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# **INSTITUTE OF GAS TECHNOLOGY**

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# **RESEARCH BULLETIN**



# PHYSICAL - CHEMICAL PROPERTIES OF ETHANE - NITROGEN MIXTURES



PREFACE

This Bulletin, the 26th in a series of publications on research conducted in the libraries and laboratories of the Institute of Gas Technology, presents the results of one phase of the determination of the physical and thermodynamic properties of natural gas components and their mixtures, data which are required for the engineering design of plants to separate the pure components of natural gas.

Investigation of the physical and thermodynamic properties of natural gas components and their mixtures was initiated in November, 1947, as a part of the Institute's Basic Research Program. The initial literature survey, and the design, construction and operation of the experimental units and their modifications, were accomplished with Institute funds.

In January, 1950, the Technical and Research Committee contributed \$5,000, under the PAR (Promotion-Advertising-Research) Plan of the American Gas Association, as a grant-in-aid for "A Study of the Physical and Physical-Chemical Properties of the Methane-Nitrogen System." In January, 1951, the Committee assumed complete financial responsibility for the "Study of the Physical-Chemical Properties of the Methane-Ethane System," Project NB-1.\* With the consolidation of departments within the American Gas Association, financial sponsorship of the program, including its extension to "Study of the Physical-Chemical Properties of the Ethane-Nitrogen System," Project NB-5, was assumed by the Pipeline Research Committee in 1953.<sup>†</sup>

The guidance and encouragement of the Supervising Committee composed of D. T. MacRoberts and M. E. Benesh, and of the Technical and Research and Pipeline Research Committees, are gratefully acknowledged. The authors wish to thank Director E. S. Pettyjohn for assistance in the design, construction and manipulation of the equipment used. John R. Hasenberg assisted in the experimental work. The editing of this Bulletin is the work of A. E. S. Neumann; the illustrations, of S. Bruno, E. Hviid, and D. Sternbach.

Chicago, Illinois July, 1955 E. S. PETTYJOHN, *Director* Institute of Gas Technology

\* PHYSICAL-CHEMICAL PROPERTIES OF METHANE-NITROGEN MIXTURES, by O. T. Bloomer and J. D. Parent. Institute of Gas Technology Research Bulletin No. 17, 1952.

THERMODYNAMIC PROPERTIES OF NITROGEN, by O. T. Bloomer and K. N. Rao. Institute of Gas Technology Research Bulletin No. 18, 1952.

Supplement to Bulletin No. 18. "Mollier Chart for Nitrogen" and "Compressibility Chart for Nitrogen," reproduced full scale (grid 10 x 10 to the inch) on heavy paper, 22" x 34".

<sup>†</sup>THERMODYNAMIC PROPERTIES OF METHANE-NITROGEN MIXTURES, by O. T. Bloomer, B. E. Eakin, R. T. Ellington and D. C. Gami. Institute of Gas Technology Research Bulletin No. 21, 1955.

Supplement to Bulletin No. 21. "Mollier Chart for Methane" and "Temperature-Entropy Chart for Methane," reproduced full scale (grid 10 x 10 to the inch and 10 x 10 to 0.75 in. respectively) on heavy paper, 22" x 34".

PHYSICAL-CHEMICAL PROPERTIES OF METHANE-ETHANE MIXTURES, by O. T. Bloomer, D. C. Gami and J. D. Parent. Institute of Gas Technology Research Bulletin No. 22, 1953.

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# ABSTRACT

This bulletin presents data on liquid-vapor phase equilibria, gas phase pressure-volume-temperature relationships, and saturated liquid and vapor densities for the ethane-nitrogen system, obtained by detailed experimental investigation with specific mixtures of ethane and nitrogen.

The liquid-vapor phase equilibrium data were determined by study of the dew and bubble point pressure-temperature relations of ten mixtures of ethane and nitrogen. During experimental runs the mixture was confined in a heavy-walled glass cell immersed in a cryostat, and stirred by a magnetically-raised and lowered steel ball. Dew and bubble points were determined by direct visual observation, and the critical region of the mixture was carefully noted if critical conditions were within the operating limits of the equipment. The range covered was from 50 to 1950 psia, and  $-297^{\circ}$ to  $+90^{\circ}$ F, the critical temperature of ethane. It was not possible to determine the highest pressure at which liquid and vapor can coexist, due to equipment limitations.

Pressure-temperature, temperature-composition and pressure-composition diagrams were prepared from the dew and bubble point data. Equilibrium vaporization ratios were determined from these diagrams, and are presented in graphical and tabular form. It is estimated that the phase equilibrium data are reliable to  $\pm 2$  psi or  $\pm 0.2^{\circ}$ F, whichever is greater.

The gas-phase pressure-volume-temperature data were determined by a study of the pressure-temperature relations of five mixtures of ethane and nitrogen at constant density. Seven or eight constant density lines (isometrics) were investigated for each mixture. The data, covering the range from the critical region to  $+110^{\circ}$ F and pressures to 4000 psia, are presented in plots of compressibility factor versus pressure, with lines of constant temperature. Compressibility factors calculated from the data are believed accurate to  $\pm 0.3\%$ .

The experimental compressibility factors have been compared with values calculated with the Benedict-Webb-Rubin equation of state, the constants for the mixtures being obtained by combining the constants for ethane and nitrogen. An empirical combination rule for the  $A_o$  term was used to adjust the method of combining constants and improve the agreement with the experimental data. A comparison of the experimental pressure-volume-temperature data with the data of Reamer *et al.*<sup>18</sup> show good agreement, with a maximum deviation of about 1.2%.

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# THE PROBLEM

The rapid growth of the natural gas industry and greater emphasis on petrochemical processes has increased interest in the separation of natural gases into component streams of high purity. Of the separation processes studied, those which would be carried out at low temperatures seem the most promising;<sup>17</sup> however, low-temperature phase equilibrium and thermodynamic data necessary for the engineering design of separation plants are incomplete.<sup>15</sup>

To help supply the needed data, the Institute of Gas Technology began, in November 1947, as a part of its basic research program, study of the liquid-vapor phase equilibria, pressure-volume-temperature relationships, and determination of the thermodynamic properties of selected mixtures of natural gas components at low temperatures.

Since the inception of this program, data on liquid-vapor phase equilibria and P-V-T relationships of the methane-nitrogen and methane-ethane binary systems have been obtained and published.<sup>6, 9</sup> The thermodynamic properties of nitrogen<sup>7</sup> and two mixtures of methane and nitrogen<sup>8</sup> have been calculated by use of a modification of the Benedict-Webb-Rubin equation of state. No phase equilibrium data were available for the ethanenitrogen system, the remaining binary combination of the three important components of natural gas: methane, ethane and nitrogen. Recently Reamer *et al.*<sup>18</sup> published data on the gas-phase P-V-T relationships of ethane-nitrogen mixtures covering temperatures from 40° to 460°F and pressures up to 10,000 psia. These are now the only data available in the literature.

The problem is, therefore, to measure the liquid-vapor phase behavior and the gas-phase pressure-volume-temperature relationships of specific mixtures of ethane and nitrogen over a wide range of concentrations, pressures, and temperatures and to present this information in a form useful for engineering calculations.



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Fig. A.-DEW AND BUBBLE POINT DIAGRAMS FOR THE ETHANE-NITROGEN SYSTEM

# SUMMARY OF RESULTS

#### I. Liquid-Vapor Phase Equilibrium Data

#### A. Dew and Bubble Points

The dew and bubble point pressure-temperature diagrams, or phase boundary curves, of six mixtures of ethane and nitrogen, dew point curves of three additional mixtures, and the bubble point curve of one other mixture were determined. These constitute the primary phase equilibria data. The compositions of the mixtures investigated are given in Table A. The experimental dew and bubble point data are presented in Table I of Tabulated Data and shown graphically in Fig. A.

Each of the curves for ethane-nitrogen mixtures 1, 2, 4, 5, 9 and 10, Fig. A, forms a loop. The lower segment of each loop represents the conditions of pressure and temperature at which the mixture in the vapor phase begins to condense upon cooling or compression and is thus the *dew point curve*. The upper segment of the loop, or *bubble point curve*, represents either the completion of condensation of the vapor, or the boiling point of the liquid. These curve segments join at the critical point of the mixture where the properties of the saturated liquid and vapor phase become indistinguishable.

All of the mixtures tested exhibit retrograde<sup>14</sup> phenomena. The 15% ethane-85% nitrogen mix-

Table A.	-CALC	ULATE	) CO	MPOS	ITION	S OF
<b>MIXTURES</b>	INVESTIC	GATED	FOR	DEW	AND	BUBBLE
	POINT	DETER	MINA	TION	S	

Mixture No.	Fig. A Curve No.	Ethane Mole %	Nitrogen Mole %
A		95.02	4 98
B	2	84.99	15.01
Ċ	3	79.98	20.02
D,	4	75.07	24.93
Da	4	75.00	25.00
E	5	68.31	31.69
Ea	5	68.28	31.72
F	6	49.82	50.18
G	7	30.00	70.00
H <sub>1</sub>	8	15.03	84.97
H <sub>2</sub>	8	14.94	85.06
J,	9a	5.10	94.90
$J_2$	9b	4.95	95.05
ĸ	10	1.98	98.02

ture has a double retrograde<sup>23</sup> region, and does not have a normal bubble point curve, as certain ethane-nitrogen mixtures are not completely miscible under liquid conditions. Mixtures containing less than 31.7% nitrogen show partial miscibility in the liquid region through certain low-temperature intervals by the formation of two distinct liquid phases, one containing about 70% and the other about 5% ethane. However, the 2% ethane-98% nitrogen mixture shows normal dew and bubble point behavior. Due to the large retrograde region





exhibited by mixtures of 50 and 30% ethane, and the very high pressures reached by the phase envelope, it was not possible to complete the phase boundary curve in the low-temperature region; the required pressures would have exceeded the 2000 psia maximum working pressure of the equilibrium cell. The portions of the phase boundary curves for these two mixtures shown as dashed lines were obtained with P-V-T apparatus.

#### **B.** Pressure-Composition Diagrams

Isothermal pressure-composition (P-X) diagrams were constructed from the phase boundary curves; the pressure values were taken from the intersection of the given constant temperature lines and the dew and bubble curves for each mixture. Fig. B presents P-X diagrams for selected temperatures from  $-260^{\circ}$  to  $+40^{\circ}$ F. The straight line sections of the  $-220^{\circ}$ ,  $-240^{\circ}$ and  $-260^{\circ}$  loops (such as BCD) represent the range of composition at constant temperature and pressure over which three phases coexist. The estimated compositions of the immiscible liquid phases at various temperatures are indicated by dashed lines. At temperatures above the maximum threephase coexistence temperature ( $-220^{\circ}$ F), but below 0°F, the loops are not closed, as equipment limitations prevented obtaining the necessary data in this (the double retrograde) region.

The dot-dash line represents the estimated pressure behavior at a temperature of  $-220^{\circ}$ F for various mixtures in the composition range between 85 and 95% nitrogen. It is expected that mixtures in the composition range of 40 to 85% nitrogen will exhibit similar phenomena at low temperatures (-80°F and below).

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Fig. C.-ISOBARIC TEMPERATURE-COMPOSITION DIAGRAMS, ETHANE-NITROGEN SYSTEM

#### C. Temperature-Composition Diagrams

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Values of the temperature at which various constant pressure lines intersect the dew and bubble point curves were read from a large-scale plot of the phase boundary curves, and are recorded in Table B. These are plotted as temperature-composition (T-X) isobars in Fig. C for pressures of 100, 300, 500, 700 and 950 psia. The straight lines on the 100, 300 and 500 psia curves (such as DEF) represent the range of compositions, at constant temperature and pressure, through which three phases coexist. Above the maximum three-phase coexistence pressure (605 psia), the T-X curves are not closed, since equipment limitations prevented accumulation of sufficient data for complete definition of this (double retrograde) region.

In the three-phase coexistence region the com-

#### PHYSICAL-CHEMICAL PROPERTIES OF ETHANE-NITROGEN MIXTURES

position of the two liquid phases and the vapor phase can be determined from Fig. C. To illustrate, at a pressure of 300 psia, and a temperature of  $-248^{\circ}$ F, any feed mixture containing 30 to 95%nitrogen will separate into two liquid phases having compositions of 27.5 and 95.5% nitrogen (points D and E), and a vapor phase containing 99.9% nitrogen (point F, Sec. A). If a mixture containing 95% nitrogen were cooled to -245°F at a pressure of 300 psia, it would exist as a liquid phase containing 24% nitrogen and a vapor phase containing 99.8% nitrogen (Sec. A). If the cooling were continued to a temperature of -248°F, the pressure being maintained at 300 psia, the liquid phase would cease to be homogeneous, and would separate into two liquid phases having compositions of 27.5 and 95.5% nitrogen, respectively. The vapor phase in equilibrium with the less dense liquid phase would have a composition of 99.9% nitrogen (V in Sec. A). Upon further cooling to a temperature of -250°F the vapor phase would have disappeared and the mixture would exist as two immiscible liquid phases  $(L_1 \text{ and } L_2 \text{ in Sec. A})$ . The three phases will coexist at 300 psia only at a temperature of  $-248^{\circ}$ F; above  $-248^{\circ}$ F there will be one liquid phase and a vapor phase, and below this temperature there will be two liquid phases and no vapor phase, the transition taking place at -248°F.

The composition of the equilibrium liquid and vapor phases at a given pressure and temperature can be read from the points at which the selected temperature line intersects the curves for the given pressure. For example, at -140°F and 100 psia the composition of the liquid phase (point B), is 97.8% ethane-2.2% nitrogen, while the equilibrium vapor phase at the same temperature and pressure (point C) is 11.5% ethane-88.5% nitrogen. Data obtained in this manner can be used to construct constant-pressure vapor compositionliquid composition (Y-X) diagrams. Y-X diagrams at 100, 300, 500 and 950 psia are shown in Fig. D. The 950 psia equilibrium curve intersects the Y = X line at the composition (85% ethane-15% nitrogen) which exhibits a critical point at this pressure. Since this pressure is greater than the critical for either component, separation into the pure components cannot be obtained under these conditions. The composition at the point of maximum obtainable separation (88% ethane-12% nitrogen) is that exhibiting a 950 psia cricondenbar.

Equilibrium vaporization ratios, K, for ethane and nitrogen in the binary system are also estab-



lished from the compositions of the vapor and liquid in equilibrium as read from the temperaturecomposition diagram, Fig. C. As an illustration, at  $-140^{\circ}$ F and 100 psia, the liquid composition (point B) is 97.8% ethane-2.2% nitrogen, and the equilibrium vapor (point C) is 11.5% ethane-88.5% nitrogen. The equilibrium vaporization ratio for ethane is 11.5/97.8 = 0.118, and for nitrogen, 88.5/2.2 = 40.2.

K values were calculated in this manner for ethane and nitrogen in the ethane-nitrogen system for selected values of temperature and pressure, and are given in Tables C and D. At the dew point temperature of the pure component for each pressure the K value is 1.000. The saturation (dew point) temperatures for the pure components are given at each pressure. For a pressure that exceeds the critical pressures of the pure components, the temperatures marked with daggers represent the critical temperatures of the system at that pressure, and the K values for ethane and nitrogen at each of these temperatures are also 1.000. The ethane equilibrium vaporization ratios are plotted as K versus pressure (Fig. E) isotherms, and the nitrogen equilibrium vaporization ratios as K versus temperature (Fig. F) isobars.

#### Table B.-SUMMARY OF DEW AND BUBBLE POINT

Proc		95.02 4.98	% C2H6	84.99% 15.01%	6 C <sub>2</sub> H <sub>6</sub>	79.98% C₂H₀ 20.02% N₂	75.07% C <sub>2</sub> H <sub>6</sub> 24.93% N <sub>2</sub>	68.31% 31.69%	$C_2H_6$ N <sub>2</sub>	49.82% C <sub>2</sub> H <sub>6</sub> 50.18% N <sub>2</sub>	30.00% C <sub>2</sub> H <sub>6</sub> 70.00% N <sub>2</sub>
Ps	sure, sia	D.P.	B.P.	D.P.	B.P.	B.P.	B.P.	D.P.	B.P.	D.P.	D.P.
1	00	-50.0t	-232.31		-278.2	_			_		-105.3
1	50	-27.7	-171.9	-35.0	-263.0	-268.8	_	-48.2	_	-69.1	- 89.7
2	00	- 98	-152.8	-18.8	-249.9	-257.4		-33.3	_	-56.1	- 78.9
2	50	- 45	-1113	- 5 5	237.4	247.4		-21.0		_45.4	- 70 1
2	00	16.9	75.6	- 5.5	-237.4	238 5	-241 1	-10.9		36.3	- 62.8
3	50	27.4	- 48.0	+ 0.1	_213.1	229.8	239.4	- 20		-28.6	- 56.7
4	00	26.9	- 40.0	25.1	200.8	221 5	-237.4	- 5.5		-20.0	- 51.5
4	50	30.0 AE 4	- 20.5	22.0	-200.8	2120	225.0	+ 5.5		-20.7	47.0
5	100	45.0	- 1.0	40.0	-107.0	204.2	-2105	12.1		-14.7	- 47.0
5	500	55.0	+ 0.4	40.0	-173.7	104.9	212.0	22.7		- 7.2	- 43.0
5	00	60.0	24.2	40.3	-157.4	-174.0	-212.7	23./	210.0	- 3.7	- 37.0
0	500	07.3	34.5	51.9	-143.4	-185.0	-205.2	28.0	-219.9	- 0.1	- 30.5
0	50	/3.0	45.8	56.9	-124.3	-1/3.9	-197.7	32.9	-214.3	+ 3.4	- 33.9
/	00	/8.2	56./	61.4	-102.8	-161.3	-190.4	36.7	-208.8	6.6	- 31.6
/	50	82.7	67.2	65.2	- 81.5	-147.8	-183.0	40.0	-203.3	9.4	- 29.7
8	00	-	76.2	68.4	- 59.9	-132.9	-174.3	42.9	-197.8	11.8	- 28.0
		-	82.1				1150	45.0	101.7		
8	50	-		70.4	- 37.2	-115.0	-165.3	45.2	-191.7	13.9	- 26.5
9	000	-		71.1	- 14.1		-154.9	47.1	-185.3	15.5	- 25.4
9	50	—	—	68.9*	+ 6.3	—	-142.6	48.5	-178.7	16.8	- 24.5
10	000	—	—	—	28.7	_	-128.3	49.0	-171.8	17.9	- 23.9
		—			64.0	-		—	_	—	
10	50	_			-	_	-112.4	49.0	-163.7	18.7	- 23.5
11	00		-	-	-	_	- 94.5	48.6*	-155.0	19.3	- 23.2
11	50		—	—	—	-	- 75.0	47.3*	-144.9	19.5	- 23.1
			—	-	-		+ 50.8			-	-
12	00	—	-	-	-	—	- 53.8	44.7*	-133.4	19.4*	- 23.0
		-	-	_	-	-	+ 45.6	_	-	-	
12	50			_	-	—	- 28.0	40.9*	-120.4	18.9*	- 23.1*
		<u> </u>		-			+ 38.3			-	
13	00	-	-	-				35.9*	-106.0	17.7*	- 23.4*
13	50	-		_	-		-	_	- 90.3	16.1*	- 23.9*
		_	-	_	-	-			+ 30.0	_	-
14	00	_			_	_	-	_	- 71.6	14.1*	- 24.6*
		_	_	_				_	+ 22.7		
14	50	-			_				- 42.0	11.6*	- 25.6*
						_	_		+ 9.1		
15	00	_	_	_					-	9.0*	- 27.0*
15	50		_		_		_		_	5.9*	- 28.6*
16	00	_	_		_		_		_	+ 2.5*	- 30.4*
16	50		_	_			_			- 1.3*	- 32.6*
17	00		_		-					- 5.75*	- 35.4*
17	50				_				_	-11.2*	- 39.4*
18	00				_			_		-19.3*	- 44.9*
18	50			-							- 53.2*

## Table C .- "K" VALUES FOR ETHANE IN THE ETHANE-NITROGEN SYSTEM

Pressure, Psia Temp. °F. 200 300 400 500 1200 100 600 700 950 \* -263.7 -240.3 -282.8 -250.6 --280 0.00120 --\_ -----\_ -260 0.00218 0.00130 \_ \_ \_ 0.200 -240 0.00583 0.00284 0.00251 -1111 0.00373 \_ -220 0.0157 0.00659 0.00440 0.00402 0.0308 -200 0.0217 0.0129 0.0107 0.00939 0.00988 0.0117 0.0194 -180 -160 -140 0.0356 0.0234 0.0198 0.0183 0.0178 0.0185 0.0200 0.0428 0.0626 0.0391 0.0304 0.0269 0.0261 0.0264 0.0285 0.0455 0.116 0.0692 0.0549 0.0487 0.0456 0.0440 0.0440 0.0531 0.0818 -120 0.0930 0.0794 0.0731 0.0717 0.0714 0.0816 0.205 0.118 0.103 0.377 0.128 0.118 0.196 0.148 0.114 0.112 0.137 0.119 - 80 - 60 - 40 - 20 0.301 0.190 0.173 0.226 0.163 0.567 0.158 0.165 0.186 0.334 0.273 0.791 0.458 0.246 0.227 0.215 0.218 0.249 Ξ 0.639 0.485 0.394 0.341 0.314 0.298 0.289 0.321 0.528 0.458 0.400 0.843 0.634 0.424 0.382 0.404 0 0.799 0.666 0.588 0.539 0.512 0.491 0.507 20 0.985 0.822 0.726 0.665 0.630 0.603 0.640 I I I 40 0.980 0.870 0.802 0.757 0.725 0.824 60 0.999 0.922 0.881 0.878 --0.973 -80 -\_ --100 \*\* 46.0 -6.2 21.6 43.0 61.0 75.8 88.3 69.11 45.5†

\* Saturation temperature for nitrogen

\*\* Saturation temperature for ethane † Critical temperature for the binary system

Processo	14.94% C <sub>2</sub> H <sub>6</sub> 85.06% N <sub>2</sub>		15.03% C2H 84.97% N2	16	4.95% C <sub>2</sub> H <sub>6</sub> 95.05% N <sub>2</sub>	5.10° 94.90°	% C₂H₀ % N₂		1.98% C2H 98.02% N2	6
Pressure, Psia	D.P.	D.P.	D.P.	D.P.	D.P.	D.P.	D.P.	D.P.	D.P.	B.P.
100	-130.6	_	_			-			-	_
150	-118.3				-154.9			-190.7		_
200	-109.6				-148.8			-183.9	—	-263.3
250	-102.6				-144.2	_				-255.9
300	- 97.0		_		-140.6	_	_	-175.6	_	-249.8
350	- 92.4		_		-137.5		_	-173.2		-244.2
400	- 88 5				-135.1	-1337		-171 2		-239.3
450	95 1				-122.2	120.0		170.0		234.7
500	- 03.1	_		_	-133.3	-130.7		149.2		230.1
500	- 02.3		_		-132.0	-127.0		149.9	_	225 5
550	- 77.7	_			-131.1	-127.7	_	-100.0	220 5*	-225.5
600	- 77.8	_	_		-130.8	-127.5		-108.8	-220.5	_
650	- 76.1				-130.3	-127.2	_	-169.2*	-216.1*	
700	- /4.6		_		-130.3	-127.1		-170.0*	-211.8*	_
750	- 73.6	—	—	_	-130.5*	-127.3*	-214.1*	-172.3*	-206.5*	
800	- 72.7				-131.3*	-127.8*	-210.9*	-177.6*	-199.3*	
	—	—	—			-				_
850	— 72.2		-		—	-128.5*	-207.5*	-	-	
900	- 71.9					-129.5*	-203.8*		—	
950	- 71.8				—	-131.0*	-199.9*			-
1000	- 71.9*		_			-132.9*	-195.6*			
				·	_					_
1050	-	- 72.2*			_	-135.5*	-190.9*	-		
1100		- 72.6*	_			-139.0*	-185.4*			_
1150		- 73.2*					-178.8*			
									_	
1200		- 73.9*			_	-151.1*	-168.0*			
	_								_	
1250		- 74.8*				_				
1200									_	
1300		- 76 1*								
1350		77.5*								
1550		11.5								
1400		80.1*	201 7*	211 5**		_				_
1400		- 00.1	-201.7	-211.5						_
1450		02 7*	100.0*	210 5**		-	_		_	
1450		- 02.7	-107.7	-217.5			_			
1500		05.0*	101.5*	222.2**	_	_				
1500	_	- 85.8*	-181.5*	-223.2**		_				
1550		- 89.3*	-1/3./*	-225.9**			NO	TE. All tompora	turor givon	in °E
1600		- 93.7*	-165.8*				140	. An tempera	t i given	in r
1650	—	- 99.4*	-157.0*	-229.9**	—		≁ Re	etrograde dew p	oints	
1700		-108.0*	-145.6*	-231.5**	-		** [	Double retrograd	e dew point	s
1750		—	_	-232.9**			+ F.	trapolated value		
1800		_	-					and pointed value		
1850			-							

# DATA INTERPOLATED TO EVEN VALUES OF PRESSURE

# Table D.-"K" VALUES FOR NITROGEN IN THE ETHANE-NITROGEN SYSTEM

				Pressure, Psi	a				
Temp. °F	100	200	300	400	500	600	700	950	1200
*		-263.7			_				-
-280	5.98	—					-		
-260	12.0	4.38	-			-		_	
-240	17.6	8.31	4.89	1.01		_			
-220	22.6	11.1	7.15	5.11	3.94	3.07		—	_
-200	28.8	13.9	9.17	6.70	5.22	4.26	3.56		
-180	32.3	16.0	10.6	7.94	6.27	5.16	4.36	3.02	
-160	36.8	18.3	12.2	9.04	7.14	5.93	5.01	3.53	_
-140	40.3	20.1	13.4	9.96	7.87	6.53	5.54	3.89	2.89
-120	42.2	21.1	14.3	10.7	8.42	6.95	5.88	4.11	3.08
-100	44.1	22.5	15.1	11.2	8.76	7.20	6.11	4.27	3.19
- 80	46.1	22.5	15.4	11.4	8.97	7.35	6.23	4.36	3.23
- 60	47.2	22.1	15.1	11.5	9.12	7.52	6.37	4.40	3.22
- 40		21.9	14.4	11.0	8.90	7.35	6.25	4.35	3.13
- 20		20.5	14.2	10.6	8.49	7.01	5.95	4.13	2.98
0			13.4	10.1	8.01	6.69	5.56	3.80	2.72
20			11.0	9.12	7.25	6.06	5.13	3.40	2.31
40				7.50	6.38	5.26	4.36	2.84	1.63
60					1.50	4.53	3.48	1.86	
80	_						2.66		
100									
**	-46.0	6.2	21.6	43.0	61.0	75.8	88.3	69.1†	45.5†
* Saturatio	on temperature f	or nitrogen	** Saturation temp	erature for ethan	e † Critica	al temperature	for the binary	system	



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Fig. E.-VAPORIZATION EQUILIBRIUM RATIOS FOR ETHANE IN THE ETHANE-NITROGEN SYSTEM

#### PHYSICAL-CHEMICAL PROPERTIES OF ETHANE-NITROGEN MIXTURES



Fig. F.-VAPORIZATION EQUILIBRIUM RATIOS FOR NITROGEN IN THE ETHANE-NITROGEN SYSTEM

#### II. Critical Data for the Ethane-Nitrogen System

The critical and maximum temperatures and pressures for mixtures of ethane and nitrogen are tabulated in Table E. In Fig. G is shown the relationship between the critical temperature and the composition expressed as mole percent nitrogen. The molecular weights of the components are nearly the same, so the critical temperature-mole or weight percent curves are nearly the same. The observed relationship is not linear, as for binary hydrocarbon systems, but gives temperatures greater than those predicted by linear combination of the critical temperatures.

Various empirical methods have been proposed for prediction of critical constants of mixtures. These correlations usually apply only to systems on which they are based, and are not very useful for predicting other systems. The rule proposed by Bloomer<sup>6</sup> expressed by the equation:

$$T_{c} \text{ of mixture} = \frac{\frac{W_{1}}{M_{1}}V_{c1}}{\frac{W_{1}}{M_{1}}V_{c1} + \frac{W_{2}}{M_{2}}V_{c2}}(T_{c1} - T_{c2}) + T_{c2}$$

 $T_c = critical temperature$ W = weight fraction M = molecular weight  $V_c =$  molal volume at the critical point Subscript (1) refers to component (1) Subscript (2) refers to component (2).

gave good agreement with the methane-nitrogen critical data. It deviated to some extent from the ethane-nitrogen data, but as shown in Fig. G the agreement is better than a linear combination of the component criticals. Through a certain range of compositions, partial liquid miscibility of the liquid phases and double retrograde behavior occur. As a result, it is not possible to predict critical temperatures for mixtures in this range.

The behavior of the mixtures containing 15, 25 and 31.7% nitrogen was anomalous in the critical region. When the data on these mixtures were plotted on an expanded scale, the P-T loops, instead of being tangent to the critical locus curve at the critical point, coincided with the curve over a considerable temperature range. Over the temperature range of coincidence the phenomenon observed in the cell changed from that of a dew point to that in which a substantial quantity of liquid



Fig. G.—Locus of Critical Temperatures for Ethane-Nitrogen Mixtures

appeared instantaneously upon cooling. The quantity of liquid which appeared increased through this range until a true bubble point was observed. The temperature range for this phenomenon was approximately 20°F for the 31.7% nitrogen mixture. Similar but less pronounced phenomena were observed for the methane-ethane system.<sup>9</sup>

The exact critical temperatures for these mixtures are in doubt because of this phenomenon. The reported value is the temperature at which the meniscus disappeared with the cell half-full of liquid. The reddish-brown opalescence normally observed at the critical point was apparently at a

Table E.—EXPERIMENTAL CRITICAL CONSTANTS OF THE MIXTURES INVESTIGATED

Composition		Critica	al Point Temp Po		num Point	um Maximun oint Press. Poir	
Mole % C₂H₀	Mole % N2	Temp °F	Press. psia	Temp °F	Press. psia	Temp °F	Press. psia
95.02	4.98	82.95	788.4	83.55	775	79.8	808.5
84.99	15.01	67.00	970.0	71.10	895	54.8	1033.5
75.07	24.93	49.10	1166.5	_	_	17.5	1290.0
68.31	31.69	33.47	1320.8	49.05	1035	- 12.0	1472.0
49.82	50.18		_	19.55	1175		
30.00	70.00	-	_	-23.05	1175		-
14.94	85.06	Does no	ot exist	-71.70	965	-125	1738.0
5.10	94.90		-	-127.10	675	-158.5	1211.5
1.98	98.02	-223.0	575.0	-169.45	615	-189.0	837.0



Fig. H.—Locus of Coexistence of Three Phases in the Ethane-Nitrogen System

maximum when the cell was half-full of liquid, and became less intense for those temperatures at which the meniscus disappeared above or below the halffull level. The approach to this region was frequently made from two directions, and for a given temperature in no instance was there a difference greater than 1.0 psia in the pressure at which the liquid phase disappeared.

#### III. Partial Miscibility in the Liquid Phase

At certain low temperatures, mixtures containing from 5-80% ethane form two immiscible liquid phases in equilibrium with a vapor phase. The locus of conditions under which the three phases coexist (pressure vs. temperature curve) is shown in Fig. H. The vapor pressure curve for nitrogen is given for reference. The maximum point at which three phases coexist is  $-220^{\circ}$ F and 605 psia. The locus terminates in the system quadruple point,  $-300.5^{\circ}$ F and 40 psia, at which two liquids, a vapor, and a solid coexist. For the 15% ethane mixture two liquid phases coexist in the region between the three-phase locus and the dew point curve at temperatures below  $-220^{\circ}$ F (Fig. A). Various other mixtures will exhibit similar behavior. When curves for all mixtures are available, the effect of temperature at constant pressure on the miscibility of the two liquid phases can be shown by cross plots of the data. The experimental data indicate that at constant pressure the effect of temperature on the solubility of the two liquid phases is slight, especially at low pressures.

### IV. Single and Double Retrograde Phenomena

Mixtures containing 1.98-95% ethane exhibited retrograde phenomena. The size of the retrograde regions encountered and the amount of liquid formed varied markedly from mixture to mixture. The following types of retrograde behavior were observed: isothermal condensation, isobaric vaporization between dew points, and isobaric vaporization between bubble points.

The 15% ethane mixture exhibited unique behavior in that (as shown in Fig. A, curve 8) no bubble point was observed on the phase envelope within the pressures attainable with the experimental equipment. With pressure reduction at constant temperature between  $-235^{\circ}$  and  $-220^{\circ}$ F from a point in the single-phase region above the dew point curve, two immiscible liquid phases formed upon isothermal condensation of the saturated vapor phase, a phenomenon termed double retrograde condensation by van der Waal.<sup>23</sup>

The phase envelopes of mixtures containing 30.00 and 49.82% ethane could not be completed because of equipment limitations, but it is expected that mixtures in the range of 10-60% ethane will exhibit behavior similar to that of the 15% mixture. The phase boundary (P-T) curves for the 5 and 68% ethane mixtures terminate in the three-phase locus and give limits beyond which the double retrograde phenomenon does not extend. Each of the retrograde processes is considered in detail in Sec. III of Discussion.

#### V. Gas Phase Pressure-Volume-Temperature Data

Constant density (isometric) pressure-temperature data for five mixtures of ethane and nitrogen were determined over the temperature range from the two-phase boundary curve to  $+110^{\circ}$ F, and pressures to 4000 psia; they constitute the primary P-V-T data. The compositions of the five mixtures investigated and the experimental data are recorded in Table II, Tabulated Data. Fig. J presents a plot of the isometric data for the 50.26% ethane-49.74% nitrogen mixture. The two-phase dew and bubble point boundary curve for the mixture is shown as a dashed line. The behavior illustrated is typical of that exhibited by the other four mixtures; seven or eight isometrics were determined for each mixture.

The nearly linear variation of pressure with temperature for the isometrics facilitates the use of this type of plot for extrapolation of experimental data to higher temperatures, and interpolation between experimental temperatures. The isometrics are nearly linear in the gas-phase as well as two-phase regions, but the slopes of the lines are different in the two regions. Phase boundary data can be obtained from the intersection of the gasphase and two-phase lines, as shown in Fig. J (the interpolated points). The phase boundary data thus obtained do not have the accuracy of the primary data obtained with dew and bubble point apparatus, as visual observation of the dew point is not made, and the isometrics are not truly linear. For all five mixtures the isometrics exhibit a slight downward curvature for densities lower than the critical density, and then exhibit a slight upward curvature at densities higher than the critical. This is in accord with the general behavior of pure substances. The isometric type of plot is not used extensively in engineering calculations; isometrics for the other four mixtures are not presented graphically.

For use in engineering calculations, the most general method of presenting the P-V-T behavior of gas mixtures is in the form of compressibility



Fig. J.—Experimental Isometric Pressure-Temperature Data for a 50.26% Ethane-49.74% Nitrogen Mixture

factor plots. The compressibility factor, z, in a modification of the ideal gas law to permit calculating the behavior of actual gases, is defined by the equation:

$$z = P/RT\rho = PV/RT$$

P = absolute pressure

R= universal gas law constant, the value of which depends only upon the units used to express the pressure, temperature, and density, and not upon the nature of the gas

T = absolute temperature

ho = 
m density of the gas in moles per unit volume

 $V = molal volume = I/\rho$ 

The compressibility factor is a measure of the deviation of a gas from the ideal gas behavior and is 1.000 for an ideal gas. Its value is readily calculated by application of the above equation to the experimentally measured pressure, temperature and density. Compressibility factors plotted versus pressure along lines of constant temperature are shown in Fig. K for five mixtures. Comparisons of these data with those obtained by an equation of state are presented in **Discussion**.





# Table F.-CALCULATED SATURATED LIQUID AND VAPOR DENSITIES FOR ETHANE-NITROGEN MIXTURES

95.02%	C₂H₀	84.9	9% C2H6	- 15.01%	N <sub>2</sub>	68.31%	C₂H₀	15.03%	C <sub>2</sub> H <sub>6</sub>	1.98%	C <sub>2</sub> H <sub>6</sub>
4.98%	N <sub>2</sub>	Run I		Run 2		31.69%	N2	84.97%	, N <sub>2</sub>	98.02°/	N2
°F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc
52.0	0.3713	61.5	0.2823	23.4	0.3961	-150.0	0.5915	-146.5	0.4247	-228.1	0.3940
32.0	0.4061	58.7	0.2974	-0.4	0.4355	-155.0	0.5967	-173.2	0.4921	-232.0	0.4288
10.0	0.4344	54.0	0.3179	-45.7	0.4923	-155.0	0.5929	-202.0	0.5528	-240.0	0.488
-20.0	0.4632	50.0	0.3315	-47.4	0.4771	-165.0	0.6029			-249.0	0.525
-20.0	0.4678	42.0	0.3545		0.5006	-172.8	0.6122			-268.0	0.583
50.0	0.4947	-45.0	0.4880	-100.0	0.5282	-184.0	0.6185	5.1%	C <sub>2</sub> H <sub>6</sub>		
	0.5202	-70.0	0.5103	-100.0	0.5303	-197.8	0.6289	94.9%	N <sub>2</sub>		
-120.0	0.5509	-100.0	0.5360	-130.0	0.5642	-207.0	0.6359	Temp	Density		
-155.0	0.5757	-130.0	0.5670	-155.0	0.5760		0.6386		gm/cc		
-187.0	0.6011	-155.0	0.5850	-184.0	0.5970	-213.0	0.6433	-155.8	0.2328		
		-184.0	0.6058	-184.0	0.6031	-220.5	0.6497	-169.2	0.2721		
		-197.8	0.6209	-220.5	0.6276	-238.0	0.6600	-193.2	0.3341		
		-220.0	0.6341	-249.0	0.6414			-221.0	0.4111		
				2764	0.6611			-230.8	0 4054		

#### Saturated Liquid Densities Calculated from Phase Equilibrium Data

Saturated Vapor Densities Calculated with Equation of State

14.94% C <sub>2</sub> H <sub>6</sub> 85.06% N <sub>2</sub>		5.10% 94.90%	$C_2H_6$ $N_2$	1.98%C <sub>2</sub> H <sub>6</sub> 98.02% N <sub>2</sub>			
Temp °F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc		
-76.7	0.1841	-200.3	0.3573	-197.6	0.2615		
-71.7	0.1305	-180.9	0.2556	-178.9	0.1838		
-76.6	0.0821	-156.4	0.2320	-172.0	0.1515		
	0.0575	-135.5	0.0487	-178.3	0.0429		
-94.8	0.0411			-188.0	0.0275		
-118.9	0.0193						
-135.0	0.0117						
-170.0	0.0090						

#### Saturated Vapor and Liquid Densities Calculated from P-V-T Data

95.03° 4.97°	% C <sub>2</sub> H <sub>6</sub> % N <sub>2</sub>	85.01 14.99	% C₂H₅ % N₂	70.27° 29.73°	% C2H6 % N2	50.26°	50.26% C₂H <sub>6</sub> 29.9 49.74% N₂ 70.0		% C <sub>2</sub> H <sub>6</sub> % N <sub>2</sub>
Temp °F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc	Temp °F	Density gm/cc
9.3	0.4251	3.0	0.4144	-13.8	0.4129	-27.4	0.3702*		0.3272*
45.7	0.3720	35.9	0.3611	12.0	0.3614		0.3197*	-40.9	0.2767*
75.8	0.2998	56.4	0.3079	30.4	0.3094	5.1	0.2679*	-28.8	0.2262*
82.9	0.2306	66.0	0.2550	40.4	0.2577	15.0	0.2161*	-23.2	0.1762*
82.1	0.1600*	69.9	0.2152	48.2	0.2068*	20.0	0.1651*	-23.8	0.1264*
72.5	0.1073*	70.1	0.1599*	50.6	0.1563*	14.5	0.1134*		0.0758*
37.3	0.0547*	60.0	0.1039*	40.8	0.1052*	-7.6	0.0628*		0.0421*
		21.5	0.0483*	12.1	0.0540*				

\* Vapor densities

#### PHYSICAL-CHEMICAL PROPERTIES OF ETHANE-NITROGEN MIXTURES



Fig. L.—SATURATED VAPOR-LIQUID DENSITIES FOR ETHANE, NITROGEN, AND SOME OF THEIR MIXTURES

## VI. Saturated Liquid and Vapor Density Data

Saturated liquid and vapor densities of some of the mixtures investigated are presented in Table F and plotted versus temperature in Fig. L. The liquid density values were obtained in the dew and bubble point apparatus as described in Experimental Procedures. The saturated vapor density values for three mixtures were obtained by extrapolation of gas phase P-V-T data along the isometric until the dew point curve was intersected. This procedure gave the dew point temperature and pressure corresponding to a known density. The required extrapolation was very slight in all cases, since isometric data were obtained at temperatures almost down to the dew point curve. Errors in interpolating data obtained with the dew point apparatus to the compositions of the mixtures investigated in the P-V-T apparatus were minimized, since the compositions of those mixtures investigated in each apparatus were almost identical. The saturated vapor density values for two other mixtures were obtained by interpolation, from the intersections of the two-phase and singlephase region isometrics. Saturated vapor densities at low pressures were also calculated by use of the equation of state.

# DISCUSSION

#### I. Estimated Accuracy of the Data

#### A. Dew and Bubble Point Data

The principal sources of error in the dew and bubble point method can be attributed to:

- 1) Inaccuracies in the pressure and temperature measurements;
- 2) Fractionation and diffusion phenomena between the liquid in the cell and the warmer gas in the piping system;
- 3) Errors in measuring the dew point due to non-equilibrium conditions and overshooting the dew point; and
- 4) Errors in the composition of the gas mixture as prepared.

Temperature fluctuations of the cryostat were controlled to  $\pm 0.01^{\circ}$ F when readings were taken, and the pressure was measured to  $\pm 0.1$  psi. The thermocouple used to measure temperature was estimated to be accurate to  $\pm 0.2^{\circ}$ F.

Diffusion between the condensed liquid in the cell and vapor in the inlet tubing system could cause an error in the bubble point by changing the composition of the liquid in the cell from the bulk composition of the gas mixture as originally prepared. The concentration of ethane in the condensed liquid in the cell would tend to increase, which would lower the bubble point pressure. When the volume of the piping system and crosssectional area of the connecting tube were reduced, this source of error was minimized. For the equipment used in this work it was found that after a continuous 8 hour run, the maximum change in composition due to fractionation was 0.3 mole percent. The maximum fractionation occurred for mixtures containing 25 and 31.7 mole percent nitrogen between the temperatures of -80 and -150°F. In all other mixtures, composition change due to fractionation was very small, and error in bubble point pressure due to this change did not exceed 2 psi.

Errors in dew point pressure measurement, due to the nonequilibrium condition existing when liquid first formed on the cell wall, were minimized by the following procedure. The pressure in the cell was very gradually increased by addition of a small quantity of gas, until liquid droplets were detected on the walls of the cell. The valve to the cell was then closed, and the bath warmed, about 0.1°F, until all liquid disappeared. The bath was again cooled to the reappearance of liquid. This was taken as the dew point. Duplicate readings on the same mixtures and in some cases on duplicate mixtures were obtained and agreed within less than  $\pm 1$  psi or  $\pm 0.1^{\circ}$ F.

The error in the calculated composition of the gas mixture was estimated to be  $\pm 0.1\%$ .

All sources of error considered, the dew and bubble points for each mixture investigated, assuming that composition of the mixtures as calculated was correct, should be accurate to  $\pm 2$  psi or  $\pm 0.3^{\circ}$ F, whichever is larger.

#### B. P-V-T Data

The important sources of error are the calibration of the volume of the high-pressure bomb  $(\pm 0.02\%)$ , the calibration of the piston gage used to measure the pressure in the high-pressure bomb  $(\pm 0.05\%)$ , and the measurement of mass in the high-pressure bomb. The measurement of mass is subject to these sources of error: volumetric calibration of buret  $(\pm 0.01\%)$ , measurement of pressure in buret  $(\pm 0.03\%)$ , measurement of temperature in buret  $(\pm 0.01\%)$ , and the compressibility factor of gas in buret  $(\pm 0.05)$ .

Estimation of the maximum probable error in the data is difficult, since most of the errors are calibration errors rather than random experimental errors. The composition of the mixtures is probably accurate to  $\pm 0.03$  mole percent. The error in the reported values of the compressibility factors is probably within the range of 0.2 to 0.3%.

#### C. Internal Consistency of the Data

A quadruple-junction and two sets of triplejunction thermocouples were calibrated with a standard platinum resistance thermometer and were used to measure and check the temperature. The thermocouples were calibrated at the temperatures of liquid nitrogen, subliming  $CO_2$ , an icewater mixture, and at intermediate temperatures by maintenance of a constant temperature with the low-temperature bath. All the calibrations were made against a standard platinum resistance thermometer that had been calibrated by the U. S. Bureau of Standards. Two deadweight gages were used to measure pressures. Volume calibration of the system was made from time to time and found to be constant. The 25 and 31.7% nitrogen mixtures were duplicated after a period of four months, and experimental data were reproduced within the experimental accuracy. Phase boundary data on two of the mixtures were obtained with the P-V-T apparatus by determination of the intersection of the isometric lines in the two-phase and single-phase regions. These data agree very well with those obtained with the dew and bubble point apparatus, and show that the experimental data are constant. Cross plots of dew and bubble point data in the form of P-X, T-X and Y-X diagrams are consistent and smooth. K values when plotted against pressure on logarithmic scale are linear.

The duplication of three-phase data and the dewbubble points of pure components indicated that no marked impurities were present. Starting with any mixture, points on the three-phase locus agreed within 1 psi and  $0.1^{\circ}$ F.

#### II. Phase Equilibria

#### A. Phase Rule

The phase rule is a thermodynamic law, first stated by Gibbs,<sup>14</sup> that relates the number of phases present to the number of components and degrees of freedom (variants) for a heterogeneous system in equilibrium.<sup>19</sup> It is assumed that the only determinative variables are temperature, pressure, and composition of the phases. The rule is applicable to heterogeneous systems in either chemical or physical equilibrium, so long as they are dynamic and reversible, in contrast to the static equilibrium of mechanics.

The phase rule states that for a heterogeneous system having C components present in P phases in equilibrium, the number of degrees of freedom, F, is, F = C - P + 2. The number of intensive variables, consisting of temperature, pressure, and compositions of the different phases, which have to be specified to completely define the state of a system, is F. For example, a single component system if in a single phase requires both the temperature and pressure to be known to define the system; if two phases are present, and either temperature or pressure is known, the other will be known; if three phases are present, both temperature and pressure will be fixed, as the three phases can exist at only a single set of conditions.

#### B. Application of the Phase Rule to Binary Systems

For systems consisting of two components the phase rule indicates a maximum of four phases in equilibrium with each other when the degree of freedom, F, is zero. This will be a unique point, known as the quadruple point of the system, and will not depend on any intensive variables. The composition of each of the four phases and the temperature and pressure will be fixed. For the ethane-nitrogen system the four phases in equilibrium at the quadruple point are liquid-1, liquid-2, solid, and vapor, designated  $L_1$ ,  $L_2$ , S and V.

Similarly, when three phases are in equilibrium, there is one degree of freedom, and any one of the intensive variables can be specified. If all three phases are true solutions, the following types of equilibria will be possible:  $L_1-L_2-V$ ,  $L_1-L_2-S$ , L-S-V,  $L-S_1-S_2$ ,  $L-V_1-V_2$ ,  $S_1-S_2-V$ , and  $S-V_1-V_2$ . Many occurrences of L-S-V phase equilibrium have been reported in the literature; for example, the methane-water,<sup>16</sup> hydrogen sulfide-water,<sup>10</sup> and methane-carbon dioxide systems.<sup>12</sup> The ethane-nitrogen system exhibits the  $L_1-L_2-V$  three-phase phenomena, and it is possible that at lower temperatures than those investigated,  $L_1-L_2-S$  equilibrium would be exhibited.

When two phases are present in a binary mixture there are two degrees of freedom, and two of the intensive variables must therefore be specified to define the system. The types of two-phase equilibrium possible are:  $S_1$ - $S_2$ , S-L, S-V,  $L_1$ - $L_2$ , L-V, and  $V_1$ - $V_2$ . The  $S_1$ - $S_2$  and S-L equilibria are important in the study of metals. Recent data for the ammonia-helium system reported by Tsiklis<sup>22</sup> have indicated the existence of  $V_1$ - $V_2$  equilibria.

The L-V equilibrium data are of most importance in the study of hydrocarbon systems. The ethane-nitrogen system exhibited L-V and  $L_1-L_2$ equilibria in the two-phase regions.

#### C. Liquid-Liquid Equilibria

If two partially miscible liquids are mixed, two liquid phases of different composition will result throughout a limited overall composition range, with both phases containing some of each component.<sup>20</sup> The addition of component A to a twophase mixture of A and B at constant temperature and pressure will increase the relative amount of the phase rich in A, and decrease that of the phase lean in A. When a two-phase two-component system is maintained at a constant pressure, sufficiently high to prevent formation of a gas phase, the system will be univariant and for each temperature there will be definite concentrations of the components in each liquid phase. As the temperature is changed, the composition of the two solutions will change, and two solubility curves will

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be obtained, showing the solubility of A in B, and B in A, as a function of temperature. The solubility may decrease or increase with increasing temperature, depending on whether heat is evolved or absorbed when one liquid is dissolved in the other. The temperature at which the two phases become completely miscible is called the *critical solution temperature*, and may exist as either a maximum, a minimum, or both. The ethane-nitrogen system exhibits phenomena indicating the existence of a maximum critical solution temperature.

The effect of pressure on the critical solution temperature depends, according to the principle of Le Chatelier and the equation of Clapeyron, on the volume change which occurs when one of the pure components is added to a nearly saturated solution. The critical solution temperature of the ethane-nitrogen system as a function of pressure is shown in Fig. H, page 11.

#### D. Liquid-Liquid-Vapor Equilibria

A two-component system existing in three phases has one degree of freedom. When one variable, such as temperature, is specified, the system becomes invariant and it can be deduced that at constant temperature the vapor pressure is constant so long as two liquid phases are present. If vapor pressure is plotted versus overall composition at constant temperature, as illustrated for the ethane-nitrogen system in Fig. 1, the curve will exhibit a horizontal portion for the region over which a vapor and two liquid phases exist. This horizontal portion may be either above or between the vapor pressures of the pure components at that temperature; it is not possible for the vapor pressure of a system of two liquid phases to be lower than that of the least volatile component. As shown in Fig. 2, in the ethane-nitrogen system the vapor pressure of the liquid-liquid occurrence lies between the vapor pressures of the pure components.

Similarly, when temperatures are plotted versus overall composition at constant pressure, the curve will exhibit a horizontal portion for the region over which a vapor and two liquid phases coexist. This horizontal portion may be either below or between the boiling temperatures of the two pure components; the three-phase coexistence temperature of a system cannot be higher than the boiling point of the least volatile component. The phase behavior of the ethane-nitrogen system at 400 psia as a function of temperature is shown in Fig. 3.



Fig. 1.—Isothermal Vapor Pressure-Composition Curves for the Ethane-Nitrogen Three-Phase Region

1. Pressure-Composition Diagram. An isothermal pressure-composition diagram for the ethanenitrogen binary system at  $-240^{\circ}$ F is presented in Fig. 2. The horizontal straight line ABC represents the three-phase pressure for this temperature. There is a break in the slope of the dew point curve at this three-phase pressure. The lines AD and BE represent the relations of bubble point pressure to composition for the two liquids. From the slope of the lines AF and BG it is seen that the liquids of this system become more miscible with an increase in pressure.

It is of interest to follow the path of an isothermal condensation on this diagram. If a gaseous mixture corresponding to  $X_i$  is compressed isothermally, the system remains entirely gaseous until the dew point is reached at H. At this point condensation commences and continues with further increase in pressure until the three-phase line is reached, beyond which all of the gas will be condensed and the system composed entirely of the two liquid phases represented by points A and B. If the pressure is still further increased, the system would move along the line JK and the only



Fig. 2.—Isothermal Pressure-Composition Diagram for the Ethane-Nitrogen System at —240°F

change in phase would be that resulting from the effect of pressure upon the miscibility of the two liquids.

During the course of such an isothermal condensation, the relative quantities of any two phases present can be determined by comparison of the lengths of such lines as MN and NP. However, at the three-phase pressure, the relative quantities of the three phases cannot be determined from this diagram. On the liquid-vapor side of this pressure, the quantities of liquid and gas phases are given by the relative lengths of the lines JC and JA, respectively. On the liquid-liquid side of this pressure, the quantities of the two liquid phases are given by the relative lengths of the lines JA and JB.

A somewhat different type of condensation is encountered at compositions between  $X_B$  and  $X_C$ , such as  $X_2$  in Fig. 2. In this case the system remains entirely gaseous until the dew point is reached at Q, where a liquid phase corresponding to T begins to separate. This process continues until the three-phase pressure is reached at R, where liquids of compositions corresponding to B and A, and a gas corresponding to C, coexist. With a minute increase in pressure, liquid A disappears and the system is made up entirely of gas of a composition corresponding to C and the liquid



Fig. 3.—Isobaric Temperature-Composition Diagram for the Ethane-Nitrogen System at 400 Psia

at B. With further increase in pressure, the quantity of the gas phase decreases, and the system becomes entirely liquid at S. At compositions from  $X_D$  to  $X_A$  normal condensation is observed, since only a liquid and a gas phase are involved.

2. Temperature-Composition Diagram. An isobaric temperature-composition diagram of partialmiscibility regions of the binary ethane-nitrogen system is shown in Fig. 3. The horizontal line ABC in Fig. 3 represents the three-phase temperature for this pressure. Lines AD and BE are bubble point lines, while DCE is a dew point curve. As shown by lines AF and BG, the mutual solubility of the liquids increases as temperature decreases.

In a distillation, the total composition of the mixture as it first boils must lie on one of three curves, DA, BE or AB: if along DA or BE the mixture is homogeneous; if along AB, it is heterogeneous. If the composition of the mixture lies on the curve DA, say at H, it will have a vapor J much richer in nitrogen. As distillation is continued, the boiling point of the remaining liquid will rise toward that of pure ethane. If the mean composition of distillate is taken to be K, somewhere between B and A the distillate will separate into two layers on condensation. If the condensed phase is now distilled, it will boil at constant temperature as long as two layers are present, giving a distillate of constant composition C while the relative quantity of the layer of composition A increases. If the distillate of composition C is subjected to fractional distillation, pure nitrogen will be obtained.

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#### III. Retrograde Behavior in the Ethane-Nitrogen System

#### A. Isothermal Retrograde Condensation

This phenomenon may be illustrated by the behavior of the mixture in the 68.31% ethane-31.69%nitrogen diagram of Fig. 4. The mixture in the single phase at A may be expanded to B, the upper dew point, at which pressure the first liquid will appear. Further pressure reduction causes continuous condensation until some point D is reached, where the liquid formed begins to vaporize, until at pressure E the entire quantity of liquid formed between B and D has been vaporized and the mixture is at its lower dew point. The condensation from B to D is retrograde, and may be further qualified as being isothermal and between dew points. From D to E normal vaporization occurs with expansion.

#### B. Isobaric Retrograde Vaporization Between Bubble Points

Referring again to the 68.31% ethane-31.69% nitrogen diagram in Fig. 4, the fluid at A may be cooled to F, at which temperature a bubble of vapor will appear and grow with further temperature reduction until some point G is reached. From G to H a temperature decrease causes normal condensation. The vaporization from F to G is retrograde, and may be further qualified as being isobaric and between bubble points. Moving in the opposite direction will cause opposite phenomena; for example, from D to B is retrograde vaporization, and G to F is retrograde condensation. The isothermal retrograde phenomenon may occur only above the critical temperature, C, and below the maximum temperature of two phases, J; the isobaric retrograde phenomenon may occur only above critical pressure, C, but below the maximum pressures of two phases, K. The retrograde phenomenon can occur only in the region corresponding to the cross-hatching.

The position of the critical point is shown between the maximum temperature, J, and the maximum pressure, K; however, this does not have to be. The point C can lie to the right, below maximum temperature J, or to the left, below maximum pressure K. The position of C below maximum temperature J has not been observed in the systems studied thus far, while location of C below maximum pressure K was observed in the 1.98% ethane-98.02% nitrogen system (curve 10, Fig. A, reproduced in Fig. 4).

#### C. Isobaric Retrograde Vaporization Between Dew Points

This phenomenon is illustrated by the behavior of the 1.98% ethane-98.02% nitrogen mixture in Fig. 4. The mixture in single phase at L may be cooled to M, where liquid will appear; on further cooling more condensation will take place until point N is reached, at which temperature the liquid



formed begins to vaporize until a temperature P is attained; there the entire quantity of liquid formed between M and N is vaporized. The vaporization from N to P is retrograde, and is further qualified as being isobaric and between dew points. Normal condensation occurs when the mixture is cooled from M to N.

#### D. Double Retrograde Condensation

In experiments on binary mixtures at high pressures it was found that two liquid layers would form, especially when one component was polar. Van der Waal discusses data on ethane-alcohol and carbon dioxide-nitrobenzene mixtures which formed two liquid layers.<sup>23</sup> A saturated vapor of systems of this type might give two liquids, instead of the usual single liquid formation, by retrograde condensation upon isothermal reduction of the pressure at temperatures above the critical. To distinguish the phenomena in which two liquids are condensed or vaporized in a retrograde manner, they were called "double retrograde" condensation or vaporization by van der Waal. The same nomenclature that has been used when a single liquid phase is condensed or vaporized applies when two liquid phases are condensed or vaporized, except for the prefix "double."

The phase boundary curve for a 15% ethane-85% nitrogen mixture in Fig. 4 shows that this mixture exhibits pronounced retrograde behavior and a tendency to form two liquid phases at or below —220°F below the phase envelope and above the three-phase locus. If the fluid in the single-phase region at Q is expanded isothermally at —228°F, it will form two liquid phases at a pressure of 1600 psia at R; on further reduction of pressure only the relative amount of the two phases will change until a pressure of 495 psia is reached at S, when a third or gas phase will appear. Below this pressure only a liquid and a vapor phase exist in equilibrium with each other.

It is believed that behavior of mixtures in the range of 10-60% ethane will be similar to that of 15% ethane-85% nitrogen. The 68.3% ethane mixture has a normal bubble point curve, which meets the three-phase locus from below at -223°F, very near the maximum coexistence temperature for three phases, while the phase boundary curve for the 5% ethane mixture exhibits a very large retrograde region and terminates in the three-phase locus curve from above at -230.0°F. For this mixture there is no clearly defined transition between dew and bubble points, since the liquid

forms two phases very close to the critical point. Any mixture containing more than 5% and less than 68.3% ethane will have the critical point much higher than  $-220^{\circ}$ F, and if it behaves normally should have a bubble point at this temperature. Normal bubble point curves will have to terminate in the three-phase locus or run below the locus, so mixtures containing more than 5% and less than 68.3% ethane should not exhibit normal bubble phenomena, but behave similar to the 15% ethane-85% nitrogen mixture.

The data of this investigation are not sufficient to show the phase boundary curve of the liquidvapor, liquid-liquid and liquid-solid regions that also terminate in the three-phase locus throughout its existence range. The locus has its lower terminus in the quadruple point for the system.

#### IV. Utility of the Data

#### A. Liquid-Vapor Phase Equilibrium Data

The liquid-vapor phase equilibrium data can be used directly to predict the pressure-temperature conditions required for the separation of mixtures of ethane and nitrogen into the pure components.

As mentioned previously, ethane-nitrogen mixtures form two immiscible liquid phases at temperatures below -220°F, pressures above the three-phase locus curve but below the dew point curve, and in the composition range of approximately 5-80% ethane. As the vapor pressure during the existence of the three phases lies between the vapor pressures of the pure components, it is possible to separate the mixture into pure components by distillation.

The degree of separation of ethane from nitrogen obtained solely by partial condensation or evaporation can be readily determined from Fig. C. Consider, for example, a mixture composed of 70% ethane-30% nitrogen, held at a pressure of 300 psia. Referring to Fig. C, the dew point will be found to be -9.2°F. Cooling below this temperature will, in the absence of supercooling, bring about condensation of liquid to an extent which depends on the temperature. Referring to the figure, it will be seen that when the above mixture is brought to a temperature of -100°F at 300 psia a partial separation will occur: a liquid composed of 94.3% ethane and 5.7% nitrogen, and a vapor 14.0% ethane and 86.0% nitrogen, will result. Comparison of the lengths of the temperature tie-line to the left and right of the feed composition permits calculation of the extent of lique-

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faction; for the above example:

$$rac{86.0-30.0\%}{86.0-5.7\%} imes 100=69.7\%$$

These figures indicate the degree of separation and liquefaction obtainable in a perfect separator.

Further separation could be obtained by use of a fractionator in which contact between a rising vapor stream and a descending liquid stream would be effected on a series of bubble cap plates or their equivalent. The data of Fig. C can be used to estimate the number of equilibrium vaporizations required for a desired separation of ethane from a given mixture of nitrogen and ethane.

The separation of a feed mixture into nearly pure ethane and up to 99.8% nitrogen can be carried out in an ordinary distillation column so long as operation is maintained above the three-phase line. To obtain a pure nitrogen product, the 99.8% nitrogen stream from this column could be chilled to below —248°F and fed to a second column. In this unit separation into pure nitrogen and a liquid of the composition indicated at E could be attained. The liquid of composition E could then be returned to the first column and retreated.

This process is more easily described by use of a Y-X diagram. Other procedures may be required for rigorous calculation, but for the sake of simplicity Fig. 5 was prepared; it is a Y-X diagram to which the McCabe-Thiele graphical method of computation has been applied. No attempt will be made to present the method in detail, and the reader is referred to standard reference works on fractional distillation.

Fig. 5 employs an equilibrium curve for a pressure of 300 psia, together with the lines used for computing the number of equilibrium vaporizations required to separate a mixture of 70% ethane and 30% nitrogen into two streams, 98% ethane-2% nitrogen and 2% ethane-98% nitrogen. Perfect separation is theoretically impossible. The numbered points on the equilibrium line show the composition of the equilibrium liquid and vapor at each theoretical vaporization; I is the top contact. A on the operating line shows the relation of the composition of the liquid I to the composition of



Fig. 5.—Equilibrium Composition Diagram at 300 Psia Showing the Determination of the Number of Theoretical Contact Stages Required to Effect a Selected Degree of Separation of Ethane and Nitrogen from a Specific Mixture

the vapor rising from vaporization at 2. There are separate operating lines for the rectifying section above the introduction of the feed, and for the stripping section. The operating lines represent material balance lines; their location depends on the heat content or enthalpy of the feed (that is, whether it is at its bubble point or only partially liquefied), and also on the reflux ratio. Reflux is obtained by condensing part of the vapor from the top of the column and returning it to the top of the column, so there will be liquid to interact with the rising vapor.

In the illustration given in Fig. 5, two theoretical equilibrium vaporization stages are required to effect the desired separation under the conditions selected. The effect of an increase in pressure will be to reduce the curvature of the equilibrium line, which will increase the number of vaporizations required for the separation. Thus, the higher the operating pressure, the greater the number of vaporizations, and, the greater the required height of the fractionator.

Also, with column operating pressure and composition of the overhead stream fixed, the maximum temperature of the refrigerant used in the reflux condenser is easily determined. This temperature must be at least as low as the dew point of the overhead product at the column pressure.

The liquid-vapor equilibrium data presented in this Bulletin and shown in Fig. 1 also serve to fix the temperature and pressure levels in heat exchangers and condensers. These conditions may be easily evaluated from the plot.

B. Gas Phase Pressure-Volume-Temperature Data

The experimental P-V-T data on the ethanenitrogen mixtures can be used to calculate the thermodynamic properties of the ethane-nitrogen system. This is most conveniently and accurately accomplished by means of an equation of state. A modification of the Benedict-Webb-Rubin equation developed at the Institute can be used with a high degree of accuracy for these calculations.

In addition, P-V-T data for the mixtures may be used to calculate the fugacity and activity coefficients of ethane and nitrogen in liquid-phase mixtures of the two. Since the fugacity of a component of a liquid solution is equal to the fugacity of the components in the gas phase in equilibrium with the liquid phase, it is only necessary to determine the fugacity of the component in the gas phase. This can be done by using the gas phase P-V-T data and the equation of state.

This latter use of the P-V-T data is of little importance for the binary ethane-nitrogen system, but is of great importance in predicting the phase behavior of ternary and multicomponent mixtures containing ethane and nitrogen.

Equation of State. A means of predicting the compressibility and the thermodynamic properties of a gas mixture is the "equation of state" method, in which the constants in the equation of state for the mixture are evaluated from constants of the pure components of the mixture. This is the method presented by Beattie *et al.*<sup>2, 3</sup> and Benedict *et al.*<sup>4, 5</sup> and is generally more accurate than the pseudocritical method. It is, however, very time-

consuming. The modified Benedict-Webb-Rubin equation of state is:

$$\begin{split} P &= RT\rho + \left(B_{o}RT - A_{o} - \frac{C_{o}}{T^{2}} - \frac{D_{o}}{T^{4}}\right)\rho^{2} + \left(bRT - a\right)\rho^{3} \\ &+ \left(\frac{c}{T^{2}} + \frac{\delta}{T^{4}}\right)\rho^{3}\left(1 + \gamma\rho^{2}\right)e^{-\gamma\rho^{2}} + a\alpha\rho^{6} \quad \text{[Equation I]} \\ & P = \text{absolute pressure} \\ R = \text{universal gas constant} \\ T = \text{absolute temperature} \\ \rho = \text{density} \end{split}$$

 $A_o, B_o, C_o, D_o, a, b, c, \delta, \alpha$ , and  $\gamma$  are empirical constants, the values of which depend on the composition of the gas mixtures. Benedict *et al.* recommended the following combining rules for determining the value of the constants for mixtures from the constants of the pure gases making up the mixture:

$$B_{om} = \sum_{i} x_{i} B_{oi} \qquad (\text{Linear combination})$$
or
$$B_{om} = \frac{1}{4} \left(\sum_{i} x_{i} B_{oi}\right) + \frac{3}{4} \left(\sum_{i} x_{i} B_{oi}^{1/3}\right) \times \left(\sum_{i} x_{i} B_{oi}^{2/3}\right) \qquad (\text{Lorentz combination})$$

$$A_{om} = \left(\sum_{i} x_{i} A_{oi}^{1/2}\right)^{2}$$

$$C_{om} = \left(\sum_{i} x_{i} C_{oi}^{1/2}\right)^{2}$$

$$a_{m} = \left(\sum_{i} x_{i} a_{i}^{1/3}\right)^{3}$$

$$b_{m} = \left(\sum_{i} x_{i} b_{i}^{-1/3}\right)^{3}$$

$$c_{m} = \left(\sum_{i} x_{i} \alpha_{i}^{-1/3}\right)^{3}$$

$$\alpha_{m} = \left(\sum_{i} x_{i} \alpha_{i}^{-1/3}\right)^{3}$$

$$\gamma_{m} = \left(\sum_{i} x_{i} \gamma_{i}^{-1/2}\right)^{2}$$

where  $x_i$  equals mole fraction of the i<sup>th</sup> component in the mixture. By analogy to these rules, the  $D_o$ and  $\delta$  terms in the modified equation should be combined by linear square root and linear cube root, respectively. This would result in the following rules for the  $D_o$  and  $\delta$  constants:

$$D_{om} = (\sum_{i} x_{i} D_{oi}^{1/2})^{2}$$

and

$$\delta_{m} = (\sum_{i} x_{i} \, \delta_{i}^{1/3})^{3}$$

#### Table 1

MODIFIED BENEDICT-WEBB-RUBIN EQUATION OF STATE CONSTANTS FOR C<sub>2</sub>H<sub>6</sub> AND N<sub>2</sub>

	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>
Mol. wt	30.047	28.014
B	0.0627724	0.0484824
A	4.15556	1.27389
C.	179,592.0	4273.00
D		$7.61781  imes 10^{6}$
b	0.0111220	0.00232373
a	0.345160	0.017844
c	32,767.0	475.000
δ	_	832,000
α	0.000243389	0.00015300
Y	0.0118000	0.006500
P =	atmospheres	
ρ=	gram moles/liter	
T=	°Kelvin (°C + 273.1	6)
R =	universal gas constant	= 0.08206

Since the  $D_{o}$  and  $\delta$  terms are zero for ethane, these rules reduce to:

and

$$\delta_m = \delta_{N_2} X_{N_2}{}^{s}$$

 $D_{om} = D_{oN_2} X_{N_2}^2$ 

where  $X_{N_2}$  is the mole fraction of nitrogen present in the mixture.

Values of the constants for ethane taken from the paper of Benedict, Webb and Rubin,<sup>4</sup> and for nitrogen from the work of Bloomer and Rao,<sup>7</sup> are tabulated in Table 1. Since the values of  $B_o$  for ethane and nitrogen are not too greatly different, the values of  $B_{om}$  obtained by the considerably more complicated Lorentz combination will be only slightly different from those obtained by the linear combination method. The Lorentz combination gives smaller values, which is in the right direction to improve the agreement between the calculated and observed values; however, the correction is only a small fraction of that required.

Pressures calculated by use of the modified Benedict-Webb-Rubin equation of state and the above combining rules, with the linear combination rule for  $B_o$ , are compared with experimentally measured pressure in Table 2. The agreement between the observed values and those calculated by this method is only fair. To improve the agreement between the calculated and the observed pressure values, an empirical correction factor for the equation of state was determined and applied successfully to methanenitrogen<sup>8</sup> and methane-ethane systems:<sup>9</sup>

$$P_{\text{corrected}} = P_{\text{calc by Eq I}} - (2x_1 x_2) (0.0625 \rho^2)$$
[Equation 2]

A similar correction factor was recently applied by Benedict and Stutler for the methane-nitrogen system.

The correction given by Equation 2 may also be obtained as an empirical correction to the combination rule for the  $A_o$  term in the equation of state:

$$A_{\rm om} = (\sum_{i} x_i A_{\rm oi}^{1/2})^2 + 0.125 x_1 x_2$$

[Equation 3]

For the ethane-nitrogen system the values of pressure calculated by the equation of state were lower than the observed values, so the sign of the correction term had to be reversed. With this correction the average error of the calculated pressures is reduced to a value only slightly greater than the average error obtained in fitting the equation to pure components.

To determine the nature of the deviation (Pobserved - Pcalculated), plots of deviation versus temperature at constant density and composition, and deviation versus density at constant temperature and composition, were prepared. No simple relationship of the deviation with temperature, density or composition was found. Unlike the methane-ethane and methane-nitrogen systems, the deviation is not independent of temperature and composition but is a function of 1/T and  $X_{N_2}$ . Also the deviation is not proportional to  $\rho^2$ , as is assumed in the empirical correction term, but to some power less than 2, of the order of 1.5. However, taking the empirical correction term to be proportional to  $\rho^2$  seems to take into account the influence of temperature, composition and density, as can be seen from the reduction in the average deviation in Table 2.

# Table 2.—COMPARISON OF EXPERIMENTAL PRESSURES WITH PRESSURES CALCULATED FROM EQUATION OF STATE (B. Averaged by Linear Combination)

Tomporature		95.03% C <sub>2</sub> H <sub>6</sub> — 4.97% N <sub>2</sub> Mixture Density in Gram Moles per Liter										
°K		1.8218	3.5735	5.3342	7.6840	10.0000	12.3409	14.1165	Deviation			
				Press	ure in Atmosp	oheres						
316.49	Experimental	35.670	53.151	62.514	72.203	90.827	157.25	294.15				
	% Error	0.41	0.15	0.39	0.15	0.36	0.00		1.20			
305.38	Experimental	33.485	48.149	53.974	58.921	69.339	121.03	242.03				
	Calculated	33.348	48.088	54.050	58.637	68.814	120.44	259.74				
	% Error	0.41	0.13	0.14	0.48	0.76	0.49	-7.32	1.39			
	Average % Error	0.41	0.14	0.27	0.32	0.56	0.25	7.14	1.30*			

\* Overall Average % Error. Excluding the 14.1165 isometric, the average = 0.32%. By use of Equation 3, the average (excluding the 14.1165 isometric) = 0.25%.

Temperature				De	nsity in Gra	m Moles per	· Liter			%
°K		1.6159	3.4824	5.3521	7.2211	8.5540	10.3262	12.1125	13.8822	Deviation
					Pressure i	n Atmospher	es			
316.49	Experimental	34.011	58.482	74.439	88.526	101.76	130.06	188.64	-	
	Calculated	33.950	58.091	73.567	87.681	100.12	125.97	180.68		
	% Error	0.18	0.67	1.18	0.96	1.64	3.24	4.40		1.75
305.38	Experimental	32.145	53.593	65.950	76.177	85.710	106.99	155.49	264.64	
	Calculated	32.104	53.307	65.403	75.421	84.174	103.19	147.51	258.57	
	% Error	0.13	0.53	0.84	1.00	1.82	3.68	5.35	2.30	1.96
294.27	Experimental	30.262	48.662	—		70.467	84.964	122.97	217.36	
	Calculated	30.235	48.457			68.352	80.613	114.22	210.12	
	% Error	0.09	0.42	-	_	3.09	5.40	7.66	3.33	3.33
	Average % Error	0.13	0.54	1.01	0.98	2.25	4.11	5.80	2.82	2.28*

85.01% C<sub>2</sub>H<sub>6</sub> — 14.99% N<sub>2</sub> Mixture

\* Overall Average % Error. By use of Equation 3, the average = 1.22%.

#### 70.27% C2H6 - 29.73% N2 Mixture

Tomperature				D	ensity in Gra	am Moles pe	r Liter			%
°K		1.8294	3.5643	5.2988	7.0070	8.7288	10.4764	12.2261	13.9505	Average Deviation
					Pressure in	n Atmosphere	es			
316.49	Experimental Calculated % Error	39.569 39.772 —0.51	66.909 66.806 0.15	89.671 88.665 1.13	111.34 109.88 1.33	137.44 135.47 1.45	176.02 172.69 1.93	238.58 233.88 2.01		1.22
305.38	Experimental Calculated % Error	37.493 37.703 —0.56	62.133 62.129 0.01	81.770 80.845 1.14	99.837 98.383 1.48	121.68 119.35 1.95	153.95 150.28 2.44	208.05 202.52 2.73	303.38 304.33 —0.31	1.33
294.27	Experimental Calculated % Error	35.431 35.615 —0.52	57.267 57.400 —0.23	73.877 72.972 1.24	88.500 86.880 1.98	106.12 103.30 2.73	132.53 127.98 3.55	178.10 171.21 4.02	262.48 260.64 0.71	1.87
238.17	Experimental Calculated % Error	33.329 33.503 —0.52	51.973 52.618 —1.23	65.685 65.042 0.99	77.130 75.369 2.34	90.930 87.325 4.13	111.42 105.82 5.29	148.50 139.97 6.10	221.16 216.77 2.03	2.83
	Average % Error	0.53	0.40	1.12	1.78	2.56	3.30	3.74	1.02	1.83*

\* Overall Average % Error. By use of Equation 3, the average = 0.86%.

(Continued on next page)

# Table 2 (Cont.).—COMPARISON OF EXPERIMENTAL PRESSURES WITH PRESSURES CALCULATED FROM EQUATION OF STATE (B<sub>o</sub> Averaged by Linear Combination)

	Density in Gram Moles per Liter											
	2.1574	3.8937	5.6697	7.4174	9.1995	10.9674	12.6908	Average Deviation				
		a.	Pressu	ure in Atmosp	heres							
Experimental	47.101	77.851	107.03	137.14	173.80	222.15	290.35					
Calculated	46.990	77.579	106.34	135.96	171.68	218.45	285.11					
% Error	0.24	0.35	0.64	0.86	1.22	2.56	1.80	1.10				
Experimental	44.631	72.918	98.945	125.50	157.66	200.40	260.96					
Calculated	44.569	72.586	98.160	124.02	155.00	195.70	254.59					
% Error	0.14	0.46	0.79	1.18	1.69	2.34	2.44	1.29				
Experimental	42.216	67.923	90.787	113.73	141.53	178.50	231.78					
Calculated	42.131	67.551	89.931	112.04	138.32	172.98	224.04					
% Error	0.20	0.55	0.94	1.49	2.27	3.09	3.34	1.70				
Experimental	38.493	60.513	78.470	96.237	117.79	146.60	188.81					
Calculated	38.291	59.749	77.136	93.425	112.42	137.68	176.46					
% Error	0.52	1.26	1.70	2.92	4.56	6.09	6.54	3.37				
Average % Error	0.23	0.66	0.99	1.61	2.43	3.52	3.53	1.86*				
	Experimental Calculated % Error Experimental Calculated % Error Experimental Calculated % Error Experimental Calculated % Error Average % Error	2.1574           Experimental         47.101           Calculated         46.990           % Error         0.24           Experimental         44.631           Calculated         44.569           % Error         0.14           Experimental         42.216           Calculated         42.131           % Error         0.20           Experimental         38.493           Calculated         38.291           % Error         0.52           Average % Error         0.23	2.1574         3.8937           2.1574         3.8937           Calculated         46.990           77.579         7.579           % Error         0.24           Calculated         44.631           72.918         72.586           % Error         0.14           Calculated         44.569           % Error         0.14           Calculated         42.131           67.923         Calculated           % Error         0.20           % Error         0.20           % Error         0.20           % Error         0.20           % Error         0.55           Experimental         38.493           Calculated         38.291           9% Error         0.52           Average % Error         0.23	Experimental         47.101         77.851         107.03           Calculated         46.990         77.579         106.34           % Error         0.24         0.35         0.64           Experimental         44.631         72.918         98.945           Calculated         44.569         72.586         98.160           % Error         0.14         0.46         0.79           Experimental         42.216         67.923         90.787           Calculated         42.131         67.551         89.931           % Error         0.20         0.55         0.94           Experimental         38.493         60.513         78.470           Calculated         38.291         59.749         77.136           % Error         0.52         1.26         1.70           Average % Error         0.23         0.66         0.99	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	50.26% C <sub>2</sub> H <sub>6</sub> — 49.74% N <sub>2</sub> Mixtu           Density in Gram Moles per Liter           2.1574         3.8937         5.6697         7.4174         9.1995           Pressure in Atmospheres           Experimental         47.101         77.851         107.03         137.14         173.80           Calculated         46.990         77.579         106.34         135.96         171.68           % Error         0.24         0.35         0.64         0.86         1.22           Experimental         44.631         72.918         98.945         125.50         157.66           Calculated         44.569         72.586         98.160         124.02         155.00           % Error         0.14         0.46         0.79         1.18         1.69           Experimental         42.216         67.923         90.787         113.73         141.53           Calculated         42.131         67.551         89.931         112.04         138.32           % Error         0.20         0.55         0.94         1.49         2.27           Experimental         38.493         60.513         78.470         96.237         117.79           Calculate	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $				

\* Overall Average % Error. By use of Equation 3, the average = 0.65%.

29.96% C2H6 - 70.04% N2 Mixture

	Density in Gram Moles per Liter											
	1.4661	2.6365	4.3900	6.1381	7.8822	9.6335	11.3803	Deviation				
			Press	ure in Atmosp	heres							
Experimental	34.941	60.915	98.224	136.00	177.23	225.26	285.40					
Calculated	34.909	60.813	98.104	135.84	176.88	224.82	283.91					
% Error	0.09	0.17	0.12	0.11	0.19	0.20	0.52	0.20				
Experimental	33.431	57.989	92.808	127.62	165.33	209.18	264.01					
Calculated	33.422	57.887	92.620	127.27	164.61	208.52	261.65					
% Error	0.03	0.18	0.20	0.27	0.44	0.32	0.89	0.33				
Experimental	31.920	55.042	87.323	119.16	153.33	192.89	242.61					
Calculated	31.922	54.949	87.113	118.68	152.33	191.29	239.40					
% Error	0.01	0.17	0.24	0.40	0.65	0.83	1.32	0.50				
Experimental	29.661	50.626	78.967	106.48	135.36	168.69	210.40					
Calculated	29.663	50.515	78.799	105.72	133.84	166.12	206.02					
% Error	-0.01	0.22	0.21	0.72	1.12	1.52	2.08	0.55				
Experimental	27.368	46.486	70.638	93.570	117.28	144.38	178.31					
Calculated	27.375	46.011	70.345	92.565	115.15	140.74	172.37					
% Error	0.03	1.03	0.41	1.07	1.81	2.52	3.33	1.46				
Experimental	25.857		-	85.370	105.22	128.30	157.28					
Calculated	25.842	—	-	83.746	102.66	123.83	150.00					
% Error	0.06	-	-	1.90	2.43	3.48	4.63	2.50				
Average % Error	0.04	0.35	0.24	0.75	1.11	1.48	2.13	0.84*				
	Experimental Calculated % Error Experimental Calculated % Error Experimental Calculated % Error Experimental Calculated % Error Experimental Calculated % Error Experimental Calculated % Error Average % Error	1.4661           Experimental         34.941           Calculated         34.909           % Error         0.09           Experimental         33.431           Calculated         33.422           % Error         0.03           Experimental         31.920           Calculated         31.922           % Error         -0.01           Experimental         29.661           Calculated         29.663           % Error         -0.01           Experimental         27.368           Calculated         27.375           % Error         -0.03           Experimental         25.857           Calculated         25.857           Calculated         25.842           % Error         0.06	I.4661         2.6365           Experimental         34.941         60.915           Calculated         34.909         60.813           % Error         0.09         0.17           Experimental         33.431         57.989           Calculated         33.422         57.887           % Error         0.03         0.18           Experimental         31.920         55.042           Calculated         31.922         54.949           % Error         -0.01         0.17           Experimental         29.661         50.626           Calculated         29.663         50.515           % Error         -0.01         0.22           Experimental         27.368         46.486           Calculated         27.375         46.011           % Error         -0.03         1.03           Experimental         25.857            Calculated         25.842         -           % Error         0.06         -	Experimental         34.941         2.6365         4.3900           Pressi         Pressi           Calculated         34.999         60.813         98.104           % Error         0.09         0.17         0.12           Experimental         33.431         57.987         92.808           Calculated         33.422         57.887         92.620           % Error         0.03         0.18         0.20           Experimental         31.920         55.042         87.323           Calculated         31.922         54.949         87.113           % Error         -0.01         0.17         0.24           Experimental         29.661         50.626         78.967           Calculated         29.663         50.515         78.799           % Error         -0.01         0.17         0.24           Experimental         27.368         46.486         70.638           Calculated         27.375         46.011         70.345           % Error         -0.03         1.03         0.41           Experimental         25.857         -         -           Calculated         25.842         -         -         -<	Experimental         34.941         60.915         98.224         136.00           Calculated         34.909         60.813         98.104         135.84           % Error         0.09         0.17         0.12         0.11           Experimental         33.431         57.989         92.808         127.62           Calculated         33.422         57.887         92.620         127.27           % Error         0.03         0.18         0.20         0.27           Experimental         31.920         55.042         87.323         119.16           Calculated         31.922         54.949         87.113         118.68           % Error         -0.01         0.17         0.24         0.40           Experimental         29.661         50.626         78.967         106.48           Calculated         29.663         50.515         78.799         105.72           % Error         -0.01         0.22         0.21         0.72           % Error         27.375         46.011         70.345         92.565           % Error         -0.03         1.03         0.41         1.07           Experimental         27.368         46.486	Experimental         33.431         57.987         92.808         127.27         164.61           Experimental         34.941         60.915         98.224         136.00         177.23           Calculated         34.909         60.813         98.104         135.84         176.88           % Error         0.09         0.17         0.12         0.11         0.19           Experimental         33.431         57.987         92.808         127.62         165.33           Calculated         33.422         57.887         92.620         127.27         164.61           % Error         0.03         0.18         0.20         0.27         0.44           Experimental         31.920         55.042         87.323         119.16         153.33           Calculated         31.922         54.949         87.113         118.68         152.33           % Error        0.01         0.17         0.24         0.40         0.65           Experimental         29.661         50.626         78.967         106.48         135.36           Calculated         29.663         50.515         78.799         105.72         13.84           % Error        0.01 <t< td=""><td>Experimental         34.941         60.915         98.224         136.00         177.23         225.26           Calculated         34.941         60.915         98.224         136.00         177.23         225.26           Calculated         34.909         60.813         98.104         135.84         176.88         224.82           % Error         0.09         0.17         0.12         0.11         0.19         0.20           Experimental         33.431         57.989         92.808         127.62         165.33         209.18           Calculated         33.422         57.887         92.620         127.27         164.61         208.52           % Error         0.03         0.18         0.20         0.27         0.44         0.32           Experimental         31.920         55.042         87.323         119.16         153.33         192.89           Calculated         31.922         54.949         87.113         118.68         152.33         191.129           % Error        0.01         0.17         0.24         0.40         0.65         0.83           Experimental         29.661         50.626         78.967         106.48         135.36         <td< td=""><td>Experimental         31.920         55.042         87.323         11.18.6         153.33         192.89         242.61           Calculated         34.941         60.915         98.224         136.00         177.23         225.26         285.40           Calculated         34.909         60.813         98.104         135.84         176.88         224.82         283.91           % Error         0.09         0.17         0.12         0.11         0.19         0.20         0.52           Experimental         33.431         57.989         92.808         127.62         165.33         209.18         264.01           Calculated         33.422         57.887         92.600         0.277         0.44         0.32         0.89           % Error         0.03         0.18         0.20         0.27         0.44         0.32         0.89           Calculated         31.920         55.042         87.323         119.16         153.33         192.89         242.61           Calculated         31.922         54.949         87.113         118.68         152.33         191.29         239.40           % Error         -0.01         0.17         0.24         0.40         0.65</td></td<></td></t<>	Experimental         34.941         60.915         98.224         136.00         177.23         225.26           Calculated         34.941         60.915         98.224         136.00         177.23         225.26           Calculated         34.909         60.813         98.104         135.84         176.88         224.82           % Error         0.09         0.17         0.12         0.11         0.19         0.20           Experimental         33.431         57.989         92.808         127.62         165.33         209.18           Calculated         33.422         57.887         92.620         127.27         164.61         208.52           % Error         0.03         0.18         0.20         0.27         0.44         0.32           Experimental         31.920         55.042         87.323         119.16         153.33         192.89           Calculated         31.922         54.949         87.113         118.68         152.33         191.129           % Error        0.01         0.17         0.24         0.40         0.65         0.83           Experimental         29.661         50.626         78.967         106.48         135.36 <td< td=""><td>Experimental         31.920         55.042         87.323         11.18.6         153.33         192.89         242.61           Calculated         34.941         60.915         98.224         136.00         177.23         225.26         285.40           Calculated         34.909         60.813         98.104         135.84         176.88         224.82         283.91           % Error         0.09         0.17         0.12         0.11         0.19         0.20         0.52           Experimental         33.431         57.989         92.808         127.62         165.33         209.18         264.01           Calculated         33.422         57.887         92.600         0.277         0.44         0.32         0.89           % Error         0.03         0.18         0.20         0.27         0.44         0.32         0.89           Calculated         31.920         55.042         87.323         119.16         153.33         192.89         242.61           Calculated         31.922         54.949         87.113         118.68         152.33         191.29         239.40           % Error         -0.01         0.17         0.24         0.40         0.65</td></td<>	Experimental         31.920         55.042         87.323         11.18.6         153.33         192.89         242.61           Calculated         34.941         60.915         98.224         136.00         177.23         225.26         285.40           Calculated         34.909         60.813         98.104         135.84         176.88         224.82         283.91           % Error         0.09         0.17         0.12         0.11         0.19         0.20         0.52           Experimental         33.431         57.989         92.808         127.62         165.33         209.18         264.01           Calculated         33.422         57.887         92.600         0.277         0.44         0.32         0.89           % Error         0.03         0.18         0.20         0.27         0.44         0.32         0.89           Calculated         31.920         55.042         87.323         119.16         153.33         192.89         242.61           Calculated         31.922         54.949         87.113         118.68         152.33         191.29         239.40           % Error         -0.01         0.17         0.24         0.40         0.65				

\* Overall Average % Error. By use of Equation 3, the average = 0.50%.

#### PHYSICAL-CHEMICAL PROPERTIES OF ETHANE-NITROGEN MIXTURES



Fig. 6.—COMPARISON OF P-V-T DATA OF REAMER et al. WITH IGT DATA FOR ETHANE-NITROGEN MIXTURES AT 40° AND 100°F

#### V. Comparison of IGT and Published Data

Recently Reamer, Selleck, Sage and Lacey<sup>18</sup> published P-V-T data on three mixtures of ethane and nitrogen in the temperature range  $40^{\circ}$  to  $400^{\circ}$ F and at pressures up to 10,000 psia. Two of their isotherms were selected for comparison with IGT data. Fig. 6 gives this comparison at  $40^{\circ}$  and  $100^{\circ}$ F in a plot of compressibility factor versus composition for constant pressures of 200, 600, 1000, 1500, 2000, and 4000 psia. The comparison at  $100^{\circ}$ F is good, with a maximum deviation of about 1.2% and an average deviation of about 0.3%. The comparison at  $40^{\circ}$ F is good for mixtures containing more than 50% nitrogen, and fair for the mixture containing 27.3% nitrogen.

At 40°F, for a 27.3% nitrogen mixture, the twophase region is entered through part of the pressure range of the Reamer investigations, and would explain the greater deviation. The phase boundary data were not available when the Reamer work was done, else conditions outside the envelope would have been picked.

# EQUIPMENT AND EXPERIMENTAL PROCEDURES

#### I. Materials Used

The ethane used was Phillips Petroleum Company's "Research Grade." It was stated to have a purity of 100.00%, and no impurities were detected in a mass spectrometer analysis.

The nitrogen used was obtained from Linde Air Products and was stated to be 99.99% pure. Mass spectrometer analysis did not show any detectable impurities.

Dew and bubble point data on both are given in Table 3.

#### II. Dew and Bubble Point Apparatus

In IGT Research Bulletin No. 176 a literature survey was presented of methods for obtaining vapor-liquid equilibrium at low temperatures. On the basis of this survey, a modified "dew and bubble point" method was chosen as particularly suited to the investigation of binary systems at low temperatures. The apparatus (Fig. 7) employed in the present work is essentially the same as that used in the study of the methane-nitrogen system, except that the cell was modified through use of an O-ring glass-to-metal connector, and a 4000 psi deadweight gage was added to the pressure-measuring system, to enable working at the higher pressures encountered in the ethane-nitrogen system and permit collection of density data on the saturated liquid phase.



#### Table 3.—DATA ON PURE COMPONENTS USED TO PREPARE THE MIXTURES

Ethane

Temp, °F	Dew Point psia	Bubble Point psia	Bubble Point from Literature
20.0	293.7	296.6	
0.0		221.6	218.9

Mass Spectrometer Analysis: 99.9+% ethane. Based on this dew and bubble point determination and IGT phase equilibrium data,<sup>9</sup> the impurity is estimated to be 0.12% methane.

#### Nitrogen

Temp, °F	Dew Point psia	Bubble Point psia	Calculated Vapor Pressure*
-235.00	459.8	461.8	464.5

Mass Spectrometer Analysis: 99.9+% nitrogen. Based on this dew and bubble point determination and IGT phase equilibrium data,<sup>8</sup> the impurity is estimated to be 0.2% methane.

\* Calculated with the Dodge and Dunbar formula:

$$\log P_{atm} = (-316.824/T) + 4.47582 - (0.0071707)(T + (2.940)(10^{-5})(T^2))$$
  
T is in °Kelvin.





Fig. 8.— Equilibrium Cell, Low-Temperature Bath Assembly

#### A. Description of Apparatus

1. Gas Measurement and Storage. All gas measurements required for preparing the mixtures and measuring the gas into the equilibrium cell were made with two high-pressure (2,000 psi) Jerguson sight gages (D, and D, in Fig. 7), each 28 in. long and of approximately 225 cc volume. They were calibrated by attaching arbitrary scales and adding mercury; fifty approximately equal increments of mercury were then withdrawn from each gage successively and weighed after the corresponding liquid levels were noted. Calibration curves were prepared from these data. The calibrations were checked at 600 psia, to observe the effect of pressure on gage volume, by applying cylinder nitrogen gas to the gages when nearly full of mercury, then withdrawing and weighing the mercury in the gage, maintaining the gage pressure constant. The volume obtained by this method agreed with the original calibration to within 0.1 cc.

The Jerguson gages were connected at the top by a manifold system, as shown in Fig. 7. All valves and fittings were of the "Aminco" highpressure type. A 1200 psi Bourdon-type gage was used to measure the manifold pressure. This gage was read to  $\pm 1.0$  psi and was calibrated frequently with the deadweight gage. For high pressure measurements this gage was isolated from the system and a 3000 psi pressure gage attached on the cylinder side of valve 9 in Fig. 7. The pressure in the gas measuring system was determined with the deadweight gage. The entire Jerguson gage and manifold system was mounted in a thermostatically-controlled air bath held constant within  $\pm 0.2^{\circ}$ F. A blower continuously circulated air over a strip heater and through the cabinet around the manifold and gages. Mercury was added to or withdrawn from the Jerguson gages by controlled changes in the pressure of the nitrogen in the mercury reservoir C.

2. Equilibrium Cell. The Pyrex glass equilibrium cell, shown in detail in Fig. 8, was constructed of heavy-wall tubing with a bore of 0.25 in. and an OD of 0.75 in. It was connected to a glass-to-metal tubing connector by a section of capillary tubing with a 1 mm bore and 6 mm OD. The cell contained a close-fitting steel ball which when raised and lowered by movement of a magnet provided excellent agitation of the fluid in the cell.

**3.** Glass-to-Metal Connector. A modification of the closure developed by Davis *et al.*<sup>11</sup> proved satis-



factory at the high pressures encountered. The advantages of the seal (shown in Fig. 9) over other types are ease of construction and assembly, and ability to absorb vibrations. The seal is effected by compression of a rubber O-ring, confined in a groove in the brass male fitting, against the flat end of the glass capillary. The glass tubing is connected to the brass adapter by a metal female coupling threaded over a brass ring mounted on the capillary tube. The end of the glass tubing is upset, and forms a thrust point for the brass ring. A teflon insert insulates the brass ring from di-

Metal-to-Glass Connector A teflon the bras rect contact with the glass and pro-

rect contact with the glass and provides even stress distribution. This seal was tested at 2000 psi for a 24-hour period without bursting or leaking. INSTITUTE OF GAS TECHNOLOGY RESEARCH BULLETIN NO. 26



Fig. 10.—Low-Temperature Bath Cooling System

4. Low-Temperature Bath. The low-temperature bath was modified from that described by Walters and Loomis,<sup>24</sup> and is diagrammed in Fig. 10. The liquids used in this bath were either propane or pentane. Liquid nitrogen, which served as the refrigerant, was forced by air pressure from the Dewar flask into the vaporization chamber **B** on top of the bath. Heat was conducted by the copper turbine tube from the bath to the vaporization chamber, where the liquid nitrogen gave up its latent heat; the turbine tube served as a "cold finger" in the bath.

The refrigeration rate was maintained constant within very narrow limits by the water column which regulated the air pressure in the liquid nitrogen Dewar, and by the needle valve and the 5gallon capacitance tank C. (The capacitance tank and needle valve are analogous to a capacitance and resistance, respectively, used in a DC electric circuit to stabilize current.) Normally, the pressure in the vaporizer B was equal to the depth of the water column M minus the hydrostatic head of the liquid nitrogen column. The pressure in C was lower by an amount equal to the resistance to flow of the vaporized nitrogen from B to C. If the liquid nitrogen vaporization rate decreased, the pressure in C tended to fall off. This lowered the pressure in B and thus created a differential pressure which forced more liquid nitrogen into B and, thereby, increased the vaporization rate. If the vaporization rate increased, the system functioned in the opposite manner. The refrigeration rate was regulated by opening and closing of the needle valve. The water column height was about 4 feet, and the water column equivalent of the liquid nitrogen column varied from about 1 to 1.5 feet, depending on the depth of the liquid nitrogen in the Dewar. Thus the pressure in C varied from about 3 to 2.5 feet of water. Since the gas flow rate through the needle valve was proportional to the square root of the pressure in C, the vaporization rate fell off only 7% as the Dewar vessel went from full to empty; this was a gradual and continuous decrease during the course of an experiment.

The temperature of the bath was maintained constant by partially offsetting the refrigeration effect with a small manually-controlled current to the nichrome heating coil wound on the outside of the turbine tube. The temperature was controllable to  $\pm 0.01^{\circ}$ F by adjustment of the variac.

5. Temperature and Pressure Measurement. The temperature of the bath, which was assumed to be the temperature inside the cell at equilibrium, was measured by a triple-junction copper-constantan thermocouple connected to an L & N type K-2 potentiometer and an L & N type E self-contained galvanometer. With this equipment, temperature changes of the order of  $0.002^{\circ}$ F were detected, and fluctuations of the bath temperature were held to less than  $0.01^{\circ}$ F.

The thermocouple was calibrated by use of a platinum resistance thermometer with a Meuller Bridge as primary standard. The resistance thermometer had been previously calibrated by the National Bureau of Standards. Readings were taken at the ice point, the normal boiling point of liquid propane ( $-43.7^{\circ}$ F), the sublimation point of carbon dioxide ( $-109.3^{\circ}$ F), the normal boiling point of carbon dioxide ( $-109.3^{\circ}$ F), the normal boiling point of carbon dioxide ( $-109.3^{\circ}$ F), the normal boiling point of liquid nitrogen ( $-320.4^{\circ}$ F), and at temperatures between  $-109.3^{\circ}$  and  $-320.4^{\circ}$ F obtained by controlling the bath temperature as described above. The calibration was believed to be accurate within  $\pm 0.05^{\circ}$ F down to  $-240^{\circ}$ F.

The pressure inside the equilibrium cell was measured with either a 1000 or 4000 psi capacity Refinery Supply Company deadweight gage. Pressure balance between the equilibrium cell and the deadweight gage was determined from the position of the mercury-gas interface in a lucite sight gage which served as one leg of a mercury manometer. Oil filled the space above the mercury in the other leg of the manometer, which connected to the deadweight gage. The volume of the gas space in the pressure-measuring system was held to a minimum by use of capillary tubing and by using a 1/16 in. ID bore in the lucite sight gage. The total volume of the piping system between valve **6** (Fig. 7) and the capillary glass tube of the equilibrium cell at bath liquid level was calibrated and found to be 1.17 cc. In the later phases of the experimental work this volume was reduced to 0.55 cc.

The deadweight gage was calibrated by comparison of its reading, when subjected to the vapor pressure of carbon dioxide at the ice-point of water, with the value  $505.56 \pm 0.02$  psia given for this point in the International Critical Tables. The relative masses of the weights used with this gage were determined by comparison with one of the weights used as a standard. It was found that the maximum deviation of any weight from the standard weight corresponded to a pressure of less than 0.05 psi. After all corrections, a reading of 505.6 psia was obtained with this gage, so it was considered quite reliable.

#### **B.** Experimental Procedures

1. Preparation of Mixtures. Two procedures for preparing mixtures were used. In Method No. 1, valves 2, 5, 7 and 8 (Fig. 7) were closed and all other valves opened. Then the spaces above the mercury level in Jerguson gage D,, and in the manifold and equilibrium cell, were evacuated by means of a vacuum pump connected by heavy rubber tubing to valve I. Nitrogen was introduced into Jerguson gage D, through valve 2 after valve I was closed. The level of mercury in the Jerguson gage, and the pressure and temperature, were recorded; the amount of nitrogen admitted was calculated with the aid of a compressibility factor chart prepared from the data of Bloomer and Rao.<sup>7</sup> Valves 2 and 4 were then closed, valve I opened, and the manifold and cell evacuated.

Ethane was then admitted into the manifold and cell through valve 2 after closing of valve 1. The amount of ethane required to give the desired composition was calculated, and approximately this amount was added through valve 4 into Jerguson gage  $D_1$  by control of the pressure drop in the manifold and cell. The piston gage was used in all cases to measure the manifold pressure. The amount of ethane admitted was calculated with the aid of a compressibility factor chart, prepared from the data of Sage and Lacey,<sup>21</sup> from the known volume of the manifold, the pressures in the manifold system, and the temperature.

After evacuation of the manifold, cell and Jerguson gage  $D_2$ , value I was closed and the contents of Jerguson gage  $D_1$ , were thoroughly mixed by repeated forcing of the gas back and forth between the two Jerguson gages and the equilibrium cell, by means of the mercury in reser-

voir C. The accuracy of this method was such that the quantity of ethane added to the nitrogen could be calculated to  $\pm 0.2\%$ .

In Method No. 2, nitrogen was introduced into Jerguson gage  $D_1$  as described above. Ethane was then introduced into Jerguson gage  $D_2$  in the same manner. The mercury level and pressure in  $D_2$  were adjusted to give the desired amount of ethane. The manifold was then evacuated after closing of valve 5, and the contents were mixed as described above. The accuracy of this method is such that the quantity of each component measured in the Jerguson gages can be determined to an estimated accuracy of  $\pm 0.2\%$ . The accuracy with which a mixture can be prepared is dependent on its composition; for example, assuming a mixture containing 30% ethane is to be prepared, the calculation is:

#### Percent ethane =

 $\begin{array}{c} (0.3000 \pm 0.0006) \ 100 \\ \hline (0.3000 \pm 0.0006) + (0.7000 \pm 0.0014) \\ = 30.00 \pm 0.08\% \end{array}$ 

In these calculations it is assumed that the ethane and nitrogen are pure, or that the impurities are known to be less than 0.01%. The maximum error would be  $\pm 0.1\%$ . Method No. 1 was used to prepare mixtures containing 10% or less of one of the components, because such small quantities of a component could not be measured accurately in the Jerguson gages.

These calculated compositions were checked by mass spectrometer analyses, but the calculated values were slightly more precise because the proximity of the ethane and nitrogen peaks on the mass spectrometer record causes interference, preventing high resolution of the components.

2. Operating Procedures. The complete P-T loop (dew and bubble point curve) for a given mixture was determined as follows: With the temperature of the cryostat held constant, gas was added slowly from Jerguson gage  $D_1$  to the evacuated equilibrium cell until the pressure was about 10 psi below the expected dew point pressure. Time for attainment of equilibrium was allowed (five minutes was found to be ample). Addition of gas to the cell was then continued so that the rate of pressure rise in the equilibrium cell was about 1-2 psi per minute. In this stage of addition the gas was added from the manifold system only, with Jerguson gage valves 4 and 5 closed. The rate of addition could then be accurately judged by the rate of pressure drop in the manifold system, as determined from the Bourdon gage A. This addition of gas was continued until the formation of minute drops of liquid could be detected on the cell wall. The cell was viewed by transmitted light, from a fluorescent tube, through 1-in.-wide windows in the Dewar vessel. Observation was facilitated by use of a 7-power magnifying glass. After liquid was first detected, a pressure increase of a few tenths of a pound resulted in the wall of the cell being covered by a film of liquid.

A deposit of iron oxide from the stirring ball on the inside of the cell wall aided the observation of the film. The minute particles impressed dimples into the film and caused refraction of the light, which made detection of the liquid film much easier. Condensation probably started on these minute particles, as the wall of the cell appeared to gradually fog up before the film formed. The dew point was taken as the pressure at which the minute drops were first detected, and could be duplicated to within at least 1 psi at lower pressures, and within 2 psi in the critical region.

After the first dew point was obtained, a series of dew points were determined at progressively higher temperatures up to the cricondentherm temperature. For temperatures above the cricondentherm, dew points were obtained by pressurizing the cell to a known pressure and then cooling the cell until liquid began to form. After liquid was detected, the cell was cooled or warmed slowly for determination of the exact dew point. For mixtures with large retrograde regions it was necessary to be certain that no liquid formed in the capillary. The foregoing procedure was followed up to the critical point.

When the mixture was cooled below the critical temperature, liquefaction occurred until only a small bubble of gas remained. The bubble point at each temperature was determined by adding gas to the cell until only a very small bubble of gas remained, and then agitating the contents until a constant pressure reading was attained. The bath was warmed until the gas bubble completely disappeared, and the bubble point taken as the pressure at which the gas bubble first appeared on cooling. Bubble points could be checked to within 1.0 psia or less. A series of bubble points were obtained at progressively lower temperatures.

Three-phase data points were obtained by use of two procedures. In the first, the liquid-liquid phase boundary pressure was obtained, by the standard bubble point method, for a given mixture as the point at which the homogeneous liquid separated into two phases. In the second procedure the bath was maintained at a constant temperature and a known amount of ethane condensed in the cell so that it was approximately one-third filled with liquid. Measured volumes of nitrogen were then added; after each addition the contents of the cell were stirred and the resulting equilibrium pressure was measured. Increments of nitrogen were added to the cell until both the low and high boundary pressures for the three-phase region for the particular bath temperature had been determined (Fig. 1). The data for the three-phase region obtained by the two procedures checked within one psi and  $0.1^{\circ}$ F.

The mass of gas in the equilibrium cell at the bubble point was determined by noting the initial and final mercury levels in the Jerguson gage, and the air bath temperature. Before making the final readings the mercury level was adjusted so the initial and final pressures in the Jerguson gage were the same. The moles of gas added to the cell were then calculated from these readings, with use of the compressibility factor data of Reamer et al.<sup>18</sup> for nitrogen-ethane mixtures. Correction was applied for the gas in the piping system connected to the cell, to obtain the moles of gas in the equilibrium cell at the bubble point. Density data for the saturated liquid phase obtained in this manner have an estimated accuracy of  $\pm 1\%$  except in the critical region, where the error may be larger.

Due to the small difference between the mercury level initially in the Jerguson gage, and that at the dew point, the values of the saturated vapor densities calculated from the gage readings would contain a large degree of uncertainty. Therefore the saturated vapor densities were not obtained.

#### III. Gas Phase P-V-T Apparatus

#### A. Description of Apparatus

The pressure-volume-temperature apparatus, presented schematically in Fig. 11 and pictured in Fig. 12, is a constant volume apparatus consisting of high- and low-pressure systems. It is similar in design and operation to the Bean apparatus used extensively in the natural gas industry to measure "supercompressibility factors."<sup>1</sup>

The low-pressure system was used to determine the mass of gas charged to and expanded from the high-pressure system. It consisted of a waterjacketed glass buret A of accurately known volume, and a glass manifold connected to the manometer B and to the high-pressure system. Gases were charged to the high-pressure system by placing the

#### PHYSICAL-CHEMICAL PROPERTIES OF ETHANE-NITROGEN MIXTURES



high-pressure bomb in liquid nitrogen and then displacing measured increments of the gases, with mercury, from the buret into the bomb at a pressure near atmospheric. When ethane-nitrogen mixtures were prepared, ethane was condensed in the bomb first and the nitrogen added subsequently. The vapor pressures of the mixtures were sufficiently low that they were completely condensed in the bomb at atmospheric pressure and liquid nitrogen temperature.

With this procedure, mixtures of any desired composition could be charged and liquefied in the high-pressure bomb. Sufficient quantities of the mixtures were liquefied in the bomb so any desired pressure up to 4000 psia could be obtained on warming the bomb and its contents to the desired minimum operating temperature. This system of charging permitted precise measurement of the volume and composition of the gases charged to any desired density.

The high-pressure system consisted of a bomb C of accurately known volume immersed in a constant-temperature bath, a combined value and tee



Fig. 12.—IGT Pressure-Volume-Temperature Apparatus

D of the "Aminco" high-pressure type, and a system for measuring the bomb pressure. The latter consisted of manifolded piston gages, E having a maximum range of 4000 psi, and F a maximum of 1000 psi. A mercury filled sight-tube, G, was used for detecting balance between the weights on the piston and the pressure in the cell.

The apparatus was operated so that isometric data were obtained. In this method the mass of gas in the bomb is held constant and the temperature is varied. At each of several temperatures the resulting pressure is measured. After securing data along one isometric, part of the gas is expanded back into the glass buret, where the mass expanded can be accurately measured. Pressure-temperature data are then taken along the second isometric. This procedure is continued, with data taken along several more isometrics, until the gas in the highpressure bomb has been expanded to atmospheric pressure. The total mass expanded from the bomb, and remaining in the bomb at atmospheric pressure, are then summed to verify the total mass initially charged to the system.

The taking of isometric rather than isothermal data offers the following advantages:

- 1) A comparable range of conditions can be covered by the isometric method with fewer gas expansions required than for isotherms, giving less opportunity for volume measurement error.
- 2) The complete range of data desired can be obtained with one sample of gas and one charging of the high-pressure bomb, whereas the isothermal method requires a recharging of the bomb for each isotherm.
- 3) The form of the data is more convenient for testing and adjusting the constants of an equation of state.

#### **B. Experimental Procedures**

1. Preparation of Mixtures. The entire PVT system was first evacuated with the high-vacuum pump. After the system was checked for leaks, the high-pressure valve was closed and the bomb placed in a small Dewar vessel containing liquid nitrogen. The needle valve on the high-pressure sample cylinder was then slowly opened, and gas added to the buret at about atmospheric pressure, gradually displacing mercury from the buret to the leveling bulb. When the mercury in the buret reached the lower etch mark and a pressure slightly above atmospheric, the valve to the sample cylinder, and the stopcock connecting the buret to the leveling bulb, were closed. About 5 minutes was allowed for the gas in the buret to come to equilibrium; meanwhile the temperature of the circulating water in the buret was determined and the barometric pressure read. The vacuum pump was disconnected from the three-way valve, and the excess pressure in the buret was relieved by very slow opening of the three-way stopcock to bleed excess gas to the atmosphere. A long piece of rubber tubing was connected to the bleed stopcock outlet to prevent any air diffusing back into the buret. After one minute the three-way stopcock was closed.

Next, the high-pressure valve to the bomb was cracked, and the gas slowly charged into the bomb. During the charging the pressure in the buret was kept at approximately atmospheric by raising the leveling bulb. Near the end of the operation the rate of charging was slowed considerably, and the gas in the buret was kept under a pressure slightly above atmospheric. When the mercury level reached the top etch mark of the buret, the stopcock at the top of the buret was closed. The highpressure valve was closed at the moment the manifold pressure became equal to atmospheric pressure as observed on the manometer. This procedure was followed so the volume of gas in the manifold and manometer would not enter into the charging calculations, since it would be under atmospheric pressure before and after the charging of the gas to the high-pressure bomb. In the event there was a small residual plus or minus pressure in the manifold from one charging cycle, an attempt was made to cancel it out in the following cycle. The above procedure constituted one charging cycle, which was repeated until the desired amount of each component gas had been charged.

2. Determination of Pressure-Volume-Temperature Relationships. This involved only the determination of the pressure at a fixed temperature, since the volume of the bomb was known and the number of moles in the bomb was calculated from the volumetric measurements made in the buret.

A series of temperatures and the corresponding gas pressures were determined for each density of gas. The density of gas was then changed by expanding part of the gas back into the low-pressure system, as discussed in Section 3 below.

To determine the pressure in the bomb, the valve connecting the mercury sight glass and the deadweight gages was carefully opened, and weight added to or removed from the gage until the mercury column in the sight glass was balanced at a fixed reference mark. The gas in the bomb was assumed to have reached the bath temperature when a constant pressure reading was obtained at a constant bath temperature.

3. Expansion of Gas to the Low-Pressure System. The expansion of gas from the high-pressure bomb to the low-pressure buret was performed in essentially the reverse of the charging operation. The mercury level was brought to the top etch mark of the buret and the manifold brought to atmospheric pressure by opening of the three-way stopcock to the atmosphere. The stopcock was then closed, and the needle valve connecting the highand low-pressure systems was opened carefully to throttle gas into the buret. The buret leveling bulb was lowered at a rate sufficient to maintain atmospheric pressure in the low-pressure system. The needle valve was closed when the mercury level in the measuring buret reached the bottom etch mark. The system was then allowed to come to equilibrium and the barometric pressure, the temperature of the buret, and the pressure in the buret above or below atmospheric as read on the manometer, were noted.

#### C. Calculation of Results

Since the pressure and temperature of the highpressure system were measured directly, the only calculation required was the determination of the moles of gas in the high-pressure bomb. This was done by a straightforward application of the ideal gas law to the measurements obtained on the lowpressure buret, using a correction for the deviation of the gas from the ideal gas law as noted before. It was also necessary to apply a small correction for that part of the high-pressure system which was not at the temperature of the low-temperature bath. This was accomplished by calculating the moles of gas, n, in this part of the system, with the equation: n = Pv/zRT

P = absolute pressure of the bomb

v = volume of the high-pressure system not in the

low-temperature bath = 0.26 cc R = universal gas law constant

T = absolute temperature

z = compressibility factor

Since this system was at room temperature, values of z for the various mixtures could be interpolated from the data of Reamer *et al.*<sup>18</sup>

The number of moles in this part of the system was then subtracted from the total moles, to obtain the moles of gas in the high-pressure system at the temperature of the low-temperature bath.

Since the volume of the high-pressure bomb was not constant, but varied with temperature, the pressure-temperature data obtained for a given number of moles in the high-pressure system were not true isometric data. True isometric data were calculated from the experimental data by plotting the experimental pressures against the corresponding density along a constant temperature line for each temperature investigated. By graphically determining the slope of this line, the rate of change of the pressure with density at constant temperature was determined for each experimental point. Then the pressures that would have existed along a true isometric were calculated:

$$P = P_{E} + (\delta P / \delta d)_{T} (d_{T} - d_{E})$$

P == pressure that would have been obtained at the true isometric density

 $\begin{array}{l} P_{\epsilon} = \text{experimental pressure at actual density in bomb} \\ (\delta P/\delta d)_{\tau} = \text{slope of the pressure versus density curve at constant} \\ \text{temperature} \end{array}$ 

 $d_{\tau} =$  density of desired true isometric  $d_{E} =$  actual density in bomb

sity of the desired true

The density of the desired true isometric was always taken as the density at an intermediate value of the series of temperature points. The pressure correction was always less than 0.5% of the observed pressure, and it is believed that no significant error was added, by this procedure, to the pressure values reported for the true isometrics.

# TABULATED DATA

# Table I.-DEW AND BUBBLE POINT EXPERIMENTAL DATA FOR ETHANE-NITROGEN MIXTURES

						ATOREO					
	N	lixture A			Mixt	ire B (cont	.1		Mixtu	re Da (con	+.)
	05 039/ C		00/ NI		04 00%/ C		·/	7	5 00º/ C	H 25 (	00% N
	95.02% C	$_{2}H_{6} - 4.9$	8% N2		84.99% C	$H_{6} = 15.0$	$1\% N_2$	/	5.00 /o C	Π <sub>6</sub> — 25.0	JU /0 142
	-	Dew Point	Bubble Point		-	Dew Point	Bubble Point	D	T	Dew Point	Bubble Point
un	lemp	Pressure	Pressure	Kun	° F	Pressure	Pressure	No.	°F	psia	psia
					- <u> </u>	psid		2-	F2 22	1122.44	
	-47.79	104.7		6a	-130.00		637.1	Ja	53.23	1123.01	1266.9
a	0.00	233.1	-	b	-155.00		564.8	0	16.14	_	1291.4
b	20.00	314.2		c	-184.00		465.4	ď	-4.87		1279.9
c	42.00	428.6		d	-197.82		412.5	e	-31.12		1241.7
3	58.71	535.1	···	e -	-220.50		520.4	f	-62.26		1181.4
1.	70.00	623.8	-	/a	50.00	582.4	1027.2	g		_	1118.9
b	78.00	698.7	10 10-10	D	23 41		990.2	h	-108.66		1056.6
c	82.06	740.7		d	-0.37	_	932.7	4a	53.30	1124.7†	
d	82.00	_	801.8	e	-45.72		829.2	Ь	33.36	-	1268.3
е	74.00	1	789.6	8.0	-47 40		828 5	c	-4.09	- 13	1280.6
f	66.00		744.3	b	-70.00	_	775.6	d	-107.07	_	10/2.9
ā	58.71	535.4		c	-100.00		706.7	e	-129.44	_	990.3
b	84.15	No phase	e separation	90	-100.00	_	708.2	T	-150.54	_	770 3
c	83.50	781.4	-	b	-130.00	_	634.6	9	-177.50		110.5
d	83.50	783.7†		c	-155.00	_	561.9		N	inturo E	
е	82.95	788.4	-	d	-184.00	-	463.9	,	0.210/ 0		100/ NI
ba	52.00	-	679.8	10a	-184.00		467.1	6	8.31% C2	$H_6 - 31.0$	69% N2
b	32.00	-	589.8	b	-220.50	_	320.5	la		79.5	-
c	10.00	-	505.1	с	-249.00		202.6	b	-60.00	117.3	
d	-20.00	-	416.6	d	-276.40		105.8	c	-40.00	175.9	
е		-	345.8	Estim	ated critical	point: 67.0	)°F. 970 psia	d	-20.00	254.3	-
7a	-20.00	169.6	416.5			4		е	0.00	361.0	_
Ь		—	292.6			C.		2a	0.00	362.4	
c	-120.00	-	239.0		IV	lixture C		b	15.00	474.6	
d	-155.00	-	197.5	7	9.98% C2	H <sub>6</sub> — 20.0	02% N2	c	25.00	562.1	
e	-187.00	_	159.3	la	-112.33		856.5	a	32.00	704 6	
stim	nated critical	point: 82.95	°F, 788.4 psia	Ь	-135.63	- 1	791.0	t	42.00	785.4	
IOI	E: Mixture c	omposition t	for Runs 1, 2	2a	-168.53	-	672.5	a	48.00	933.7	_
	and 3 was 94	4.98% C <sub>2</sub> H <sub>6</sub>	- 5.02% N <sub>2</sub>	3.2	-210.00		467.4	h	48.00	1128.6†	_
				h	-221 39	- 27	400.4	3.0	42 00	784 5	-
		D		c	-228.00	- de	360.9	b	49.00	987.8	_
	N	lixture B		d	-240.00		292.4	c	49.00	1008.3†	-
8	34.99% C2	H <sub>6</sub> — 15.0	01% N2	4a	-260.00		190.7	4a	-60.00	119.2	
la	-70.00	77.3		b	-267.84		155.5	b	-150.00	_	1125.3
b		113.2		с	-276.40	<u> </u>	118.7*	с	-155.00		1097.3
c		164.3	_	d	-284.16	-	88.0*	5a	-155.00	-	1100.4
d	-10.00	232.0	-					Ь	-165.00		1039.4
е	10.00	318.5	· · · · · · · · · · · · · · · · · · ·		M	ixture D.		с	-172.82	-	993.4
2a	25.00	399.5	·		75 070/ 0	LL 240	20/ NI	d	-184.00		909.4
b	37.00	478.0	-		15.01% C	$n_6 - 24.9$	3% N2	e	-197.82	—	799.4
с	50.00	582.2	-	la	-151.85	-	908.4	Ť	-207.00	—	/13.9
d	58.71	667.1	-	b	-159.36	-	880.4	6a	-207.00	-	716.8
e	66.00	758.0	-	c	-178.50	—	776.9	b	-213.00		661.8
Ba	66.00	760.2	-	d	-197.82	-	656.4	c	-220.50		594.3
Ь	70.00	836.4	—	2a	-220.50	-	492.3	7a	-228.00	-	496.2*
C	71.11	888.0	_	b	-238.00	_	360.5	D	-232.00		453.7*
d	71.11	898.3	-	c	-249.00	-	285.2	C	-238.00		389.2*
e	/0.00	936.11	-	d	-260.00	_	210.0*	Estim	ated crit. p	oint: 33.47°F	, 1320.8 psia
t	69.00	949.41	-								
g	68.00	960.11	-		M	ixture $D_2$			M	ixture E <sub>2</sub>	
n	05.72	703.7		7	5 00º/ C	H _ 25 (	00% N	6	8.28% C <sub>2</sub>	H <sub>6</sub> — 31.	72% N2
a	58.71	668.9	101/-	'	J.00 /0 C2	116 - 25.0	/0 142	la	-36.90	686.4	
b	61.47		1016.5	la	54.37	1109.11	_	b	44.31	807.6	_
C	58./1	-	1029.0	b	52.07	1137.2	—	c	44.09	1209.91	
a	54.00	-	1033.1	c	50.11	1155.4†	-	d	33.47	1320.8	
f	42.00		1027.9	d	49.10	1166.2†	—	е	21.22		1409.8
	45.00		022.0	2a	44.03	-	1215.1	f	-0.62	_	1466.9
h	-45.00		833.9 774 F	b	34.25	_	1265.2	g	-21.80	-	1469.9
c	-100.00	_	706.5	c	20.17	_	1289.7	h	-41.16		1450.4
-				L L							

\* Two liquid phases

† Retrograde dew points

# Table I (continued).—DEW AND BUBBLE POINT EXPERIMENTAL DATA FOR ETHANE-NITROGEN MIXTURES

	Mixtu	re E <sub>2</sub> (con	+.)		Mixtur	e H1 (cor	nt.)	Mixture J <sub>1</sub>			
1	58.28% Ca	H_ 31.7	2% N2		15.03% C2	H 84.9	7% N2		5.10% C2	H <sub>6</sub> — 95.9	70% N2
	// //	Dew Point	Bubble Point		70 -	Dew Point	Bubble Point			Dew Point	<b>Bubble Point</b>
Run	Temp	Pressure	Pressure	Run	Temp	Pressure	Pressure	Run	Temp	Pressure	Pressure
No.	°F	psia	psia	No.	°F	psia	psia	No.	°F	psia	psia
2			1407.0	5.	01.10	1581.61	_	La	-135 53	356.5	_
Za	-9.03		1471 7	h	-120.03	1736.41		2a	-135.53	354.4	
c	-59.56		1425.5	c	-129.32	1736.4		b	-130.60	938.7†	—
d			1351.7	d	-137.60	1724.6†		с	-134.89	1040.2	—
е	-116.63		1264.0	6a	-103.63	1678.8	-	d	-139.80	1110.7†	
f	-136.84		1178.9	b	-119.36	1735.7†	-	e	-145.10	1164.7†	—
g	-155.66	-	1081.0	с	-140.36	1715.3		t	-155.49	1209.71	_
				d	-146.45	1697.5†	-	3a	-129.64	487.8	
	h.	livturo E		е	-153.27	1668.81		D	-127.30	779 5+	_
	IV	intruie i	100/ NI	7a	-106.49	1693.6†		d	-156.37	1205.01	_
	49.82% C <sub>2</sub>	$_{2}H_{6} = 50.$	18% N2	b	-147.20	1694.11	_	e	-162.17	1210.4	_
La		97.8		c	-157.92	1640.1	_	f	-166.38	1203.0	
b	-70.00	146.6		a	-173.19	1554.01	_	4a	-155.49	1210.7†	
c		228.4		f	-181.90	1497.8		b	-169.15	1192.7†	-
d		342.8		a	-194.74	1424.6		c	-173.10	1176.7†	—
2a	-15.00	441.5		ĥ	-201.95	1399.6		5a	-172.29	1185.0†	
b	0.00	601.9	-	i	-206.10	1395.6†	-	b		1136.0†	
с	8.00	725.9	-	i	-221.71	1473.6†	-	c	-186.94	1086.51	_
d	14.01	855.I		8a	-106.80	1695.7†	-	d	-192.93	1028.51	_
е	16.33	930.6		b	-119.90	1734.2	—	e	-200.32	944.5	
3a	14.68	862.8		с	-148.25	1689.7†	_	T	-220 30	648.0+	_
b	15.85	911.2		d	-164.19	1609.6†	—	h	-229.62	484.241	
С	18.72	1049.0		e	-176.32	1532.21	_	i	-230.80		467.04
				f	-186.00	14/2./†		6a	-155.75	1209.21	
	N	lixturo G		g	-191.90	1430.21		b	-169.15	1195.7	
	IV	intruie O	000/ NI	n :		1390.71		с	-193.18	1023.5†	
3	30.00% C <sub>2</sub>	$H_{6} = 70.0$	00% N2	-	-208.50	1388.71	_	d	-221.04	635.2	_
La	-112 79	84.1		k	-214.21	1412.2		Estim	nated crit. p	oint: -230.	0°F, 482 psia
b	-99.74	117.3		1	-220.20	1469.2	—				
22		171.0		m	-223.57	1508.7†	—		N	lixture $J_2$	
b	-70.00	250.2		9a		1623.3†	-		4.95% Ca	$H_{c} = 95.0$	05% Na
c		364.5		b	-159.06	1639.7		1.5	148 88	82.4	/0 1
3.a	-54.89	365.3	-	с	-191.08	1441.2†		h	-154.59	152.0	_
4-	-45.15	474 7		d	-206.60	1393.5		22	-145.86	230.7	
Ta	20.72	E42 1		e	-211.35	1398.71		b	-136.06	378.8	
b	-30.72	734 3	_	t	-218.16	1437.01		с	-131.46	530.4	<u> </u>
C	-26.31	857.0		g	-223.47	1505.01		d	-130.27	679.7†	-
d	-24.02	973.7		:	231.04	1687.51		е	-130.41	740.3†	—
е	-23.02	1148.1		÷	-233.60	1775.5		f	-131.55	812.2†	_
6a	-24.11	971.4						3a	-146.62	223.0	_
b	-23.79	1190.6						b	-135.90	380.2	
					M	ixture H <sub>2</sub>				Atuluna V	
	14				14 94º/ C.	H 85	06% Na		1 000/ 01		100/ NI
	IVI				14.74 /0 02		/0 /12		1.98% C2	$H_6 - 98.0$	$JZ /_{0} IN_{2}$
1	15.03% C <sub>2</sub>	H <sub>6</sub> — 84.	97% N2	la	-135.00	86.7		la	-198.61	100.9	_
La	00.00	576.3		2a	-118.94	147.8	_	2a	-172.00	742.6	
b	-76.00	636.1		b	-104.14	238.8	_	b	-178.94	803.6	_
c	-72.19	818.2		c		321.4		c	-184.00	832.6	_
d		1102.3 †		3a		322.2		a	-193 56	824.1	
2a		826.4		b		385.0		f	-197.60	807.6	
b	-72.13	1092.8†		d		546 1		g	-203.71	772.5	_
c		1391.6†		e	-76.00	636.7		h	-210.00	719.6	—
d		1479.1		1-	74 50	637.2	_	3a	-190.86	835.3	
е		1553.3†	-	44	72 19	853 1		b	-208.75	732.7	-
3a		1246.2†	-	0	-71.72	957.1		C	-220.52	600.7	
b	90.18	1561.4†		d	-71.82	1009.41		d	-222.66	578.8	
с	96.46	1629.1†	—	e	-72.73	1113.1		e	-223.30	·	5/2.1
d	-102.02	1667.4†		5.0	-94.84	322.9		+	-228.10		523.5
e	-106.95	1695.81	-	4.	85.00	451.6		g	-232.00		301 7
t	-113.58	1722.47		b	76.60	636.6	_	:	249.00	_	306.2
4a		1395.6†	-	D		030.0		;	-268.00	_	170.3
b		1607.51						4a	-188.00	166.9	_
c	-119.96	1735.17	_		+ Retroor	ade dew poi	nts	b	-178.30	259.9	
a	-125.04	1730.01			Inchogi	and as h pon		-		and the second	

# Table II.-EXPERIMENTAL P-V-T DATA AND COMPUTED COMPRESSIBILITY FACTORS

Tempe	rature	Pi	ressure	Density	Compressibility Factor	Temp	perature	P. 04.77	ressure	Density	Compressibility Factor
°V	° E	Peta		gm moles		°V	° E	Pata		gm moles	P/PTO
		rsia		1000 cc	<u>z = r/kip</u>	<b>K</b>		rsia		1000 cc	<u>z=P/KIP</u>
			Ist Isometric			a sector			6th Isometric		
316.49	110.00	4322.8	294.148	14.0856	0.804079	316.49	110.00	1091.1	74.244	5.3265	0.53670
294.27	70.00	2795.3	190.208	14.1165	0.557987	305.30	90.00	707.2	05.747	5.3521	0.49172
283.17	50.08	2028.8	138.286	14.1261	0.421286				7th Isometric		
266.54	20.09	909.8	61.9080	14.1784	0.1996296	316.49	110.00	857.8	58.369	3.4718	0.64735
			2nd Isometric			305.38	70.00	716.0	53.492	3.4824	0.61413
294.27	70.00	1256.6	85.506	12.3601	0.2864818	2/4.2/	70.00	710.0	40.720	3.4070	0.57616
283.17	50.09	754.9	51.3677	12.41310	0.1780867				8th Isometric		
305.38	90.00	1777.3	120.938	12.34090	0.391059	316.49	110.00	499.4	33.982	1.6141	0.81064
305.38	90.00	2311.0	121.033	12.3408	0.391370	294.27	70.00	472.4	32.144	1.6159	0.79382
510.47	110.00	2311.0	157.254	12.32410	0.471300	283.17	50.08	417.5	28.409	1.6199	0.75473
			3rd Isometric								
316.49	110.00	1334.8	90.8274	9.98705	0.3501769		Comme	-111 7	0 270/ C LI	20.7	00/ NI
305.38	90.00	1019.0	67.339	9.99998	0.2766980		Compo	sition: /	0.27% C2H	6 - 29.1	3% N2
			4th Isometric			205 20	00.00		Ist Isometric		1
305.38	90.00	865.9	58.9208	7.68396	0.3059927	305.38	70.00	4445.4	302.490	13.9385	0.86601
316.49	110.00	1061.1	72.2033	7.64854	0.3634849	283.17	50.08	3262.4	221,992	13.9629	0.68420
			5th Isometric			273.16	32.00	2730.9	185.826	13.9762	0.59316
316.49	110.00	918.7	62.5136	5.3160	0.4527907	252.60	5.00	1669.1	113.575	14.0148	0.39096
305.38	90.00	793.2	53.9739	5.3342	0.4037774				2nd Isometric		
			6th Isometric			316.49	110.00	3490.6	237.520	12.2023	0.74949
305.38	90.00	707.6	48,1492	3.57348	0.537681	305.38	90.00	3050.0	207.539	12.2136	0.67808
316.49	110.00	781.1	53.1505	3.56420	0.574186	294.27	70.00	2617.3	178.096	12.2261	0.60336
			7th Icomotrie			283.17	50.08	2188.1	148.891	12.2403	0.52348
216.40	110.00	524.2	2E 4404	1 91990	0 755001	2/3.10	32.00	1012.0	123.355	12.2002	0.44900
305.38	90.00	492.1	33.48530	1.821600	0.733548				3rd Isometric		
294.27	70.00	459.7	31.2806	1.824045	0.710169	316.49	110.00	2577.7	175.401	10.4529	0.64611
						294.27	70.00	1947.6	132.526	10.4644	0.58605
						283.17	50.08	1641.1	111.670	10.4928	0.45800
									4th Isometric		
						316.49	110.00	2013.3	136.996	8 7047	0 60599
	Compo	sition: 8	4.99% C₂H	<sub>6</sub> — ا5.01	% N2	305.38	90.00	1785.6	121.502	8.7173	0.55620
						294.27	70.00	1559.5	106.117	8.7288	0.50355
		20514	Ist Isometric	13 0577	0 75447	283.17	50.08	1338.4	91.072	8.7446	0.44820
305.38	90.00	3851.4	262.071	13.85//	0.75467				5th Isometric		
283.17	50.08	2503.6	170.359	13.8822	0.52812	316.49	110.00	1631.8	111.037	6.9845	0.61212
274.83	35.00	2013.1	136.982	13.8934	0.43718	305.38	90.00	1465.0	99.687	6.9935	0.56881
260.94	10.00	1175.6	79.994	13.9235	0.26831	294.27	70.00	1300.6	88.500	7.0070	0.52314
			2nd Isometric			203.17	50.08	1135.0	11.232	7.0214	0.4/336
316.49	110.00	2760.5	184.165	12.0927	0.59810				6th Isometric		
305.38	90.00	2277.8	154.994	12.0989	0.51121	316.49	110.00	1314.2	89.426	5.2794	0.65221
294.27	70.00	1807.2	122.972	12.1125	0.42043	305.38	90.00	1200.1	81.662	5.2888	0.61615
283.17	50.08	1345.3	91.541	12.1308	0.32475	283.17	50.08	966.3	65.753	5.2988	0.57749
			3rd Isometric			200.17	50.00			0.0002	0.03300
316.49	110.00	1907.3	129.783	10.3139	0.48451				7th Isometric		
305.38	90.00	1572.3	106.988	10.3262	0.41345	316.49	110.00	980.7	66.732	3.5521	0.72337
294.27	70.00	1251.9	85.186	10.3420	0.34362	294 27	70.00	716.0	48 720	3.5581	0.69600
			4th Isometric			283.17	50.08	764.5	52.021	3.5694	0.62720
316.49	110.00	1493.6	101.633	8.5422	0.45811				046 Jan 1		
305.38	90.00	1259.6	85.710	8.5540	0.39984	214 40	110.00	E00 4	an isometric	1.0050	0.00015
294.27	70.00	1037.1	70.570	8.5/04	0.34099	316.45	90.00	550.5	37.494	1.8252	0.83315
			5th Isometric			294.27	70.00	520.7	35.431	1.8294	0.80220
316.49	110.00	1299.2	84.405	7.2074	0.47229	283.17	50.08	490.2	33.356	1.8314	0.78381
305.38	90.00	1119.5	76.177	7.2211	0.42097						

Composition: 95.03% C2H6 - 4.97% N2

Composition: 84.99% C<sub>2</sub>H<sub>6</sub> - 15.01% N<sub>2</sub> (cont.)

# FOR ETHANE-NITROGEN MIXTURES

# Composition: 29.96% C2H6 - 70.04% N2

	Compos	sition: 5	0.26% C₂H	s — 49.74	1% N2	Temp	erature	P	ressure	Density	Compressibility Factor
Tempe	rature	P	ressure	Density	Compressibility Factor	°K	°F	Psia	atm	gm moles 1000 cc	$z = P/RT\rho$
		-		1			-				
0.14	0.	n ·		gm moles	P/PTO		00.00	4140 7	Ist Isometric	11.2204	0.00001
K		Psia	atm	1000 cc		305.38	90.00	4168.7	283.662	11.3394	0.99804
			1st Isometric			283.17	50.08	3553.6	241.807	11.3611	0.91595
205 29	00 00	4743 4	288 452	12 6655	0.90882	266.54	20.09	3092.0	210.397	11.3803	0.84526
294 27	70.00	3826.9	260.404	12.6774	0.85063	249.83	-10.00	2626.8	178.743	11.3996	0.76483
283.17	50.08	3406.2	231.777	12.6908	0.78596	238.72		2320.0	157.866	11.4127	0.70612
266.54	20.09	2785.4	189.535	12.7127	0.68164	227.60	-50.00	2018.5	137.350	11.4258	0.64363
249.83	-10.00	2176.2	148.081	12.7373	0.56708	222.05	-60.00	18/2.0	127.382*	_	_
238.72	-30.00	1808.8	124.081*			210.47		1776.0	117 447*	_	_
227.60		1686.0	107 084*	_	_	197.05	-105.00	1538.6	104.695*	_	
210.47	-/0.00	15/5./	107.004								
			2nd Isometric						2nd Isometric		
305 38	90.00	3254 0	221 421	10.9429	0.80745	305.38	90.00	3295.5	224.245	9.5980	0.93224
294.27	70.00	2939.5	200.204	10.9547	0.75682	294.27	70.00	3063.6	208.465	9.6072	0.89858
283.17	50.08	2623.2	178.498	10.9674	0.70041	283.17	50.08	2829.1	192.508	9.61/5	0.86141
266.54	20.09	2158.1	146.849	10.9875	0.61105	200.54	10.09	24/9.1	144 652	9.6335	0.73121
255.35	0.00	1855.8	126.279	11.0020	0.54776	238.72	-30.00	1891.3	128.695	9.6605	0.68005
249.83	-10.00	1/16.5	116.800*	_	_	233.16	-40.00	1774.6	120.754*		
238.72		1571.0	100.157*	_	_	227.60		1692.6	115.174*	—	_
227.00	30.00	1 17 1.7	100.107			216.49	-70.00	1565.5	106.526*	—	
			3rd Isometric			199.83	-100.00	1367.5	93.0525*	—	-
305 38	90.00	2546.7	173.292	9.1780	0.75346				3rd Isometric		
294.27	70.00	2314.1	157.465	9.1884	0.70969	305 38	00.00	2593.8	176 497	7 8530	0 89686
283.17	50.08	2079.9	141.528	9.1995	0.66206	294.27	70.00	2422.6	164.848	7.8611	0.86841
266.54	20.09	1754.7	118.039	9.2171	0.58551	283.17	50.08	2249.4	153.062	7.8696	0.83702
260.94	10.00	1621.2	110.316	9.2232	0.55858	266.54	20.09	1989.3	135.363	7.8822	0.78516
255.38	0.00	1534.0	104.423*	_	_	249.83	-10.00	1726.3	117.467	7.8957	0.72569
247.03		1364.0	92.814*	_		244.27	-20.00	1638.6	111.500	7.9004	0.70391
230.72		1501.0	72.011			238.72		1550.3	07 200*	7.9048	0.08125
			4th Isometric			216.49	-70.00	1316.5	89.582*	-	_
305 38	90.00	2012.9	136,969	7.4084	0.73778	210117	,				
294.27	70.00	1844.3	125.497	7.4174	0.70065				4th Isometric		
283.17	50.08	1673.6	113.881	7.4268	0.65989	305.38	90.00	1991.1	135.486	6.1149	0.88415
266.54	20.09	1418.1	96.496	7.4412	0.59289	294.27	70.00	1870.6	127.286	6.1216	0.86107
260.94	10.00	1349.3	91.814*		_	283.17	50.08	1748.4	118.971	6.1281	0.83548
249.83		11325	77.062*	_	_	266.54	20.09	1377 0	93 699	6.1381	0.74337
230.72	50.00	110210	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,			244.27	-20.00	1313.8	89.398	6.1535	0.72477
			5th Isometric			238.72	-30.00	1258.1	85.608	6.1585	0.70961
305.38	90.00	1571.3	106.920	5.6627	0.75347						
294.27	70.00	1454.1	98.945	5.6697	0.72270				5th Isometric		
283.17	50.08	1335.5	90.875	5.6767	0.68892	305.38	90.00	1440.6	98.027	4.3807	0.89295
266.54	20.09	1155.8	78.647	5.6874	0.63223	294.27	70.00	1362.5	92.712	4.3853	0.87551
260.94	10.00	1098.6 004 E	14.155*	_	_	265.17	20.09	1164.2	79.219	4.3969	0.82374
249.03		902.8	61 432*	_	_	249.83	-10.00	1042.7	70.951	4.4038	0.78588
200.72	30.00	102.0						1000 (1000) (1000) (1000)	(1) I I I		
			6th Isometric						6th Isometric	0 / 21 5	0.00007
305 38	90.00	1143.0	77.776	3.8892	0.79802	305.38	90.00	893.6	57 041	2.0315	0.92207
294.27	70.00	1071.6	72.918	3.8937	0.77552	294.27	70.00	808 0	55.042	2.0340	0.89844
283.17	50.08	999.1	67.984	3.8982	0.75052	266.54	20.09	745.0	50.694	2.6404	0.87779
266.54	20.09	891.2	60.424	3.9048	0.70748	249.83	-10.00	679.9	46.264	2.6442	0.85344
260.94	10.00	838.6	57.063*	_	_				7th looperte		
249.83		140.4 667 A	45.414*	_	_		00.00	FIG C	7th Isometric	1 4/14	0.05131
130.11	-30.00	007.4	10.111			305.38	90.00	512.0	34.839	1.4614	0.95131
			7th Isometric			294.27	50.00	490.3 468 F	33.303	1.4628	0.93704
205 20	00.00	401.0	47.020	2 1520	0 87150	263.17	20.08	435.9	29.661	1.4661	0.92497
305.38	70.00	655.4	44 597	2.1553	0.85688	249.83	-10.00	402.8	27.409	1.4685	0.91042
283.17	50.08	620.0	42.188	2.1574	0.84155	238.72	-30.00	380.7	25.905	1.4695	0.89989
266.54	20.09	566.4	38.541	2.1607	0.81552	227.60	50.00	358.5	24.394	1.4708	0.88802
255.35	0.00	529.6	36.037	2.1629	0.79514	216.49	-70.00	321.2	21.856	1.4725	0.83551
		*	Two-phase regi	on				*	Two-phase regi	on	

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