{CH}_4)^\infty)$. The smooth locus $K(\text{N}_2(\text{CH}_4)^\infty)$ is shown in Figure 1.

A cross plot of the data along isobars K vs. reciprocal temperature is shown in Figure 4. The smooth locus of $K(\text{N}_2(\text{CH}_4)^\infty)$ is again evident. Below the critical temperature of nitrogen, the vapor pressure of nitrogen is the limiting condition. Methane at these conditions is also shown in Figures 1 and 4 as $K(\text{CH}_4(\text{N}_2)^\infty)$.

After the preparation of Figure 4, values at -270°F were read and cross plotted onto Figure 1 to locate the curve labeled (Extrapolated) -270°F . The extrapolated values are given in Table IV. The data of Cheung and

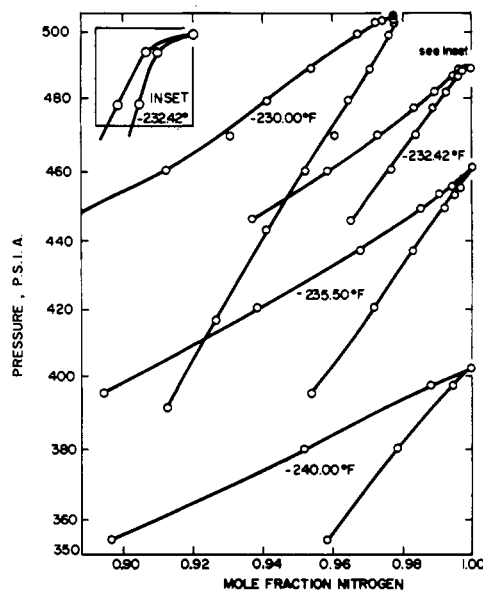


Figure 6. Pressure vs. composition (P - x,y) on expanded scale near nitrogen critical

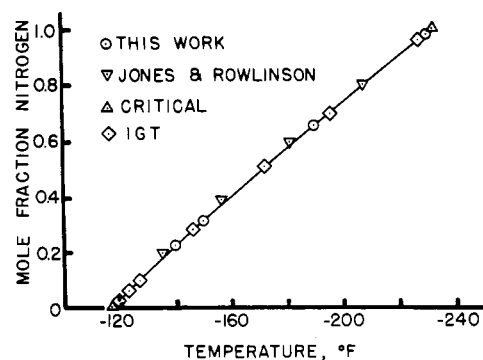


Figure 7. Critical composition-temperature locus for nitrogen-methane system showing comparison with other investigations

Table III. Experimental Data of Nitrogen–Methane System
More significant figures are given to avoid round-off error

Press, psia	Nitrogen mole fraction		K-values		Press, psia	Nitrogen mole fraction		K-values	
	Liquid	Vapor	N ₂	CH ₄		Liquid	Vapor	N ₂	CH ₄
$T = -130.00^{\circ}\text{F} = -90.00^{\circ}\text{C} = 183.15\text{K}$					$T = -210.45^{\circ}\text{F} = -134.71^{\circ}\text{C} = 138.44\text{K}$				
529 ^a	0.00000	0.00000	2.234 ^b	1.00000	86.4 ^a	0.00000	0.0000	9.55 ^b	1.0000
576	0.02544	0.04931	1.938	0.97551	100.25	0.01852	0.1499	8.094	0.8661
598	0.04160	0.07742	1.861	0.96263	119	0.04106	0.2724	6.634	0.7588
623	0.05676	0.09635	1.697	0.95803	150	0.08104	0.4183	5.162	0.6330
654	0.07848	0.1251	1.594	0.9494	200	0.1490	0.5568	3.737	0.5208
674	0.09106	0.1357	1.490	0.9509	300	0.3037	0.6983	2.299	0.4333
689	0.1060	0.1425	1.344	0.9592	392	0.4593	0.7677	1.671	0.4296
700	0.1165	0.1449	1.244	0.9679	498	0.6430	0.8146	1.267	0.5193
703	0.1175	0.1425	1.213	0.9717	548	0.7295	0.8367	1.147	0.6037
711 ^c	^d	^d	1.0000	1.0000	560	0.7466	0.8392	1.124	0.6346
					588.1 ^c	0.820 ^b	^d	1.000	1.0000
$T = -140.00^{\circ}\text{F} = -95.56^{\circ}\text{C} = 177.59\text{K}$					$T = -230.00^{\circ}\text{F} = -145.56^{\circ}\text{C} = 127.59\text{K}$				
441 ^a	0.000000	0.00000	2.95 ^b	1.00000	46.2 ^a	0.000000	0.0000	12.84 ^b	1.0000
450	0.004056	0.01200	2.959	0.99202	51.2	0.009745	0.1144	11.74	0.8943
500.5	0.03257	0.07937	2.437	0.95162	75.0	0.04714	0.3786	8.031	0.6521
534	0.05547	0.1266	2.282	0.92469	99.8	0.09116	0.5318	5.834	0.5096
574	0.08284	0.1693	2.044	0.90573	200	0.3040	0.7662	2.520	0.3359
609	0.1097	0.2023	1.844	0.8960	298	0.5475	0.8564	1.564	0.3173
650	0.1391	0.2286	1.643	0.8960	392	0.7825	0.9129	1.167	0.4005
676	0.1613	0.2459	1.524	0.8991	417	0.8353	0.9263	1.109	0.4473
700	0.1816	0.2495	1.374	0.9170	443	0.8822	0.94096	1.067	0.5012
709	0.1929	0.2488	1.290	0.9307	460	0.91223	0.95213	1.044	0.5454
720	0.2026	0.2458	1.213	0.9458	470	0.93085	0.96037	1.032	0.5731
722 ^c	0.2272	0.2272	1.000	1.0000	480	0.94122	0.96436	1.024	0.6063
					489	0.95404	0.97090	1.018	0.6329
					499	0.96737	0.97606	1.0090	0.7337
					502	0.97242	0.97809	1.0058	0.7944
					503	0.97407	0.97788	1.0039	0.8531
					504.5 ^c	0.97766	0.97766	1.0000	1.0000
$T = -150.00^{\circ}\text{F} = -101.11^{\circ}\text{C} = 172.04\text{K}$					$T = -232.42^{\circ}\text{F} = -147.10^{\circ}\text{C} = 126.25\text{K}$ (Critical of nitrogen)				
364 ^a	0.000000	0.00000	3.312 ^b	1.0000	446	0.93650	0.96511	1.0305	0.5494
370.5	0.005951	0.01938	3.257	0.9865	460	0.95840	0.97636	1.0187	0.5687
390	0.01689	0.05251	3.108	0.9638	470	0.97298	0.98340	1.0107	0.6144
401	0.02446	0.07397	3.024	0.9492	478	0.98330	0.98880	1.0056	0.6707
453	0.05764	0.1532	2.657	0.8986	482.5	0.98927	0.99250	1.0033	0.6990
500	0.09245	0.2157	2.333	0.8642	487	0.99466	0.99614	1.0015	0.7228
550	0.1287	0.2646	2.056	0.8440	488.5	0.99661	0.99747	1.000863	0.7463
598	0.1657	0.3009	1.816	0.8379	489 ^c	1.0000	1.0000	1.0000	1.0000
703	0.2599	0.3445	1.326	0.8857					
730 ^c	0.3156	0.3156	1.000	1.0000					
$T = -170.00^{\circ}\text{F} = -112.22^{\circ}\text{C} = 160.93\text{K}$					$T = -235.50^{\circ}\text{F} = -148.50^{\circ}\text{C} = 124.65\text{K}$				
239 ^a	0.000000	0.00000	4.864 ^b	1.00000	396	0.89406	0.95340	1.0664	0.4399
250	0.009750	0.04452	4.567	0.96489	420	0.93870	0.97170	1.0351	0.4617
276.5	0.02968	0.1221	4.114	0.90475	437	0.96766	0.98290	1.0157	0.5288
301	0.04895	0.1835	3.749	0.8585	449	0.98504	0.99165	1.0067	0.5582
358	0.09572	0.2986	3.112	0.7756	453	0.99052	0.99474	1.00426	0.5549
394.5	0.1257	0.3471	2.761	0.7468	455	0.99427	0.99663	1.00237	0.5881
455	0.1774	0.4130	2.328	0.7136	461 ^a	1.00000	1.00000	1.00000	0.628 ^b
526	0.2457	0.4671	1.901	0.7065					
598	0.3128	0.5131	1.640	0.7085					
647	0.3683	0.5284	1.435	0.7466					
701	0.4382	0.5296	1.209	0.8373					
709	0.4514	0.5181	1.148	0.8784					
710	0.4527	0.5178	1.144	0.8811					
718 ^c	0.486 ^b	^d	1.000	1.0000					
$T = -190.00^{\circ}\text{F} = -123.33^{\circ}\text{C} = 149.82\text{K}$					$T = -240.00^{\circ}\text{F} = -151.11^{\circ}\text{C} = 122.04\text{K}$				
149.5 ^a	0.00000	0.0000	6.745 ^b	1.0000	32.11 ^a	0.000000	0.00000	14.60 ^b	1.0000
179	0.02838	0.1529	5.388	0.8718	40.5	0.016538	0.19633	11.87	0.8172
202.5	0.05140	0.2404	4.677	0.8006	50.0	0.03514	0.3466	9.863	0.6772
249.5	0.09849	0.3683	3.739	0.7007	75.0	0.086024	0.5588	6.496	0.4827
299	0.1503	0.4579	3.047	0.6380	99.8	0.1411	0.6655	4.717	0.3895
300	^e	0.4615	^f	^f	200	0.4283	0.8411	1.964	0.2779
396.5	0.2579	0.5779	2.241	0.5688	284.75	0.7093	0.91093	1.284	0.3064
495	0.3778	0.6480	1.715	0.5657	300.25	0.7524	0.92247	1.226	0.3131
594	0.5034	0.6867	1.364	0.6309	311	0.7837	0.93085	1.188	0.3197
649	0.5866	0.6878	1.172	0.7552	354	0.8962	0.95888	1.067	0.3961
664 ^c	0.6528	0.6528	1.000	1.0000	380	0.95136	0.97851	1.0285	0.4418
					398.25	0.98804	0.99464	1.0066	0.4482
					403 ^a	1.0000	1.000000	1.000	0.4991 ^b

Table III. Continued

Press, psia	Nitrogen mole fraction		K-values	
	Liquid	Vapor	N ₂	CH ₄
$T = -255.00^{\circ}\text{F} = -159.44^{\circ}\text{C} = 113.71\text{K}$				
17.36 ^a	0.000	0.000	16.90 ^b	1.000
30.2	^c	0.4151	^d	^e
50.0	0.089407	0.6491	7.206	0.3854
75.0	0.1671	0.7660	4.584	0.2809
100	0.2609	0.8290	3.178	0.2314
149.5	0.4984	0.8990	1.804	0.2014
200.2	0.7495	0.94505	1.261	0.2194
199.5	0.7491	0.94428	1.261	0.2221
222.5	0.8580	0.96449	1.124	0.2500
250	0.95585	0.98739	1.033	0.2856
262 ^a	1.000	1.000	1.000	0.3076 ^b

^a Saturation conditions. ^b Extrapolated. ^c Critical conditions. ^d Critical composition not determined. ^e Experimental difficulty. ^f Liquid composition was not determined owing to change of nitrogen refrigeration. ^g Could not sample liquid phase at this low pressure.

Table IV. Extrapolated Data of Nitrogen-Methane System
 $T = -270^{\circ}\text{F}$

Press, psia	K-values	
	N ₂	CH ₄
8.5	19.1	1.00
50	4.36	0.206
75	2.590	0.150
100	1.760	0.128
150	1.080	0.154
169	1.00	0.191

Wang (7) at 40 psia and -271°F show excellent agreement with these extrapolated values.

An example of the liquid-vapor composition data is shown in Figure 5. It is evident that retrograde condensation occurs above -150°F up to the critical temperature of methane. Also shown on the figure is a comparison with the work of Bloomer and Parent (2, 3) at -150° and -240°F . More extensive comparisons are not feasible. Even for these, dew-bubble point data had to be interpolated over substantial temperature ranges.

Figure 6 shows, on an expanded scale, the pressure-composition behavior for the four isotherms near the critical temperature of nitrogen. The same "pinch" effect noted in the paraffin binaries (26) is evident. As analytical techniques improve, continuity in transition regions for equilibrium conditions becomes apparent. "Nature" is both systematic and reasonable.

Critical exponent. A rather stringent test of the data was made by evaluating the critical exponent β from the data in the critical region as had been done on the paraffin hydrocarbon binaries (25, 29). A value ca. $\frac{1}{3}$ was obtained; this evaluation utilized pressure and composition differences, which indicates the reliability of the data. An experiment for accurate determination of critical exponents from vapor-liquid equilibria would require specially

designed equipment with much better pressure measurements.

An additional comparison is shown in Figure 7 for the critical temperature vs. critical composition. Our data are consistent with the dew point-bubble point data of IGT (9). A considerable disparity is evident with the data of Jones and Rowlinson (11), who observed critical conditions by slowly warming sealed glass tubes. A note in their article in the preparation of the sample states, "if nitrogen was not one of the components" for estimating residual quantities in the gas manifold. Evidently (from Figure 7), this led to a greater error in composition than their estimate of 0.002 in mole fraction.

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