

Liquid-Vapor Equilibrium in the System Normal Hydrogen-Helium

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(Received 18 October 1963)

Liquid-vapor equilibrium phase compositions for the binary system normal hydrogen-helium have been determined for 11 isotherms in the range 15.50°–32.50°K and at pressures up to 500 psia. The vapor recirculation method of obtaining equilibrium was used in conjunction with a liquid hydrogen vapor-pressure controlled cryostat. Analyses were made on a mass spectrograph. The results are presented in both tabular and graphical form, and the general behavior of the system discussed. An agreement with some previous investigations is demonstrated, and conflicts in existing data are resolved. Some problems of theoretical correlation of the data are discussed.

I. INTRODUCTION

THE liquid-vapor phase equilibrium of the hydrogen-helium system is of interest for a number of reasons. High-pressure gaseous helium is often used in the transfer of liquid hydrogen from storage tanks. The possibility of using hydrogen-helium mixtures in bubble chambers to study the interaction of elementary particles with helium nuclei has also been cited.¹ Further, the liquid-vapor equilibrium of the two elements with the lowest critical temperatures is of particular interest from a theoretical point of view.

Two previous investigations of liquid-vapor equilibrium in the hydrogen-helium system have been reported, the first of which is a Ph.D. thesis by S. R. Smith² conducted at Ohio State University in 1952. Smith reported equilibrium phase compositions at temperatures of 17.40°, 20.39°, and 21.80°K, and for pressures up to 875 psia. His experimental data have been tabulated in two recent publications.^{3,4}

Recently, Roellig and Giese¹ reported helium solubility in liquid hydrogen at nine isolated points. They obtained temperature indirectly by calculating the partial pressure of hydrogen from experimentally determined liquid and vapor phase compositions, assuming that Raoult's law is valid for the liquid⁵ and ideal gas behavior for the vapor.

Comparison of the limited data from these two sources shows poor agreement, especially in the liquid phase, where Roellig and Giese show helium concentrations exceeding those of Smith by as much as a factor of 10. Eckert and Prausnitz⁶ pointed out that the assumption of ideal behavior in the liquid and vapor phases led to significant errors in the temperatures reported by Roellig and Giese. They recalculated the temperatures using a better model and obtained

temperatures differing from the published values by as much as 2.7°K. The use of these corrected temperatures improves the agreement with Smith's data somewhat; however, the wide discrepancy in liquid compositions still exists. Roellig and Giese concluded from their data that the solubility of helium decreases with increasing temperature, while the data of Smith, over a more limited temperature range, show the opposite behavior, although in a somewhat inconsistent manner.

Equilibrium liquid and vapor phase compositions for the normal hydrogen-helium system have been obtained at 11 temperatures in the range 15.50°–32.50°K, and at pressures up to 500 psia. Investigation of the system using equilibrium hydrogen instead of normal hydrogen is now in progress. It is anticipated that differences in the results will be measurable but small.

II. EXPERIMENTAL APPARATUS

A vapor-recirculating equilibrium apparatus with a vapor pressure controlled liquid hydrogen bath, based on a design by Dodge and Dunbar, was constructed and used for this work. Samples of the liquid were withdrawn through stainless-steel capillary tubing, while a portion of the equilibrium vapor was isolated in the external portion of the circulation loop and sampled at room temperature. Sample compositions were determined by mass spectrometry.

Equilibrium temperatures were measured with a calibrated platinum resistance thermometer in conjunction with a G-2 Mueller bridge and reflecting galvanometer. Secondary temperatures were measured by gold-cobalt vs copper differential thermocouples referenced to the resistance thermometer. Temperature control to within $\pm 0.005^\circ\text{K}$ or better was maintained at all isotherms except those of 15.50° and 17.07°K, for which the temperature control was $\pm 0.02^\circ\text{K}$ or less.

Equilibrium pressures were measured to within ± 0.5 psi by means of a 0–500 psi calibrated 16 in. Heise gauge.

A detailed description of the experimental apparatus will be published elsewhere.

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¹ L. O. Roellig and C. Giese, *J. Chem. Phys.* **37**, 114 (1962).

² S. R. Smith, Ph.D. thesis, Ohio State University, 1952.

³ I. Brazinsky and B. S. Gottfried, NASA Tech. Note D-1403 (1962).

⁴ D. E. Drayer and T. M. Flynn, NBS Tech. Note 109 (1961).

⁵ C. A. Eckert and J. M. Prausnitz, *J. Chem. Phys.* **39**, 246 (1963).

TABLE I. Summary of experimental data.

Temperature (°K)	Liquid		Vapor		Temperature (°K)	Liquid		Vapor			
	Pressure (psia)	Mole % He	Mole % H ₂	Mole % He		Mole % H ₂	Pressure (psia)	Mole % He	Mole % H ₂	Mole % He	Mole % H ₂
15.50	49.5	93.78	6.22	26.00	400.0	6.64	93.36	68.58	31.42
	75.0	0.29	99.71	95.51	4.49		500.0	8.48	91.52	70.02	29.98
	100.0	0.46	99.54	96.31	3.69	29.00	127.0	0.91	99.09	14.03	85.97
	125.0	0.51	99.49	96.77	3.23		151.0	1.50	98.50	21.92	78.08
	150.0	0.55	99.45	97.02	2.98		175.0	2.20	97.80	27.75	72.25
	175.0	0.64	99.36	97.14	2.86		200.0	3.07	96.93	32.93	67.07
	200.0	0.71	99.29	97.29	2.71		250.0	4.59	95.41	39.54	60.46
	250.0	0.82	99.18	97.41	2.59		300.0	6.21	93.79	43.70	56.30
300.0	0.87	99.13	97.48	2.52	400.0	9.63	90.37	47.95	52.05		
17.07	56.5	0.36	99.64	89.67	10.33	500.0	13.35	86.65	49.20	50.80	
	75.0	0.43	99.57	91.86	8.14	30.60	300.0	7.29	92.71	30.32	69.68
	100.0	0.57	99.43	93.30	6.70		400.0	13.24	86.76	32.60	67.40
	125.0	0.72	99.28	94.12	5.88	450.0	17.95	82.05	30.36	69.64	
	150.5	0.80	99.20	94.64	5.36	31.00	176.5	1.49	98.51	11.28	88.72
	175.0	0.89	99.11	95.03	4.97		199.0	2.51	97.49	15.59	84.41
	200.0	1.00	99.00	95.15	4.85		250.0	4.78	95.22	22.58	77.42
	250.0	1.14	98.86	95.56	4.44		300.0	7.49	92.51	26.57	73.43
	300.0	1.31	98.69	95.82	4.18		325.0	8.73	91.27	27.55	72.45
	400.0	1.51	98.49	95.90	4.10		350.0	11.03	88.97	27.85	72.15
20.40	35.0	0.34	99.66	53.60	46.40	375.0	12.93	87.07	27.59	72.41	
	50.0	0.41	99.59	65.45	34.55	400.0	15.64	84.36	25.78	74.22	
	75.0	0.61	99.39	75.40	24.60	413.0	20.87	79.13	21.85	78.15	
	100.0	0.84	99.16	80.30	19.70	31.50	177.0	1.27	98.73	7.67	92.33
	125.0	1.05	98.95	83.20	16.80		200.0	2.30	97.70	11.94	88.06
	150.0	1.30	98.70	84.80	15.20		225.0	3.61	96.39	15.64	84.36
	175.0	1.54	98.46	86.03	13.97		250.0	4.83	95.17	18.35	81.65
	200.0	1.67	98.33	87.13	12.87		275.0	6.26	93.74	20.30	79.70
	250.0	2.05	97.95	88.41	11.59		300.0	8.18	91.82	21.37	78.63
	300.0	2.36	97.64	88.97	11.03	325.0	10.47	89.53	21.49	78.51	
	400.0	2.96	97.04	90.08	9.92	351.0	16.59	83.41	17.58	82.42	
	500.0	3.39	96.61	90.35	9.65	31.90	174.5	0.81	99.19	4.00	96.00
23.00	50.0	0.38	99.62	37.00	63.00		200.0	2.07	97.93	8.31	91.69
	75.0	0.75	99.25	53.44	46.56		220.0	3.17	96.83	11.75	88.25
	100.0	1.15	98.85	62.90	37.10		238.5	4.29	95.71	13.86	86.14
	125.0	1.36	98.64	67.87	32.13		250.5	4.99	95.01	14.82	85.18
	150.0	1.72	98.28	71.75	28.25		261.5	15.62	84.38
	175.0	2.15	97.85	74.35	25.65	275.5	6.87	93.13	16.19	83.81	
	200.0	2.39	97.61	76.30	23.70	289.5	8.71	91.29	16.35	83.65	
	250.0	2.91	97.09	78.78	21.22	300.0	10.10	89.90	15.88	84.12	
	300.0	3.55	96.45	80.55	19.45	308.5	12.02	87.98	
	400.0	4.58	95.42	82.34	17.66	32.50	188.5	0.98	99.02	3.12	96.88
500.0	5.46	94.54	83.30	16.70	200.0		1.68	98.32	4.80	95.20	
26.00	81.0	0.67	99.33	22.60	77.40		220.0	3.10	96.90	7.45	92.55
	100.0	0.97	99.03	33.50	66.50		242.0	5.09	94.91
	125.0	1.43	98.57	43.37	56.63		250.0	5.99	94.01
	150.0	1.92	98.08	49.77	50.23		258.0	6.75	93.25
	200.0	2.86	97.14	56.90	43.10						
	250.0	3.64	96.36	62.67	37.33						
300.0	4.76	95.24	65.65	34.35							

III. EXPERIMENTAL RESULTS

For a binary system the phase rule shows that the equilibrium liquid and vapor phase compositions are invariant at fixed pressure and temperature. The data may be represented graphically by two surfaces on a three-dimensional pressure-temperature-composition diagram, each surface representing a single phase. The two surfaces merge along a critical curve, consisting of points at which the two phases become indistinguishable. It is customary to describe the equilib-

rium surfaces graphically by showing their projections on one or more of the three P - T - x coordinate planes.

The experimental results of this investigation are summarized in Table I and shown graphically in Figs. 1-6. Figure 1 shows a plot of isotherms on a P - x diagram. Of particular interest are the liquid phase compositions, shown on an expanded scale in Fig. 2. Figures 3 and 4 show isobars in the T - x plane, with 4 being the expanded-scale liquid region. A P - T diagram obtained by cross plotting data from P - x and T - x

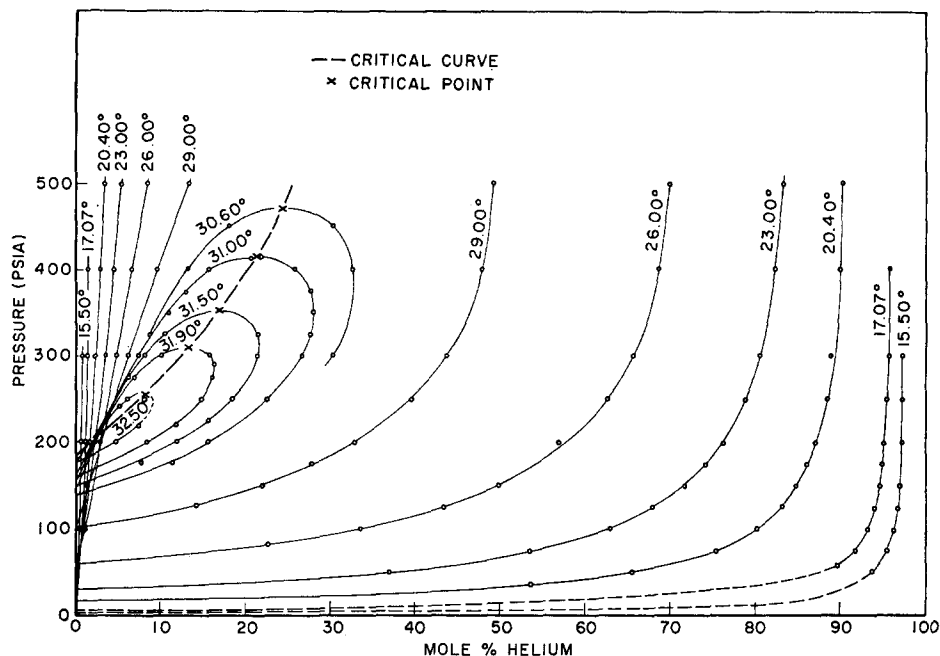


FIG. 1. Isothermal pressure-composition diagram.

diagrams is given in Fig. 5, and the equilibrium constants, the ratios of vapor-phase to liquid-phase mole fractions, are shown in Fig. 6.

The behavior of this system is seen to be typical of binary systems in which the critical temperatures of the components are far apart. Similar behavior is exhibited, for example, by the systems nitrogen-hydrogen and nitrogen-helium. The closed loops in Fig. 1 represent temperatures for which the critical point occurs at a pressure below 500 psia. These loops show a region of retrograde condensation of the first type, which is that portion of the loop lying to the right of a vertical line through the critical point. The region in which the liquid lines cross (Figs. 1 and 2) is one of retrograde condensation of the second type. On the $T-x$ diagrams, this appears as a region in which individual liquid lines (isobars) have both a positive and a negative slope. This region is seen to be restricted to helium concentrations of 4% or less, and to pressures below about 230 psia. Over most of the range covered in this study, the data exhibit reverse order solubility, which is defined as an increase in solubility of a constituent with increasing temperature at constant pressure.

The critical curve locus indicated in Figs. 1, 3, and 5 has been estimated from a study of the trend of the data on $P-x$, $T-x$, and $P-T$ plots. The loops at 31.00° and 31.50°K were almost completely closed with experimental data points, which served to define the shape of loops at nearby temperatures. The critical curve obtained from this diagram was cross plotted on $T-x$ and $P-T$ diagrams and found to be consistent with the data as it appears on those diagrams. On the $P-T$ plot, this critical curve or envelope is tangent to each of the curves of constant composition, with the point

of tangency representing the junction of the dew- and bubble-point curves for that composition.

IV. COMPARISON WITH PREVIOUS WORK

Comparisons of the present data with those of Smith² and of Roellig and Giese¹ are shown in Figs. 7

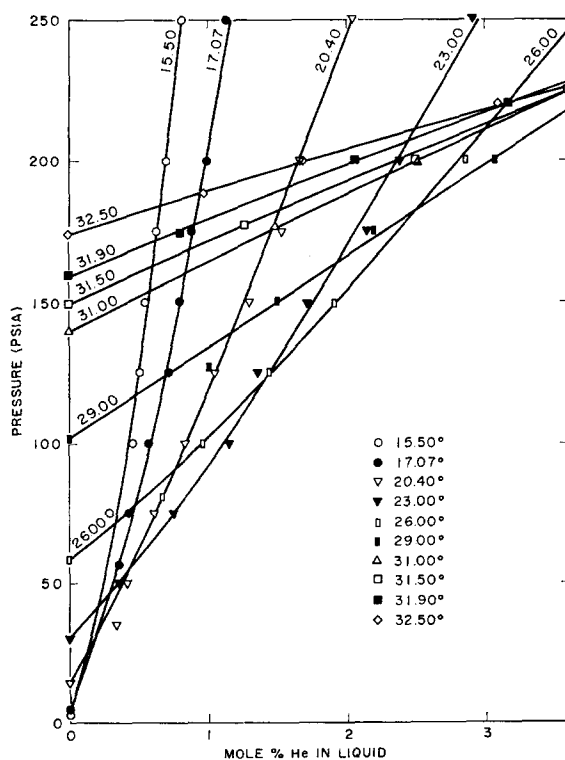


FIG. 2. Isothermal pressure-composition diagram showing liquid region on expanded scale.

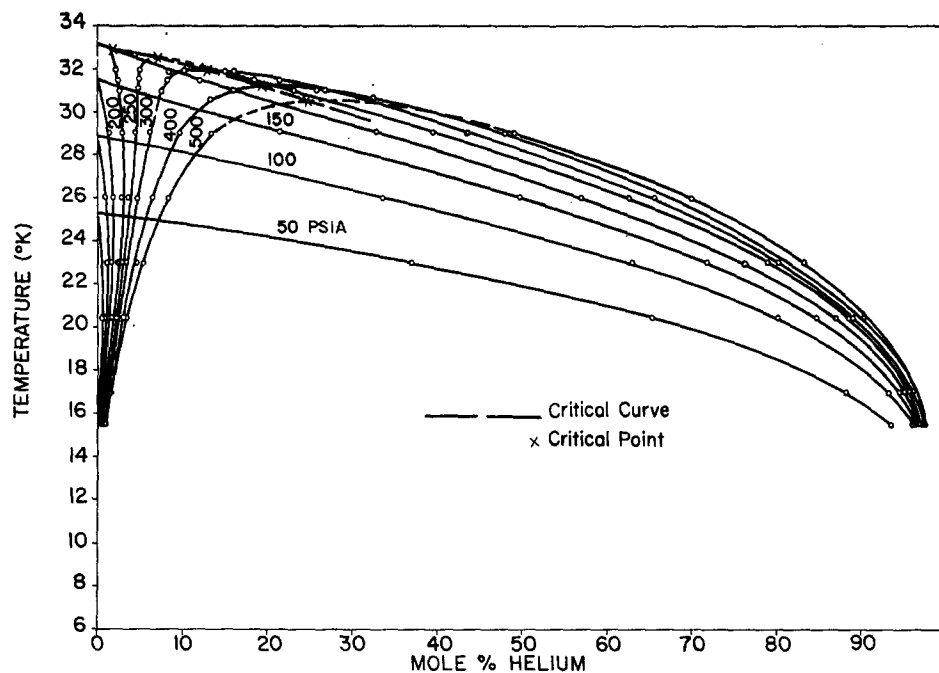


FIG. 3. Isobaric temperature-composition diagram.

and 8. The 20.4°K isotherm of Smith was duplicated in the present work, enabling a direct comparison to be made, and agreement is seen to be quite good. For the comparison with Smith's data at 17.4° and 21.8°K, isotherms from the present data were obtained by

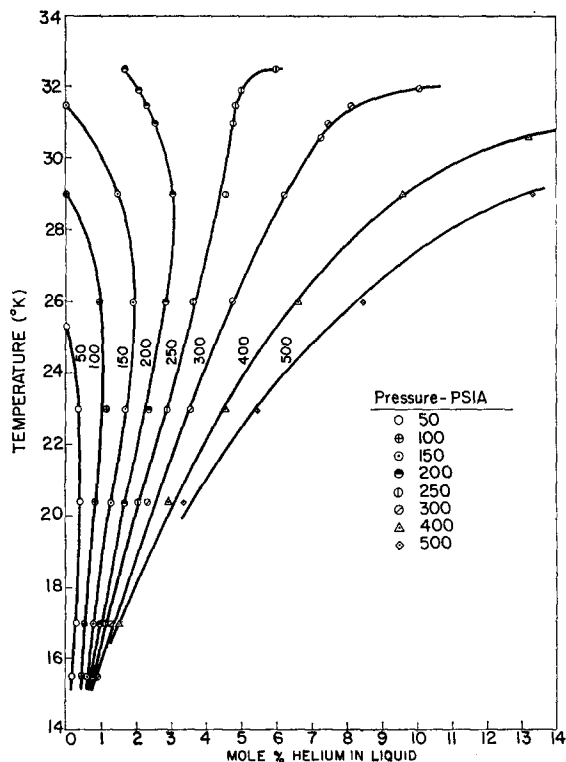


FIG. 4. Isobaric temperature-composition diagram showing liquid region on expanded scale.

interpolation on a large-scale $T-x$ diagram. The agreement for these isotherms is poorer than that at the normal boiling point 20.4°K. While there is considerable scatter in Smith's data, a smooth curve through his points appears to agree with this work if his temperatures are adjusted downward by about 0.5°K. His temperatures may well be in error by this amount since they were measured with a single copper-constantan thermocouple referenced in an ice bath. Corruccini⁶ has analyzed Smith's data by several qualitative methods and concluded that the data are not particularly consistent.

Several of the isolated points of Roellig and Giese have been plotted in Figs. 7 and 8, using the corrected temperatures of Eckert and Prausnitz.⁵ The agreement with this work is uniformly good for the vapor phase. In the liquid phase, agreement is fair at temperatures around 26°K, while at lower temperatures Roellig and Giese show unusually large helium concentrations, some of which fall outside the limits of Fig. 7. Corruccini has also concluded that this behavior cannot be correct.

V. THEORETICAL CONSIDERATIONS

Brazinsky and Gottfried³ attempted to show the consistency of Smith's data by comparison of the calculated values of hydrogen fugacity for the two phases. Eckert and Prausnitz⁵ and Corruccini have pointed out that the test is insensitive because of the small amount of helium in the liquid. It can be shown that most of the commonly used variations of the Gibbs-Duhem equation suffer from the same shortcoming, and are inconclusive when applied to the data

⁶ J. Corruccini (unpublished note, 1963).

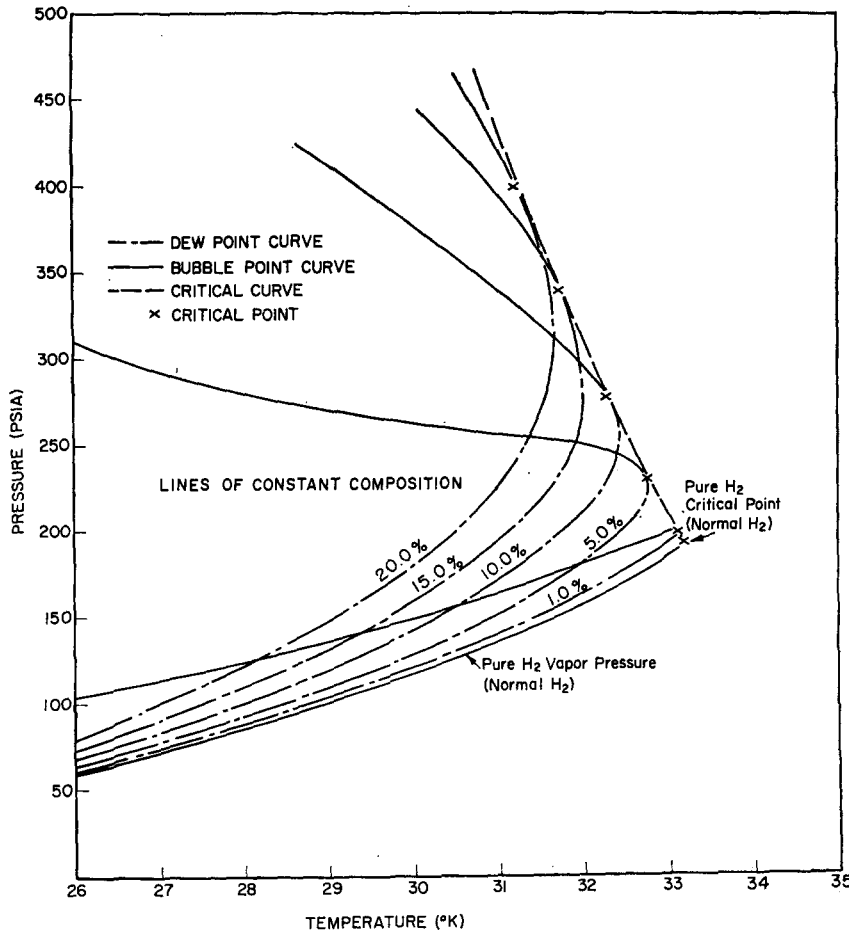


FIG. 5. Pressure-temperature diagram.

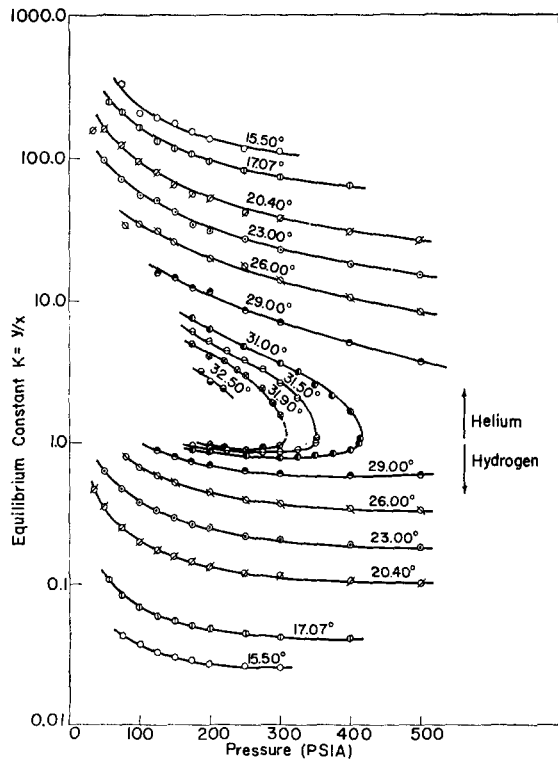


FIG. 6. Equilibrium K values.

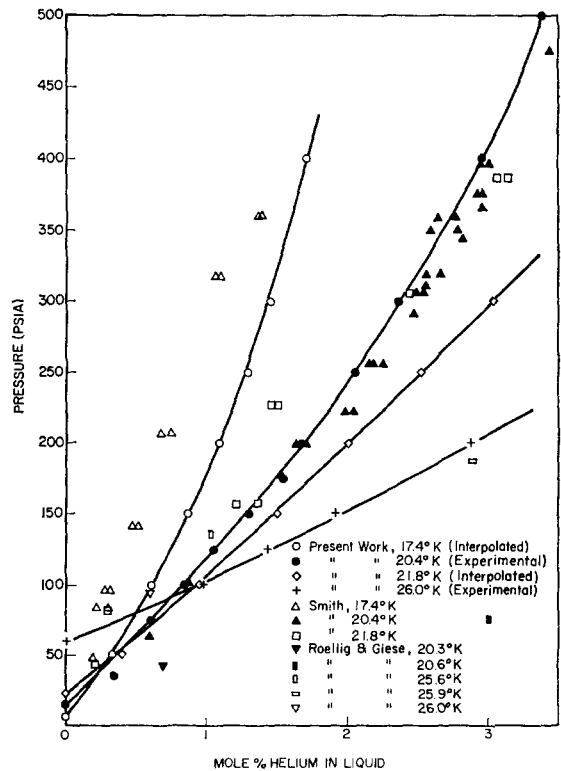


FIG. 7. Comparison with previous work, liquid-phase data.

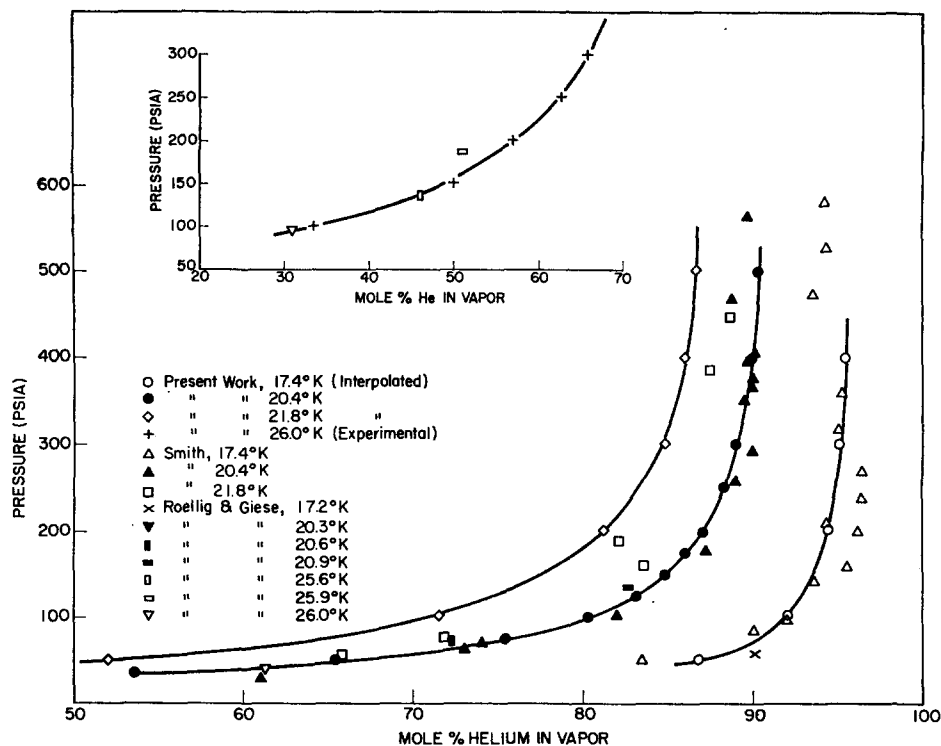


FIG. 8. Comparison with previous work, vapor-phase data.

at lower temperatures. At the higher temperatures the mole fraction of helium in the liquid becomes appreciable, approaching that in the vapor phase. Accurate data on the partial molal properties for each component in the liquid are then required for precise application of the thermodynamic consistency tests. Such data are not available and the problem is further complicated by the fact that both hydrogen and helium show poor correlation with the generalized reduced property tables developed by Hougen, Lyderson *et al.* This precludes the use of pseudoreduced critical con-

stants in estimating mixture properties. The theoretical aspect has not been investigated further at the present time.

ACKNOWLEDGMENTS

The authors express their gratitude to the National Aeronautics and Space Administration, George C. Marshall Space Flight Center, Huntsville, Alabama, for financial support of this investigation. The authors also gratefully acknowledge the valuable advice and assistance given by the Linde Company on this project.