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

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Experimental data at −110°, −150°, −190°, and −210°F are reported for the nitrogen-ethane system over the entire concentration range. Considerable experimental difficulty occurred for vapor-phase ethane concentrations less than 0.001 mole fraction at the lowest temperature.

Lower and lower temperatures are becoming necessary in the processing and operations of the gas industry. The increased cost of low-temperature facilities and operation has laid increased emphasis on the precision and validity of the basic data which govern low-temperature processes. This investigation was undertaken to provide highly accurate vapor-liquid equilibrium data for effecting removal of nitrogen by distillation from natural gas and to provide basic data for the design of LNG liquefaction cycles.

The first system investigated was the binary nitrogen–methane system (*5*). The ternary system was then investigated, and it was found that the binary data on nitrogen–ethane were insufficient; the binary nitrogen–ethane system was then investigated at four temperatures. Finally, measurements were made on the ternary nitrogen–methane-ethane at −190°F and 100 psia.

The data on the nitrogen–methane system were reported (*5*). The data on the ternary at −190° and −210°F are available in the monograph (*4*), but these data will not be published in the periodical literature until additional investigations can be made with improved equilibrium and analytical equipment.

Previous Work

Three earlier investigations are listed in Table I. Eakin et al. (*3*) used a bubble point-dew point apparatus for a wide range of investigations up to 1850 psi. Chang and Lu (*2*) reported two isotherms measured with the vapor recycle method. Their vapor-phase concentrations of ethane at −150°F are two to three times that obtained by Eakin et al. Both Eakin et al. and Chang and Lu observed two liquid phases at −240°F and lower temperatures. Some scattered data below −220°F were reported by Yu et al. (*6*).

Apparatus

The equipment was the same as for the nitrogen–methane system (*5*) with minor changes.

Ethane was charged directly to the cell from the high-pressure storage cylinder. For the ethane and ternary investigations, it was found necessary to modify the valving on the equilibrium cell so that nitrogen could be charged directly through the vapor sample line to remove traces of ethane. The vapor sample line was a horizontal bore in the side of the equilibrium cell; during the preliminary ethane investigation, the analyses gave much too high values for the ethane concentration in the vapor phase which decreased with time. The change in the valving for charging the system helped to solve this problem, but an additional change had to be made in the capillary sample line for the vapor phase which extended into the center of the cell. The vapor sample line originally had a dead volume of about 0.1 cc; this was decreased to about 0.003 cc by inserting a fine capillary tube of 0.007 in. i.d. into the $^1/_{16}$-in. capillary vapor sample line.

The analytical chromatograph column was 11 ft long as compared to 14 in. for the nitrogen–methane system.

The experimental method was the same as for the nitrogen–methane system, but there was much difficulty in obtaining the ethane in the vapor phase. For the ethane vapor analysis, the final vapor analysis was used, since a trace of liquid in the vapor sample line to the cell would require considerable time to eliminate with the vapor sample. This problem required redesign of the cell and has been incorporated in a new vapor liquid equilibrium apparatus now in use for methane–heavy hydrocarbon investigations.

Materials Used

The ethane 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

The error analysis is the same as reported previously. The larger error of 1% in the concentration applies here for ethane concentrations less than 1%.

Results

Four isotherms, at −110.00°, −150.00°, −190.00°, and −210.00°F, were investigated for the nitrogen–ethane system. The data are tabulated in Table II. No lower temperatures could be investigated with the present equipment owing to limitations in the sampling system and in the analytical system for determining the vapor concentration of ethane. Considerable experimental problems arose at low (less than 1%) ethane concentrations; these have been considered in the design and construction of a new equilibrium apparatus. Suitable modifications to the analytical train along with the new equilibrium unit should enable investigations in the lower temperature region to be made. Note that Table II at −190°F includes smoothed values for the two highest pressures.

The experimental data were plotted on expanded scales as log *K* vs. log *P* (Figure 1), as liquid-vapor com-

Table I. Previous Vapor-Liquid Investigations of Nitrogen–Ethane System

Investigators	Year reported	Temp, °F	Pressures
Eakin et al. (*3*)	1955	−300 to 90	50–1850 psia
Chang & Lu (*2*)	1967	−151 & −240	Full isotherms
Yu et al. (*6*)	1969	−255 to −220	260–591 psia

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Table II. Experimental Data of Nitrogen-Ethane System

More significant figures are given to avoid round-off error

Press, psia	Nitrogen mole fraction		K-values	
	Liquid	Vapor	N_2	C_2H_6
$T = -110.00°F = -78.89°C = 194.26K$				
25.4[a]	0.000000	0.0000	165.[b]	1.0000
51.0	0.005715	0.4862	85.06	0.5168
100.3	0.01612	0.7146	44.32	0.2901
200	0.03722	0.8360	22.46	0.1704
400	0.08081	0.8966	11.09	0.1125
602	0.1273	0.9126	7.168	0.1002
808	0.1756	0.9154	5.215	0.1026
1002	0.2225	0.9126	4.103	0.1123
1302	0.3024	0.8977	2.968	0.1467
1415	0.3338	0.8885	2.662	0.1673
1744	0.4534	0.8355	1.843	0.3009
1760	0.4577	0.8304	1.815	0.3127
1898	0.5510	0.7714	1.400	0.5091
1946	0.6472	0.7144	1.1039	0.8093
1953[c]	0.6746	0.6746	1.0000	1.0000
$T = -150.00°F = -101.11°C = 172.04K$				
7.0[a]	0.00000	0.0000	565.[b]	1.00000
52.5	0.01229	0.8449	68.77	0.15702
100.6	0.02320	0.9132	39.37	0.08884
199.0	0.04863	0.94746	19.48	0.05522
200.0	0.04845	0.94778	19.56	0.05488
400	0.09903	0.96368	9.731	0.04031
606	0.1552	0.96635	6.228	0.03983
802	0.2090	0.96215	4.604	0.04785
998	0.2689	0.95600	3.555	0.06018
1311	0.3755	0.92771	2.471	0.1158
1500	0.4327	0.9012	2.083	0.1741
1750	0.5626	0.8138	1.447	0.4257
1812	0.6341	0.7704	1.215	0.6276
1818[c]	0.7080	0.7080	1.000	1.0000
$T = -190.00°F = -123.33°C = 149.82K$				
1.4[a]	0.00000	0.00000	2000.[b]	1.00000
50.0	0.01563	0.96043	61.43	0.04020
100.5	0.03178	0.97867	30.79	0.02203
150.0	0.04796	0.98411	20.52	0.01669
200.3	0.06400	0.98752	15.43	0.01333
300	0.09698	0.98937	10.20	0.01177
400	0.1343	0.98985	7.369	0.01172
500	0.1685	0.98834	5.866	0.01402
601	0.2058	0.98656	4.793	0.01693
805	0.2839	0.98097	3.455	0.02657
1002	0.3531	0.95918	2.717	0.06310
1289	0.4336	0.9001	2.076	0.1763
1728[c]	0.7083	0.7083	1.000	1.0000
1289[d]	0.465	0.9001	1.94	0.187
1728[c,d]	0.732	0.732	1.000	1.000
$T = -210.00°F = -134.44°C = 138.71K$				
0.5[a]	0.00000	0.00000	4400.[b]	1.00000
51.2	0.01882	0.98645	52.43	0.01381
100.0	0.03870	0.99164	25.63	0.008698
150	0.05790	0.99338	17.16	0.007028
200	0.0776	0.99409	12.80	0.006412
300	0.1192	0.99444	8.342	0.006314
400	0.1637	0.99420	6.074	0.006940
500	0.2120	0.99308	4.685	0.008788
1002	0.3740	0.96216	2.573	0.06044
1000	0.3897	0.95515	2.451	0.07348

[a] Saturation conditions. [b] Extrapolated. [c] Critical conditions. [a] Recommended smoothed values.

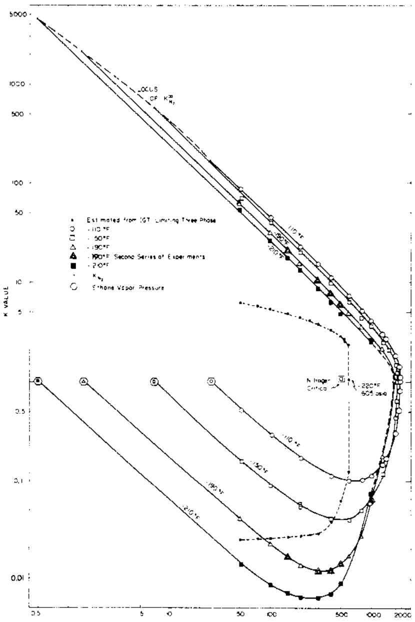

Figure 1. Isothermal K-value vs. pressure for nitrogen–ethane system

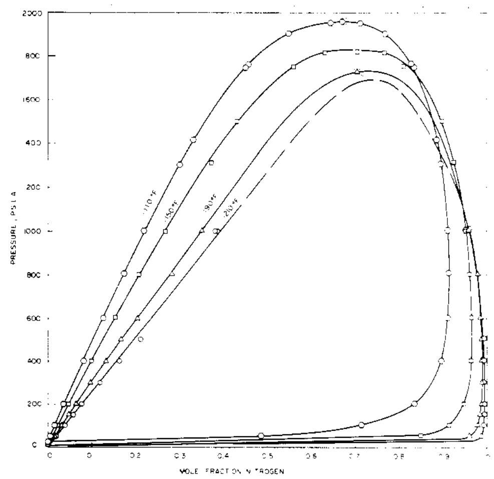

Figure 2. Isothermal pressure vs. composition (P-x,y) for nitrogen–ethane system. Dashed line: "best guess"

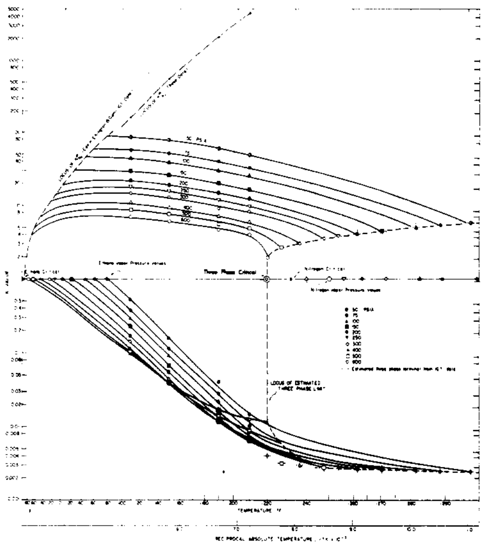

Figure 3. Isobaric K-values vs. temperature for nitrogen-ethane system. This and Figure 1 prepared on much larger scale, about 1-m square

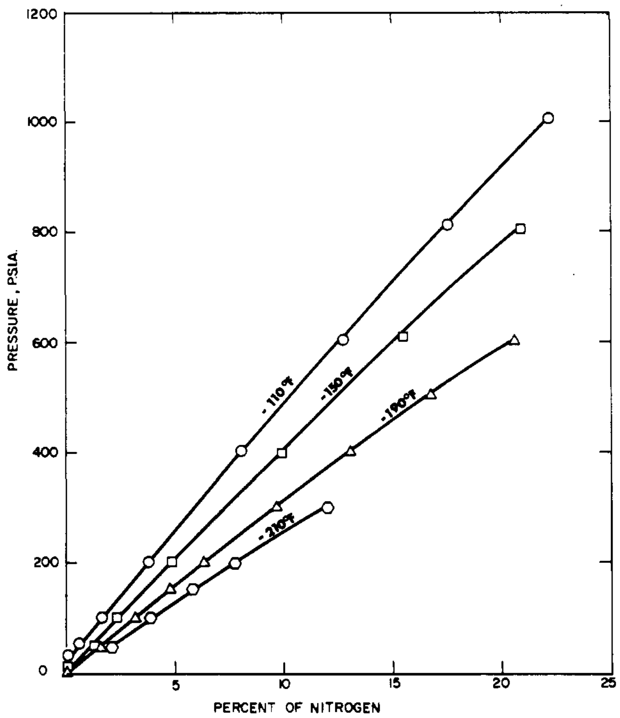

Figure 4. Liquid-phase composition as function of pressure for nitrogen-ethane system on expanded scale

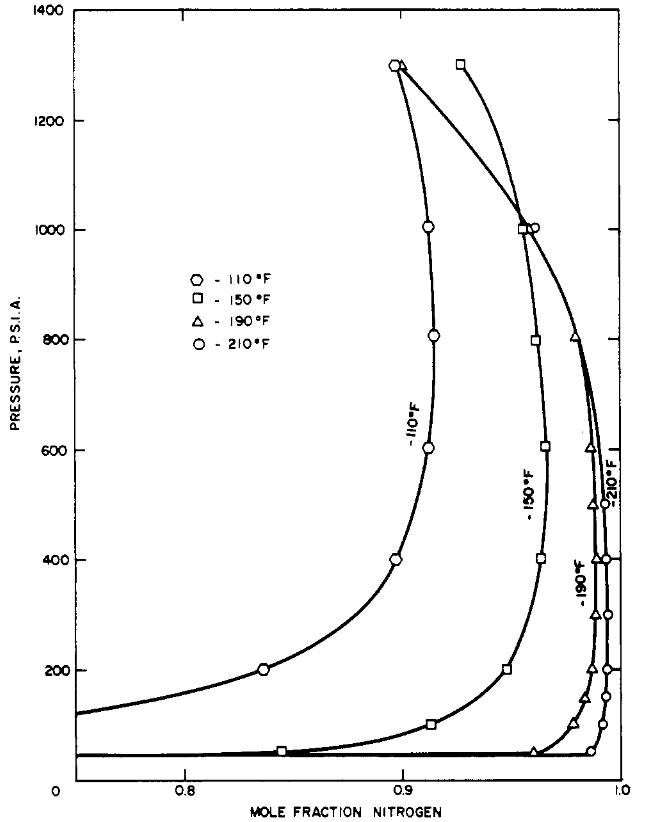

Figure 5. Vapor-phase composition as function of pressure for nitrogen-ethane system on expanded scale

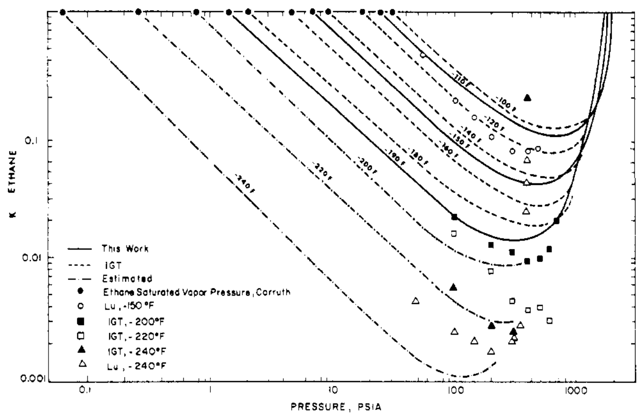

Figure 6. Comparison of existing K-value data for nitrogen-ethane system

positions in Figure 2, and as cross plots as log K vs. $1/T$ in Figure 3. In addition, the liquid and vapor concentrations are shown on an expanded scale in Figures 4 and 5.

Comparisons

The three previous investigations of this system are listed in Table I. Our data are consistent with that of Eakin et al. (*3*) at the two higher temperatures, but the data of Eakin et al. are more scattered at the lower temperatures. The data of Chang and Lu (*2*) for ethane did not extrapolate to the vapor pressure of ethane (*1*). The data of Yu et al. (*6*) fall at lower temperatures than this investigation.

A comparison of the ethane K-values is shown in Figure 6. The agreement with Eakin et al. (*3*) is satisfactory above −190°F, but the lower temperature bubble-point data of IGT (*3*) are scattered and not consistent with values estimated from this work and the ethane vapor-pressure data of Carruth.

Acknowledgment

Phillips Petroleum Co. contributed the ethane for this investigation.

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Received for review November 21, 1973. Accepted May 22, 1974. The Natural Gas Processors Association, National Science Foundation, American Gas Association, and Columbia Gas Systems Service Corp. provided financial support.

Excess Free Energies and Entropies at 45°C for Ternary System Acetonitrile–Benzene–Carbon Tetrachloride

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Excess free energies are determined from measurements of liquid-vapor equilibrium over the whole range of composition at 45°C for the ternary system acetonitrile(1)–benzene(2)–carbon tetrachloride(3), and excess entropies are calculated from these excess free energies and excess enthalpies obtained previously. The excess free energies can be represented simply in terms of binary contributions and are positive at all compositions; there is no ternary azeotrope. The excess entropies are negative except for solutions very dilute in acetonitrile. Constants are given for the calculation of these properties and the corresponding excess partial molar quantities.

Excess enthalpies for the ternary system acetonitrile–benzene–carbon tetrachloride at 45°C have been reported previously (*6*). This is a system in which one component (acetonitrile) is highly polar and in which there is a pair of components (acetonitrile–carbon tetrachloride) which may serve as a cosolvent system in facilitating separations of hydrocarbons (*5*). In spite of the moderate complexity of the system, the excess enthalpy for the ternary system could be predicted from binary contributions without the need of ternary constants.

In this paper the excess free energy of the system at 45°C is similarly investigated, and the results are used together with those for the excess enthalpy to determine the excess entropy of the system.

Experimental

Purification of the materials used was mainly by distillation, as described previously (*6*). BDH "Analar" acetonitrile was first dried and then fractionated twice over phosphorus pentoxide. BDH "Analar" carbon tetrachloride was first dried over the pentoxide. Fisher "Certified Reagent" benzene was first washed with concentrated sulfuric acid and then neutralized, dried, and fractionated over the pentoxide. The relative densities ($d^{25}{}_4$) and refractive indices ($n^{25}{}_D$) of the purified components are given in Table I. The values of these properties all lie within the ranges given by Timmermans (*14*), with the exception of the value of $n^{25}{}_D$ for benzene, for which the range given is 1.4979–1.4981. Also given in the table are the vapor pressures (p^*) measured at 45°C with the equilibrium apparatus described below, and the second virial coefficients (B) at 45°C (*1, 2*).

The excess free energies were calculated from liquid-vapor equilibrium measurements made in a condensate-recirculation equilibrium still of the Gillespie type used previously (*8*). Measurements were made at 45°C for the three binary systems and the ternary system. For the ternary system, a series of solutions with fixed ratios of benzene and carbon tetrachloride was used and acetonitrile added to make a pseudobinary system.

The liquid and vapor (condensate) samples removed from the equilibrium still were analyzed by gas-liquid chromatography by use of a Burrell K-1 chromatograph, together with a thermal conductivity cell as detector and a column utilizing Carbowax 400. The precision of the method was determined by analyzing a number of binary and ternary solutions of known composition. The standard deviation in the mole fractions of all components determined in this way was 0.002.

Results and Discussion

The liquid-vapor equilibrium measurements for the binary systems and the values of the excess free energies calculated from them are not reported in detail, since the latter agree with the equations given by Brown and Smith (*1, 2*) and by Scatchard and Ticknor (*12*) as follows (with g^E the excess free energy in cal/g mol and x mole fraction): acetonitrile(1)–benzene(2) system (*2*):

$$g_{12}{}^E = x_1x_2[643.3 - 8.1\ (x_1 - x_2) + 70.1\ (x_1 - x_2)^2] \quad (1)$$

benzene(2)–carbon tetrachloride(3) system (*12*):

$$g_{23}{}^E = x_2x_3[75.9 - 0.85\ (x_3 - x_2)] \quad (2)$$

carbon tetrachloride(3)–acetonitrile(1) system (*1*):

$$g_{31}{}^E = x_3x_1[1134.3 + 118.9\ (x_3 - x_1) + 162.2\ (x_3 - x_1)^2 + 99.5\ (x_3 - x_1)^3] \quad (3)$$

The standard deviations of the fits of the experimental data obtained here to these equations were 0.7, 0.1, and 1.1 cal/g mol, respectively. These values are within or close to the values given in the work leading to Equations 1–3. We conclude that these equations may be used to represent binary data for comparison with the measured ternary data, and that the chromatographic method of analysis is suitable.

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