Phase Equilibria in Natural Gas Systems

Data for Two Helium-Bearing Natural Gases

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IN 1958 the Bureau of Mines Helium Activity proposed a policy for the conservation of helium, vitally needed in the nation's atomic energy and space programs. During the summer of 1960 a helium conservation bill passed both houses of Congress and was signed by the President on September 13, 1960. The resulting legislation, which becomes effective March 1, 1961, calls for the construction of additional plants, either by private companies or the U.S. Bureau of Mines, to produce crude helium from natural gases now going to fuel markets. This impure helium will be purchased by the Government and stored in its Cliffside field near Amarillo, Tex.

This article, which contains heretofore unavailable information on the phase equilibria of helium-bearing natural gases, is offered as an aid to private companies interested in participating in the Helium Conservation Program.

Although the technical literature contains many references to phase behavior of multicomponent hydrocarbon mixtures, there are few references to low-temperature phase equilibrium data for natural gas systems containing helium. Brown and Stutzman (*3*, *9*) presented vaporization coefficients and phase equilibrium data for a natural gas containing 0.3% of helium at 100 p.s.i.a. and at temperatures from −130° to −240° F. These workers disregarded the helium content of the equilibrium liquid phases—an important factor in helium extraction. Davis and others (*4*) studied two natural gases containing helium. A third gas studied, also containing helium, was prepared synthetically. Helium content of the gases ranged from 0.3 to 1.0%. These workers presented pressure-temperature data, but did not analyze the equilibrium phases.

The purpose of the present investigation was to obtain analyses of equilibrium liquid and vapor phases at pressures from 100 to 500 p.s.i.a. and temperatures ranging generally from −100° to −250° F. for both the gas serving as feed to the Amarillo helium plant during the period of this study and for a "helium-conservation" gas (hereinafter designated HC), which was of interest as a representative helium source in the conservation program. Helium contents of the gases as studied are approximately 2.3 and 0.75%, respectively. From these data, solubility of helium in the equilibrium liquid phases, per cent condensed, and equilibrium coefficient data for methane, nitrogen, and helium were determined.

EXPERIMENTAL APPARATUS AND PROCEDURES

The apparatus employed in this study was a Bureau of Mines phase equilibrium apparatus, with windowed cell, built-in temperature control, and stirring device. The apparatus, procedures, and sampling techniques employed in its operation were described in an earlier report (*2*). Continuous samples of the equilibrium vapor phases are passed through a thermal-conductivity analysis apparatus and recorder to establish the fact that true physical equilibrium conditions are obtained before samples are withdrawn for analysis. Gas analyses were made by means of a mass spectrometer (Consolidated Electrodynamics Corp.), modernized to C.E.C. Model 21-103 by means of conversion kits. Analytical data are considered accurate to within ±0.1%. Special analyses for helium, when present in concentrations below the optimum range for the mass spectrometer (0.5%), were made by means of a special helium analysis apparatus (*6*). This apparatus yields data considered accurate to within ±0.01%.

COMPOSITIONS OF MIXTURES STUDIED

The compositions of the gases studied are summarized in Table I. Data are reported on a carbon dioxide- and water-free basis, these components having been removed from the gas before conducting phase studies. Compositions are given both as 12- and four-component systems. In presenting the system as one of four components, ethane and heavier hydrocarbons are lumped into an ethane-plus fraction, and argon is included with nitrogen. The gases are identified as Cliffside gas, from the Government-owned field of the same name, and as HC gas. Data pertaining to depth of the producing structure, geological formation, etc., for Cliffside gas were presented in an earlier publication (*1*). Specific data pertaining to the source, formation, etc., for HC gas cannot be released at this time, but it can be stated that it is representative of certain helium-bearing natural gases found in the Texas and Oklahoma Panhandles and in southwestern Kansas.

PRESENTATION AND DISCUSSION OF DATA

Phase Equilibrium Data. Experimental phase equilibrium data for the two systems studied are presented in Tables II and III. The vapor-phase data are treated as four-component systems, but values also are given for ethane alone. Liquid-phase data are presented as six-component systems; the butane-plus fraction contains butane and heavier hydrocarbons. The tables also include data for the per cent of total helium dissolved in the equilibrium liquid phases, and smoothed K values for methane, nitrogen, and helium.

Some of the phase equilibrium data contained in the tables are plotted in Figures 1 to 3. Figure 1 is a plot of the phase data for Cliffside gas at 200 p.s.i.a., and data for HC gas at 300 p.s.i.a. are shown in Figures 2 and 3. The latter figures show in more detail the general phase behavior of ethane-plus in the vapor, and of ethane, propane, and butane-plus in the liquid. This will be of interest to indus-

Table I. Composition of Gases Studied (CO₂- and H₂O-Free Basis), Mole Per Cent

	Cliffside Gas		HC Gas	
Component	12-component system	4-component system	12-component system	4-component system
Methane	66.6	66.6	71.7	71.7
Ethane	3.8	6.7	6.6	12.2
Propane	1.9	. . .	3.8	. . .
n-Butane	0.6	. . .	0.9	. . .
Isobutane	0.1	. . .	0.5	. . .
n-Pentane	0.1	. . .	0.1	. . .
Isopentane	0.1	. . .	0.2	. . .
Cyclopentane	Trace[a]	. . .	Trace[a]	. . .
Hexanes plus	0.1	. . .	0.1	. . .
Nitrogen	24.3	24.4	15.2	15.3
Argon	0.1	. . .	0.1	. . .
Helium	2.3	2.3	0.75[b]	0.75[b]
CO_2 content of original untreated gas	0.7	. . .	Trace[a]	. . .

[a] Less than 0.05%.

[b] Analyzed by special helium analysis apparatus (*6*).

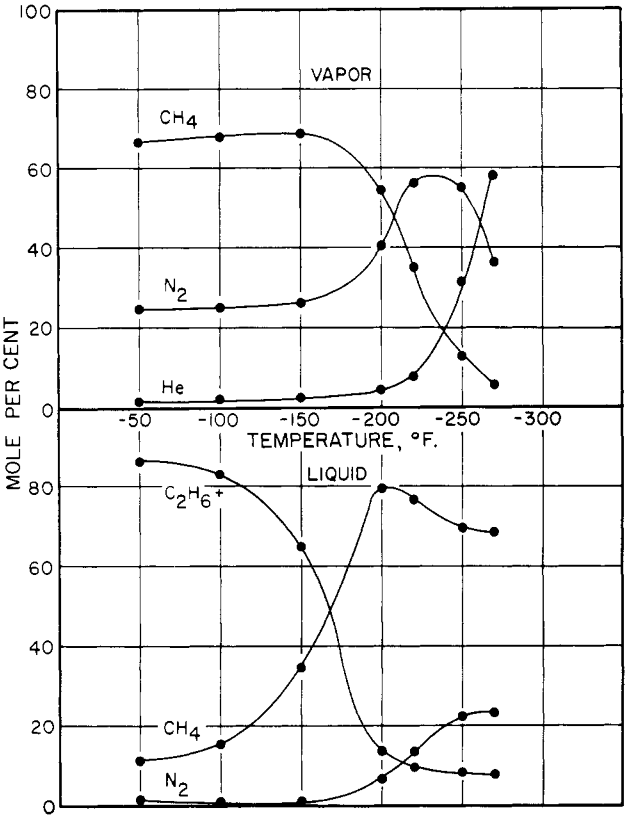

Figure 1. Vapor-liquid data on Cliffside gas at 200 p.s.i.a.

tries considering possible separation of LPG fractions as a by-product in the extraction of helium from natural gas. Solubility data for helium in the equilibrium liquid phases are presented graphically in a later section.

The ranges of temperature and pressure studied cover those required for commercial extraction of helium from natural gas. At the Amarillo plant, the first separation is effected at approximately 225 p.s.i.g. and −275° F. Referring to the plot for the 200-p.s.i.a. isobar (Figure 1), it is noted that the equilibrium vapor phase should be approximately 60 to 40 helium-nitrogen, with a small amount of methane. This vapor composition is obtained in actual practice. After a small amount of rectification at lower temperatures, during which methane is scrubbed out, the vapor is removed as crude helium and serves as the raw material for final purification.

Per Cent Condensed Data. Data relating to per cent of

(Continued on page 10)

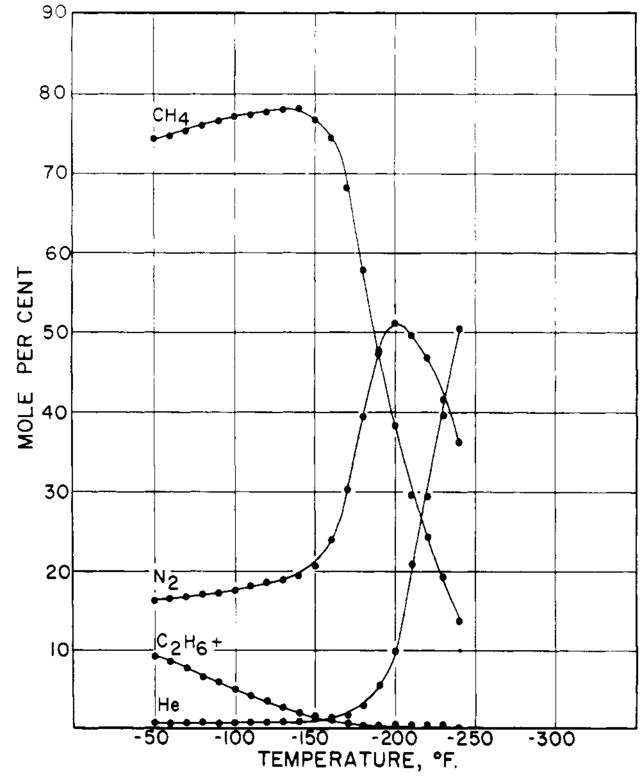

Figure 2. Equilibrium vapor phase compositions of HC gas at 300 p.s.i.a.

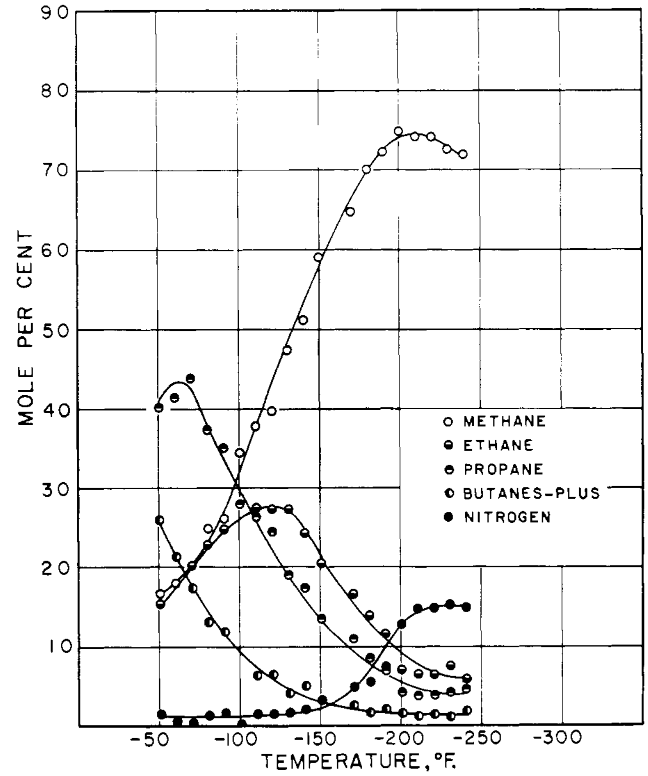

Figure 3. Equilibrium liquid phase compositions of HC gas at 300 p.s.i.a.

Table II. Phase Equilibrium Data, Cliffside Gas

Pressure, P.S.I.A.	Temp., ° F.	Vapor Composition, Mole %					Liquid Composition, Mole %						% of Total He in Liquid	Smoothed K Values		
		CH_4	C_2H_6	C_2H_6+	N_2	He	CH_4	C_2H_6	C_3H_8	C_4H_{10}+	N_2	He		CH_4[a]	N_2[b]	He[c]
100	−50	66.5	3.7	6.2	25.0	2.3	7.8	6.2	18.2	66.3	1.5	0.003	. . .	8.05	17.0	720
	−100	67.1	3.6	5.3	25.2	2.4	8.0	10.5	32.8	47.8	0.9	0.002	. . .	7.90	28.0	1100
	−150	68.8	2.4	2.6	26.3	2.3	18.0	31.1	33.1	17.8	0.0	0.002	. . .	3.88	. . .	1180
	−200	68.5	0.4	0.4	28.6	2.5	45.9	27.5	15.4	11.2	0.0	0.002	. . .	1.43	. . .	750
	−250	23.6	0.1	0.1	66.4	9.9	78.0	5.2	2.3	1.7	12.8	0.011	0.37	0.320	4.95	850
	−270	10.8	0.0	0.0	65.5	23.7	71.9	4.2	2.1	1.8	20.0	0.027	1.06	0.140	3.30	1250
200	−50	67.0	3.6	5.7	25.1	2.2	11.7	9.6	23.0	54.5	1.2	0.022	. . .	5.73	20.1	115
	−100	68.0	3.3	4.1	25.6	2.3	15.5	17.1	33.0	33.6	0.8	0.011	. . .	4.39	34.0	215
	−150	69.2	1.6	1.7	26.7	2.4	34.7	29.3	21.3	14.5	0.2	0.009	. . .	2.00	95	260
	−200	55.1	0.1	0.1	40.8	4.0	79.6	7.9	3.6	2.3	6.6	0.020	0.37	0.728	6.09	150
	−220	35.8	0.1	0.1	56.2	7.9	77.0	5.2	2.4	2.3	13.1	0.044	1.36	0.474	4.26	225
	−250	13.1	0.0	0.0	55.6	31.3	69.7	4.2	1.9	2.1	22.1	0.069	2.79	0.228	2.38	420
	−270	5.2	0.0	0.0	36.3	58.5	68.7	4.1	1.8	1.6	23.8	0.089	3.72	0.090	1.74	600
300	−50	67.2	3.7	5.7	24.8	2.3	17.4	11.0	23.1	47.2	1.2	0.068	. . .	4.20	21.0	55
	−100	68.2	3.1	3.7	25.7	2.4	26.0	20.6	27.1	25.0	1.2	0.018	. . .	2.86	21.2	128
	−150	68.2	1.2	1.3	27.9	2.6	45.1	24.3	16.2	13.2	1.2	0.014	0.07	1.40	17.0	135
	−175	62.7	0.4	0.4	33.8	3.1	75.0	10.8	5.1	3.8	5.3	0.036	0.41	0.910	6.90	95
	−200	39.1	0.1	0.1	52.7	8.1	73.6	6.9	3.8	2.9	12.7	0.054	1.69	0.543	4.15	115
	−220	25.8	0.1	0.1	56.7	17.4	72.6	4.4	2.0	1.3	19.6	0.111	4.21	0.369	2.83	170
	−250	10.5	0.0	0.0	41.2	48.3	68.7	4.1	1.9	1.4	23.7	0.158	6.56	0.150	1.80	295
400	0	66.8	3.7	6.4	24.5	2.3	17.6	10.4	20.5	50.1	1.4	0.023	. . .	3.80	. . .	. . .
	−50	68.0	3.6	5.4	26.4	2.2	17.9	11.7	24.8	43.5	2.1	0.080	. . .	3.45	20.2	31
	−100	68.5	2.7	3.4	25.7	2.4	34.7	21.1	23.5	19.1	1.6	0.026	0.08	2.13	15.3	96
	−150	66.8	0.9	1.0	29.5	2.7	66.5	16.6	8.6	4.9	3.4	0.027	0.18	1.10	7.40	100
	−190	38.3	0.1	0.3	52.8	8.6	73.6	4.9	2.3	2.3	16.8	0.127	4.11	0.450	3.25	76
	−200	32.6	0.1	0.2	52.8	14.4	72.1	4.6	2.2	1.8	19.1	0.180	6.66	0.446	2.79	87
	−250	7.7	0.0	0.0	33.5	58.8	68.7	4.0	1.8	1.3	23.9	0.279	11.7	0.105	1.41	229
500	0	66.9	3.7	6.4	24.4	2.3	23.3	9.7	18.3	46.4	2.3	0.026	. . .	2.90	. . .	. . .
	−50	67.5	3.4	5.3	24.9	2.3	25.8	13.0	23.3	35.4	2.4	0.096	. . .	2.60	16.5	20
	−100	68.5	2.6	3.0	26.2	2.3	37.0	20.5	21.7	19.1	1.7	0.041	. . .	1.78	11.5	62
	−135	67.7	1.3	1.4	28.3	2.6	60.6	17.1	10.9	7.6	3.8	0.043	0.22	1.16	6.70	75
	−150	62.6	0.7	0.8	33.1	3.5	72.1	10.1	5.6	4.0	8.2	0.041	0.62	0.910	4.90	70
	−175	46.6	0.3	0.3	45.7	7.4	74.0	5.5	2.5	1.9	15.9	0.175	5.37	0.600	3.10	44
	−200	27.2	0.1	0.1	50.1	22.6	70.0	4.3	2.0	1.4	21.9	0.347	13.8	0.389	2.20	65
	−250	5.9	0.0	0.0	27.3	66.8	67.9	3.8	1.9	1.8	24.2	0.363	15.3	0.082	1.16	170

[a] Average deviation between experimental and smoothed data, for all conditions, is 5%.
[b] Average deviation between experimental and smoothed data, below −200° F., is 3%.
[c] Average deviation between experimental and smoothed data, for all conditions, is 13%.

Table III. Phase Equilibrium Data for HC Gas

Pressure, P.S.I.A.	Temp., °F.	Vapor Composition, Mole %					Liquid Composition, Mole %						% of Total He in Liquid	Smoothed *K* Values		
		CH_4	C_2H_6	C_2H_6+	N_2	He	CH_4	C_2H_6	C_3H_8	C_4H_{10}+	N_2	He		CH_4[a]	N_2[b]	He[c]
100	−100	75.0	6.1	8.1	16.1	0.8	9.4	18.1	39.7	32.7	0.1	0.001	...	7.72	...	...
	−125	76.2	4.9	6.0	17.0	0.8	12.0	24.7	36.9	26.3	0.1	0.001	...	5.85	...	...
	−150	78.5	3.0	3.2	17.5	0.8	19.1	34.4	30.5	16.0	0.0	0.001	...	4.11	...	...
	−175	79.2	1.3	1.4	18.5	0.9	29.9	34.3	23.6	12.2	0.0	0.002	...	2.52	...	...
	−200	77.5	0.4	0.4	21.0	1.1	60.8	21.1	12.4	5.3	0.4	0.002	0.09	1.40	...	...
	−225	52.1	0.1	0.2	45.0	2.7	77.5	9.0	5.5	3.4	4.6	0.010	0.97	0.670	10.0	...
	−250	24.7	0.1	0.1	65.9	9.3	73.6	8.1	5.1	3.2	10.0	0.008	0.98	0.300	5.45	...
	−275	9.7	0.1	0.1	46.5	43.7	70.5	7.5	5.2	3.6	13.2	0.030	3.93	...	3.40	...
200	−100	76.3	4.8	5.8	17.0	0.9	18.4	23.1	30.9	27.5	0.1	0.007	...	4.02	...	...
	−125	77.7	3.5	3.8	17.6	0.9	24.7	29.4	29.8	16.0	0.1	0.002	...	2.95	...	...
	−150	78.6	1.8	1.9	18.6	0.9	42.8	30.6	19.4	7.0	0.2	0.002	...	2.00	...	...
	−175	74.9	0.5	0.5	23.5	1.1	64.1	17.7	10.8	6.1	1.3	0.004	0.17	1.27	20.5	...
	−200	55.0	0.2	0.2	41.6	3.2	73.1	11.2	6.7	3.4	5.6	0.011	1.13	0.735	8.05	...
	−225	31.5	0.2	0.4	52.4	15.7	69.0	8.9	6.3	3.7	12.1	0.040	5.09	0.400	4.76	...
	−250	14.7	0.3	0.5	43.2	41.6	70.4	7.1	4.5	3.1	14.9	0.062	8.13	0.215	3.02	...
300	−50	74.2	5.9	9.0	16.1	0.7	16.8	15.6	40.1	26.1	1.4	0.009	...	4.44	12.4	76
	−60	74.5	5.9	8.4	16.4	0.7	18.2	18.3	41.6	21.4	0.5	0.015	...	4.10	20.4	56
	−70	75.0	5.6	7.5	16.8	0.7	17.6	20.3	44.0	17.8	0.3	0.051	...	3.65	28.6	43
	−80	75.7	5.2	6.6	16.9	0.8	25.2	22.9	37.5	13.2	1.2	0.014	...	3.20	33.0	39
	−90	76.4	4.7	5.8	17.1	0.7	26.2	24.9	35.2	12.1	1.6	0.020	...	2.82	31.2	40
	−100	76.9	4.1	4.9	17.4	0.8	34.7	32.0	28.2	4.8	0.2	0.051	...	2.47	26.6	42
	−110	77.1	3.6	4.1	18.0	0.8	38.0	27.8	26.5	6.3	1.4	0.013	...	2.14	21.4	48
	−120	77.5	2.9	3.3	18.4	0.8	39.9	27.6	24.7	6.4	1.4	0.014	...	1.87	17.1	60
	−130	77.7	2.3	2.6	18.8	0.9	47.7	27.6	19.1	4.0	1.6	0.011	...	1.66	13.7	78
	−140	77.8	1.7	1.9	19.4	0.9	51.1	24.3	17.6	5.0	2.0	0.010	...	1.50	11.1	85
	−150	76.2	1.1	1.5	21.2	0.9	59.1	20.4	13.7	3.6	3.2	0.010	...	1.32	9.15	84
	−160	74.1	0.7	0.8	23.9	1.2	69.6[d]	8.5[d]	8.3[d]	1.5[d]	12.2[d]	0.013	0.68	1.21	7.55	75
	−170	67.8	0.4	0.5	30.1	1.6	64.8	16.8	11.0	2.5	4.8	0.056	4.12	1.04	6.36	58
	−180	57.6	0.2	0.2	39.4	2.8	70.0	14.1	8.7	1.6	5.5	0.065	6.50	0.813	5.38	50
	−190	47.1	0.2	0.3	47.4	5.2	72.2	11.7	7.0	1.9	7.1	0.055	6.30	0.637	4.60	58
	−200	38.1	0.1	0.2	52.0	9.7	74.7	7.0	4.0	1.3	12.9	0.093	11.51	0.503	3.98	108
	−210	29.5	0.1	0.2	49.5	20.8	73.9	6.4	3.7	1.1	14.8	0.092	11.81	0.410	3.50	198
	−220	24.0	0.1	0.2	46.7	29.1	73.6	6.4	3.8	1.3	14.8	0.117	15.23	0.329	3.10	280
	−230	19.0	0.1	0.2	41.4	39.4	72.4	7.4	4.1	0.9	15.1	0.116	15.23	0.255	2.76	360
	−240	13.5	0.0	0.0	36.2	50.3	71.8	6.8	4.6	1.7	15.0	0.113	14.93	0.191	2.50	435
400	−100	77.2	3.6	4.2	17.7	0.9	35.6	29.8	23.0	11.6	0.0	0.008	...	2.14	...	...
	−125	78.1	2.2	2.4	18.7	0.8	53.9	23.6	16.1	5.3	1.1	0.008	...	1.58	15.3	...
	−150	72.1	0.9	1.0	25.5	1.4	64.8	15.7	10.8	5.1	3.6	0.018	1.13	1.09	7.90	...
	−175	52.7	0.4	0.5	41.7	5.1	74.7	7.7	4.5	2.1	10.9	0.068	7.84	0.700	4.38	...
	−200	33.5	0.3	0.7	45.3	20.5	72.9	6.8	3.7	1.6	14.8	0.191	24.77	0.425	2.88	...
	−225	17.1	0.1	0.3	33.3	49.3	73.3	6.8	3.6	1.3	14.8	0.198	26.10	0.244	2.02	...
	−250	8.4	0.1	0.2	22.0	69.5	72.4	6.7	3.6	1.2	15.8	0.158	20.89	0.137	1.52	...
500	−100	77.1	3.3	3.8	18.1	1.0	43.9	22.9	20.4	11.4	1.4	0.011	0.37	1.69	12.6	...
	−125	76.0	1.8	2.0	20.9	1.1	59.7	18.8	13.5	5.2	2.8	0.016	0.69	1.26	8.30	...
	−150	66.2	0.8	0.9	30.6	2.3	68.2	11.1	8.7	5.1	6.9	0.060	5.54	0.875	4.95	...
	−175	46.4	0.3	0.3	42.9	10.4	71.5	7.2	4.8	3.2	13.1	0.185	23.30	0.568	3.30	...
	−200	14.1	0.1	0.2	38.5	47.2	72.7	6.6	3.6	1.6	15.2	0.352	46.53	0.342	2.21	...
	−225	9.6	0.1	0.1	27.8	62.5	71.7	6.5	3.5	1.2	16.8	0.329	43.57	0.195	1.52	...
	−250	6.0	0.0	0.0	17.5	76.6	72.1	6.6	3.6	1.3	16.1	0.215	28.47	0.106	1.09	...

[a] Average deviation between experimental and smoothed data, for all conditions except 500 p.s.i.a., at −150° to −250° F., is 4%.

[b] Average deviation between experimental and smoothed data, −200° F. and lower, is 6%.

[c] Average deviation between experimental and smoothed data is 36%.

[d] Bad sample, results discarded.

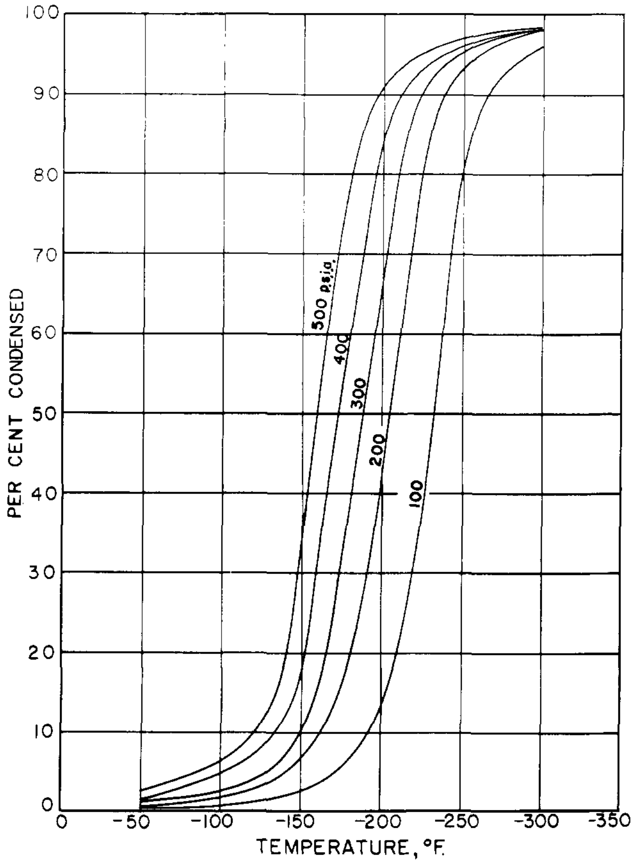

Figure 4. Isobaric condensation data on Cliffside gas

gas condensed, over the temperature and pressure range of the present study, were computed by means of the "classical" procedure, as described by Standing (*8*), for determination of vapor-liquid equilibrium data. The system was treated as containing four components: methane, ethane-plus, nitrogen, and helium. Smoothed experimental values of K for each of these components and assumed values of L (fraction condensed) and V (equal to $1 - L$) were substituted into the equation for each pressure-temperature condition. The method employed in obtaining the smoothed K values is discussed in the section on Equilibrium Coefficients. Correct L values were indicated when the summation for the four components was equal to unity. The experimental data were plotted as isobars, and smooth curves drawn through the points. Condensation curves for Cliffside gas are reproduced in Figure 4. Reference to the 200-p.s.i.a. isobar (Figure 4) shows that approximately 96% of the gas is condensed at conditions existing at the crude separator at the Amarillo plant.

Helium Solubility Data. A factor of extreme importance in the design of helium-separation plants is the solubility of helium in equilibrium liquid phases at conditions at which the initial separation of helium is effected. This represents a potential loss of helium, unless "stripping" procedures are employed to recover the dissolved helium.

Figures 5 and 6 are plots of experimental data (from Tables II and III) for the solubility of helium in equilibrium liquid phases for Cliffside and HC gases, respectively. In the Cliffside system it is noted that each isobar exhibits a well-defined minimum value, and at higher pressures (500 p.s.i.a.) a maximum appears. In the HC data maxima are well defined at 400 and 500 p.s.i.a., and minima do not appear except in the single case of the 300-p.s.i.a. isobar, where the study was continued to warmer temperatures (-50° F.). In the range -50° to -150° F. for this isobar, there is some question about the validity of the appearance of the first maximum because data in this range were scattered. Two of the experimental points (-70° F. and -100° F.) were abnormally high. In addition, the experimental value for HC gas at 100 p.s.i.a. and -250° F. was low. All other data for both gases fit the curves reasonably well. For the Cliffside system only four experimental points failed to fit the smooth curves. These points are marked with arrows in the figure.

The helium content of the equilibrium liquid phases may also be expressed in terms of percentage of the total helium contained in the system (vapor plus liquid) at each pressure-temperature condition. Expressing the data in this manner is of particular interest in helium separation, for it indicates the maximum extraction efficiency that might be obtained. These data were computed for the Cliffside and HC systems and are plotted in Figures 7 and 8. At the Amarillo plant, where helium is separated from natural gas at 225 p.s.i.g. and -275° F., Figure 5 indicates that the liquid phase should contain about 0.1% helium. Figure 7 shows that this corresponds to about 4% of the total helium.

Choice of conditions for the initial separation of helium from HC gas would have to be considered carefully. Assuming, arbitrarily, that the same conditions are chosen for this gas as are now employed at the Amarillo plant, reference to Figures 6 and 8 shows that the liquid phase would contain less than 0.1% helium, but approximately 15% of the total helium would be lost by solution. Thus, assuming no further loss of helium, separation efficiency could not exceed 85%.

In selecting conditions for extraction of helium from natural gas, it would appear that the initial separation should be made at conditions where the solubility of helium in the liquid is low. One may choose, for example, 100 p.s.i.a. and -125° F. However, if these conditions were chosen for Cliffside gas, reference to Table II shows that the crude helium stream would contain much less than 60%

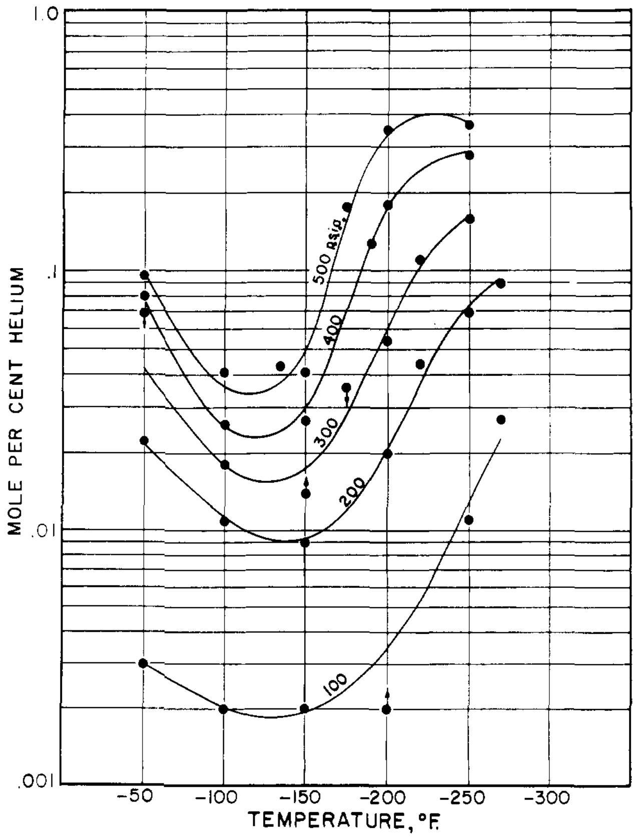

Figure 5. Solubility of helium in equilibrium liquid phases, Cliffside gas

helium. Thus, it is necessary to strike a happy medium and select operating conditions yielding a high purity crude, yet consistent with an acceptable loss of helium by solution in the liquid. To produce an acceptable crude stream, the gas must be fairly highly condensed (ca. 95%). In bureau helium operations at all plants, operating conditions are selected to meet this requirement; the total loss of helium in the liquid phase is kept low enough to be acceptable without the necessity of stripping the liquids.

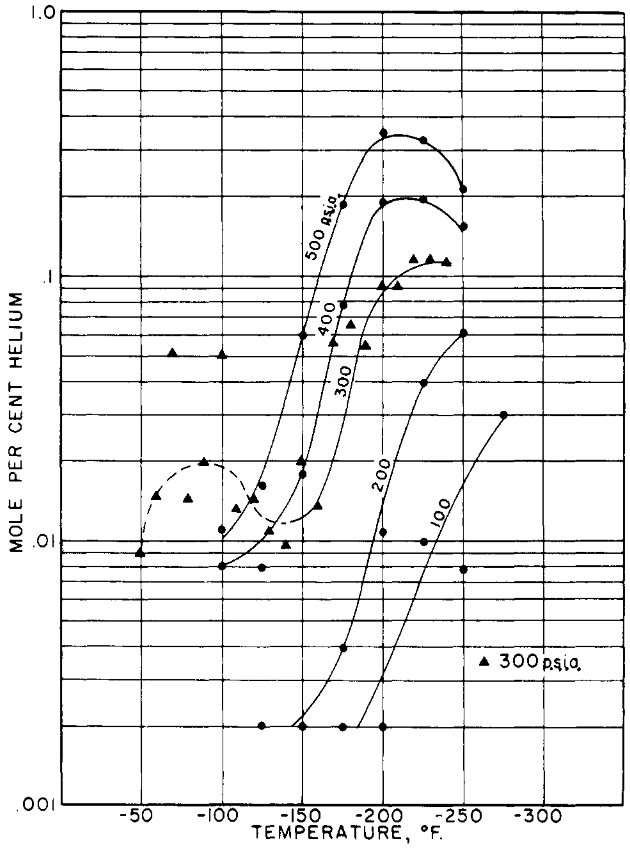

Figure 6. Solubility of helium in equilibrium liquid phases, HC gas

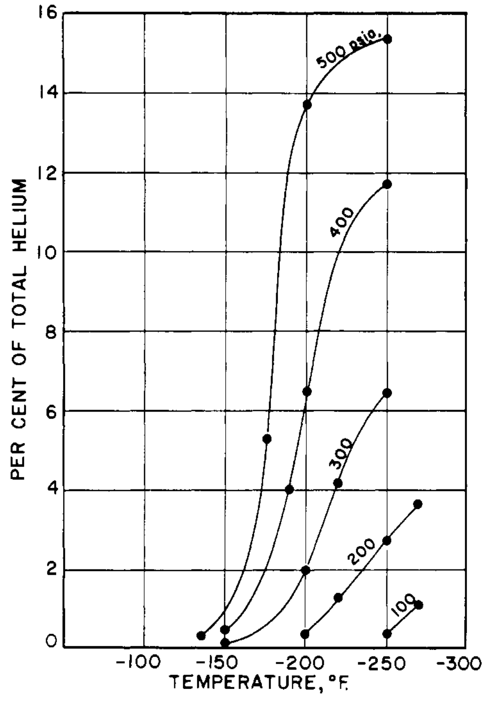

Figure 7. Per cent of total helium in liquid, Cliffside gas

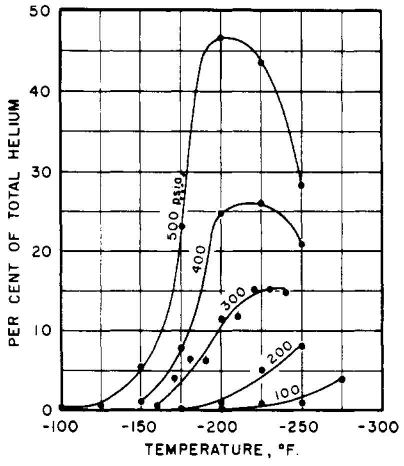

Figure 8. Per cent of total helium in liquid, HC gas

Equilibrium Coefficients. Equilibrium vaporization coefficients, $K = y/x$ (in which y is the mole fraction of the component in the vapor phase and x is its fraction in the liquid), are of importance not only in the separation of helium from natural gas, but in the entire petroleum industry. Only a few workers have presented K data for natural gas systems containing helium. Brown and Stutzman (*3*) completed a correlation of K data for methane, ethane, and nitrogen from systems of widely differing compositions. Gore, Davis, and Kurata (*7*) presented phase relationship data for two natural gases (not containing helium). They employed a modified dew point-bubble point apparatus, and, because the equilibrium phases were not analyzed, did not obtain equilibrium coefficient data. Later, Davis and others (*4*) published the results of a similar study with two natural gases containing helium, and for a third mixture, synthetically prepared, also containing helium. P-T diagrams were given, but because the phases were not analyzed, K data were not derived.

METHANE. Isobaric plots of smoothed experimental data for methane for Cliffside and HC gas are given in Figures 9 and 10. The data were derived by smoothing the experimental vapor and liquid data and obtaining the K data by reading the y and x values from these smoothed curves. Brown and Stutzman's (*3*) correlated data at 100 and 500 p.s.i.a. are also presented in the figures for comparison.

At all pressures, the K data decrease with decreasing temperature. At 400 and 500 p.s.i.a. the data for the Cliffside and HC gases are in excellent agreement; the curves nearly superimpose, when the data are plotted on a single graph. At 300 p.s.i.a. agreement is good; the curves run almost parallel to each other, and the HC data are approximately 8% lower than the values for Cliffside gas. At 200 and 100 p.s.i.a. this situation is reversed, and the HC data are higher than Cliffside data. The data agree well at these pressures at −250° F., but as the temperature is increased, the HC values rise steadily above the Cliffside data, until at −10° F. they are 17% higher at 200 p.s.i.a., and 12% higher at 100 p.s.i.a. Comparing Cliffside data with the Brown and Stutzman data, agreement is considered good for the 100-p.s.i.a. isobar over the middle temperature range. Indications are that disagreement would increase at both warmer and colder temperatures than those studied; at 100 p.s.i.a. and −100° F. Cliffside gas K values showed an indication of leveling off that was not demonstrated by the correlated data. At 500 p.s.i.a., disagreement is greatest over the middle temperature range, and Cliffside data are approximately 25% higher than B-S data at −150° F.

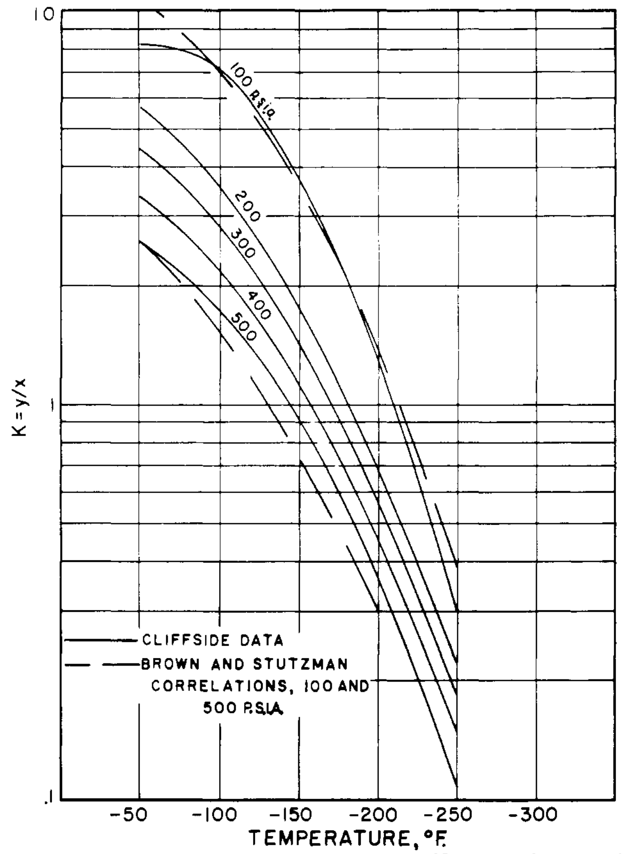

Figure 9. Equilibrium vaporization coefficients for methane in Cliffside gas, with Brown and Stutzman correlated data

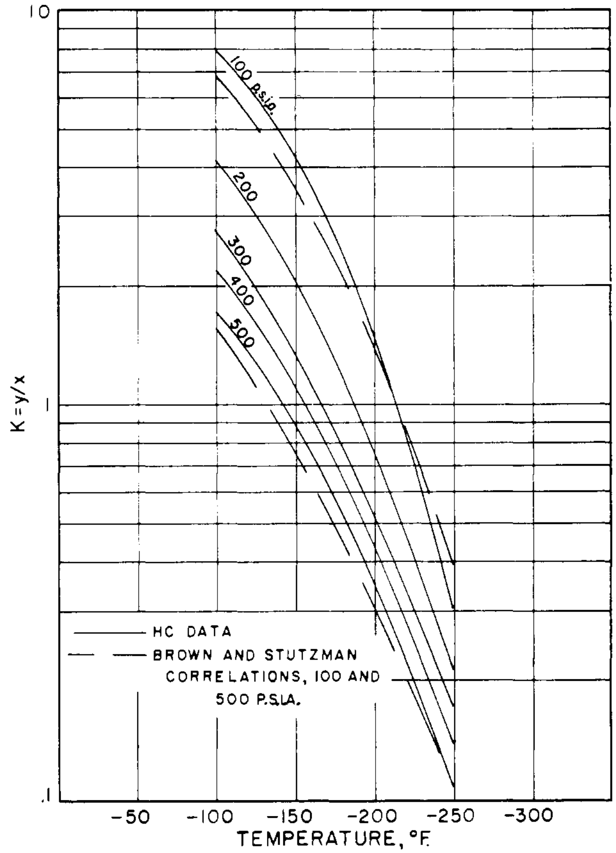

Figure 10. Equilibrium vaporization coefficients for methane in HC gas, with Brown and Stutzman correlated data

NITROGEN. Smoothed K data for nitrogen for both Cliffside and HC gas are shown in Figure 11. Brown and Stutzman's correlated data at 500 p.s.i.a. are included for comparison. For the 100-p.s.i.a. isobar in the Cliffside system, K values were indeterminate in the temperature range of approximately −130° to −210° F. because it was impossible to obtain sufficiently accurate analytical data for nitrogen concentrations in the liquid phases. In this temperature range the nitrogen content in the liquid phases drops nearly to zero, and a satisfactory method of analysis was not available to determine these low concentrations of nitrogen in the presence of large amounts of hydrocarbons. As mentioned earlier, all analyses in this study were made by means of a mass spectrometer (except for the special helium analyses), and the mass spectrometer data indicated zero for nitrogen in liquid in this area.

Brown and Stutzman's correlated data at 100 p.s.i.a. (not plotted in Figure 11) do not show this indeterminate area. HC gas also indicated indeterminacy at 100 p.s.i.a., although the study was not carried to temperatures above −100° F., and the "warm end" plot was not defined. Indeterminate values also were obtained for the 200-p.s.i.a. isobar for Cliffside gas (dashed curve in the figure). Agreement generally is considered good between the HC and Cliffside data for all isobars. At 300 p.s.i.a., however, HC data indicated a maximum at approximately −75° F. This maximum is so well defined that it is considered significant. Cliffside data, on the other hand, "leveled off" at the higher temperatures.

Agreement with the Brown and Stutzman correlated data at 500 p.s.i.a. is not considered good. Their data were consistently lower than the experimental data obtained in the present study. Greatest deviation was obtained around −100° F., where the B-S data were 42% lower than the Cliffside data.

HELIUM. Smoothed K data for helium in Cliffside gas are presented in Figure 12. The data for HC gas (Table III) are not plotted because some of the values for helium in the liquid phases were less than 0.005 mole % and are of questionable accuracy. It is generally considered, in this work, that when the helium concentration in the liquid is in the range 0.005 to 0.01 mole %, the values are reproducible to approximately ±40% of the value. K values, therefore, are not included in the table for cases where the helium concentration is less than 0.005 mole %. The experimental analytical value is shown, however, regardless of its magnitude, as it may be of interest in making engineering calculations.

Referring to Figure 12, it is observed that each curve shows a maximum at approximately −125° F. Each isobar also shows a minimum value, which is displaced toward warmer temperatures with increasing pressure.

The "derivation" of Figure 12 may be discussed with the aid of the solubility data for helium in liquid, Figure 5. Considering the 500-p.s.i.a. isobar in Figure 5, between −50° and −122° F. the solution of helium decreases to a minimum value. Because the helium content of the vapor remains virtually unchanged over this temperature range, the resulting equilibrium coefficients approach a maximum, as shown in Figure 12. The helium solubility curve shows a "flat" minimum between approximately −100° and −125° F., and because the helium content of the vapor is constant in this region, there results a correspondingly flat maximum in K. Between −150° and −175° F., although the helium contents of both vapor and liquid phases are increasing, the latter is increasing at a faster rate than the former; hence the K values pass through a minimum. Beginning at −175° F. and continuing to colder temperatures, the helium content of the vapor increases more rapidly than the solution of helium; consequently, the K values increase.

Experimental equilibrium coefficient data for helium in natural gas have not been published heretofore. However, Davis and others (*4*), in discussing phase data of two helium-bearing natural gases, called attention to the marked effect of small amounts of helium on the bubblepoint and stated that "the effect is marked only at the low temperatures, presumably due to the fact that the *K* for helium gas goes through a maximum as temperature is decreased."

The probable truth of their assumption may be discussed with the aid of Figure 12. The lowest temperatures studied represent conditions where 90 to 95% of the gas is condensed. In this temperature range *K* values increase rapidly. However, at the true bubble point (100% condensed) no vapor phase would be present, and *K* values would be indeterminate. But at conditions extremely close to the bubble point, where an infinitesimal vapor phase would exist, the composition of the vapor would be essentially 100% helium. The helium content of the coexisting liquid phase would be almost identical to the helium concentration in the feed gas. A limiting value of *K* equal to 1.00/0.023 or 43.5, would occur. Because *K* values for all isobars in Figure 12 are much higher than this limiting value at the lowest temperatures studied, then at still lower temperatures the curves must pass through a maximum, then decrease, until all isobars join at the bubble point at the limiting *K* value.

The above discussion concerns the behavior of the *K* factor for helium at temperatures near the bubble point. If the behavior of *K* data for other components, such as nitrogen, methane, or ethane, are to be studied as the temperature is lowered to the bubble point, it would be necessary to consider the "enhancement factor," as discussed by Dokoupil, van Soest, and Swenker (*5*). Briefly, this enhancement factor may be defined as an increase in the vapor pressure of the condensable component in the liquid phase above the value normally expected, when the liquid phase containing the condensable component is in equilibrium with a vapor phase containing a high concentration of a noncondensable component, such as helium. additional helium-bearing natural gases. Future work planned at this laboratory includes studies at higher pressures and temperatures, to delineate *P-T* curves. In addition, a detailed study of *K* values for helium would be particularly helpful.

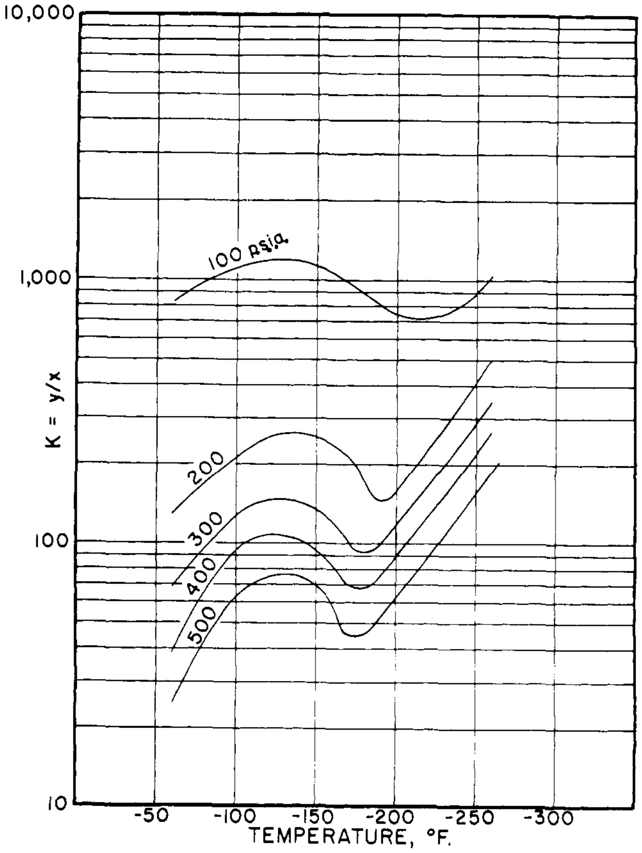

Figure 12. Equilibrium vaporization coefficients for helium in Cliffside gas

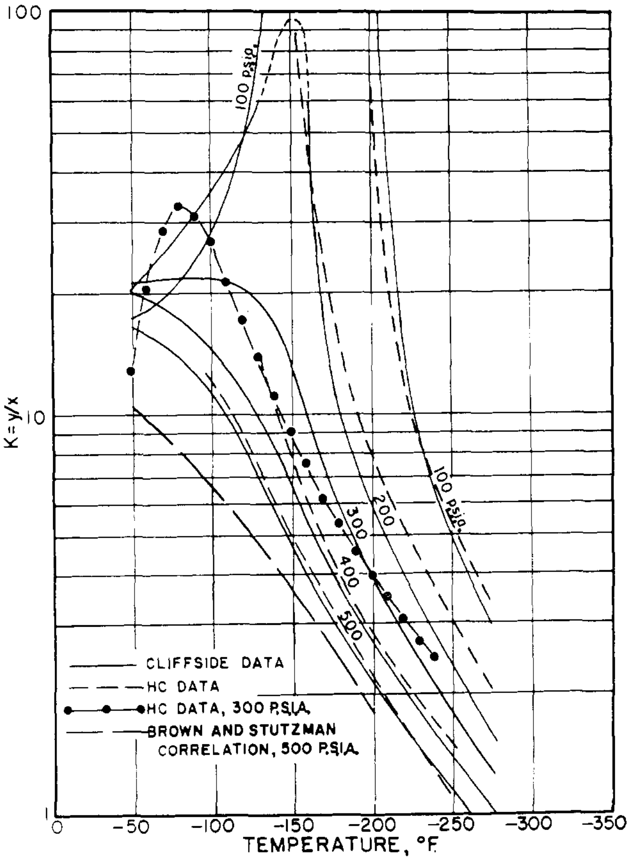

Figure 11. Equilibrium vaporization coefficients for nitrogen

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