

## Liquid-Vapor Equilibrium in the System Equilibrium Hydrogen-Helium

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Liquid-vapor equilibrium-phase compositions for the binary system 20.40° equilibrium hydrogen-helium have been determined for six isotherms in the range 20.40°–31.50°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 comparisons with those reported previously for the system normal hydrogen-helium have also been made.

### I. INTRODUCTION

**L** IQUID-vapor-phase equilibrium in the system hydrogen-helium is of interest for several reasons. The transfer of liquid hydrogen from storage tanks is commonly achieved by pressurization with helium gas, some of which dissolves in the liquid. The possible use of hydrogen-helium mixtures in bubble chambers to study the interaction of elementary particles with helium nuclei has also been proposed. Further, the liquid-vapor equilibrium of the two elements with the lowest critical temperature is of particular interest from a theoretical point of view, since both hydrogen and helium exhibit large quantum effects.

The present investigation is a continuation of the work reported previously<sup>1</sup> for the system normal hydrogen-helium in the range 15.50°–32.50°K, at pressures to 500 psia. That study was undertaken to resolve a number of discrepancies and inconsistencies, especially in liquid-phase compositions, in the results to two earlier investigations of that system.<sup>2,3</sup>

Hydrogen at room temperature, which is termed normal hydrogen, has a composition of 75% ortho-H<sub>2</sub>, 25% para-H<sub>2</sub>. During the commercial liquefaction process, hydrogen is catalytically converted from this normal composition to the equilibrium composition at 20.40°K (0.21% ortho-H<sub>2</sub>, 99.79% para-H<sub>2</sub>), which in this paper is referred to simply as equilibrium hydrogen. Thus nearly all practical applications of liquid hydrogen involve equilibrium hydrogen. For this reason, it was considered important to extend the investigation to include measurements of liquid and vapor compositions for the system equilibrium hydrogen-helium, and thus determine the nature and extent of any differences between the two systems. These values have been measured in the present study for six isotherms in the range 20.40°–31.50°K, at pressures from hydrogen saturation to 500 psia.

### II. EXPERIMENTAL APPARATUS

The experimental apparatus and instrumentation used in this study are basically the same as used in the previous work.<sup>1</sup> The equilibrium apparatus is of the vapor-recirculation type, with the equilibrium cell maintained in a vapor-pressure-controlled liquid-hydrogen cryostat. Liquid samples were withdrawn from the cell through stainless steel capillary tubing, while a portion of the equilibrium vapor was isolated in the external portion of the recirculation loop and sampled at room temperature. Sample compositions for both phases were determined by mass spectrometry.

The supply of 20.40° equilibrium hydrogen was obtained by one of two alternate means: by converting room-temperature hydrogen catalytically using hydrous ferric oxide in a small reactor located in the cryostat; or, by collecting a quantity of boiloff hydrogen vapor from the cryostat. Analyses of the hydrogen for ortho-para content were made using a thermal conductivity analyzer. No differences in experimental results could be detected for points run using the alternate sources of equilibrium hydrogen.

Equilibrium temperatures were measured with a calibrated platinum resistance thermometer, using a Type G-2 Mueller bridge. Secondary temperatures were measured by gold-cobalt-vs-copper differential thermocouples. Bath-temperature control was maintained by the vapor-pressure control system to within  $\pm 0.005^\circ$  at all six isotherms investigated.

Equilibrium pressures were measured to within  $\pm 0.5$  psi using a 0–500 psi calibrated 16-in. Heise gauge.

### III. EXPERIMENTAL RESULTS

The experimental results of this investigation are summarized in Table I and presented graphically in Figs. 1–3. Figure 1 shows the six isotherms on pressure-composition coordinates, and indicates the over-all range of the investigation. Of particular interest to the various applications of these results are the liquid phase compositions, which are shown on an expanded-scale  $P-x$  plot in Fig. 2. Equilibrium constants for the

<sup>1</sup> W. B. Streett, R. E. Sonntag, and G. J. Van Wylen, *J. Chem. Phys.* **40**, 1390 (1964).

<sup>2</sup> S. R. Smith, Ph.D. thesis, Ohio State University, 1952.

<sup>3</sup> L. O. Roellig and C. Giese, *J. Chem. Phys.* **37**, 114 (1962).

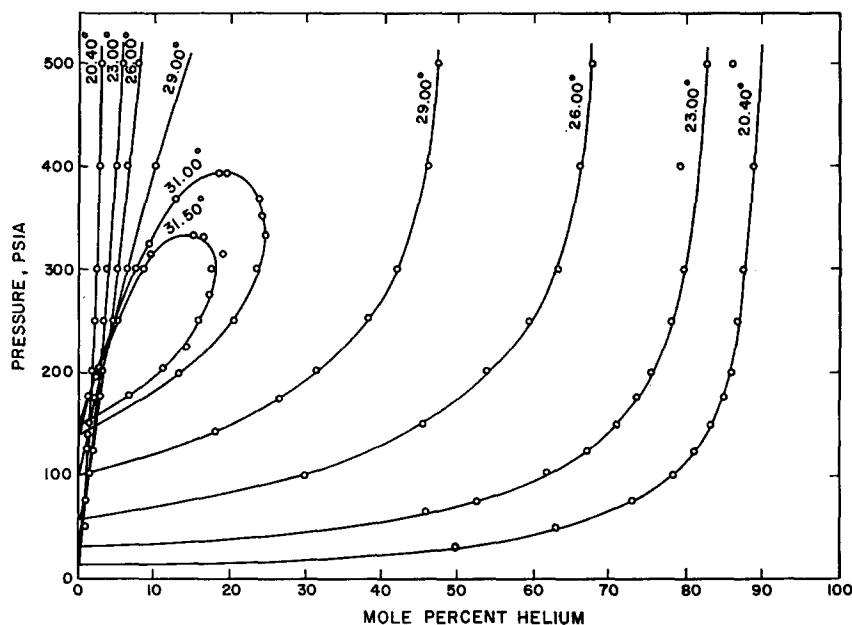


FIG. 1. Isothermal pressure-composition diagram for the system 20.40° equilibrium hydrogen-helium.

components, defined as the ratio of vapor-phase to liquid-phase mole fractions, are given in Fig. 3.

The results for this system are seen to be very similar to those for normal hydrogen-helium, as was anticipated, and the systems have the same general behavior and characteristics. Liquid-phase compositions, commonly the source of experimental difficulties in phase

equilibrium studies, seem to be very self-consistent, and show little scatter, as evidenced by the expanded-scale plot of liquid composition in Fig. 2. This is also apparent from the helium  $K$  values of Fig. 3, where any scatter in the small liquid-phase helium mole fractions would

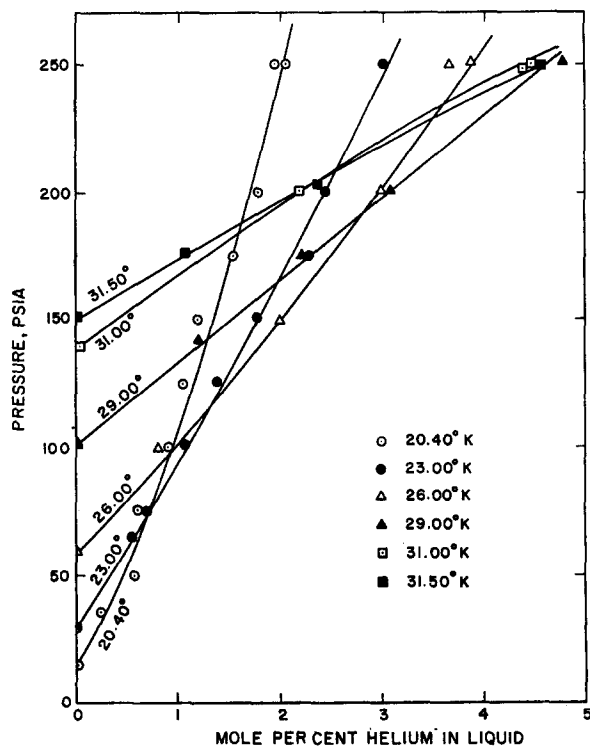


FIG. 2. Isothermal pressure-composition diagram showing liquid region on expanded scale.

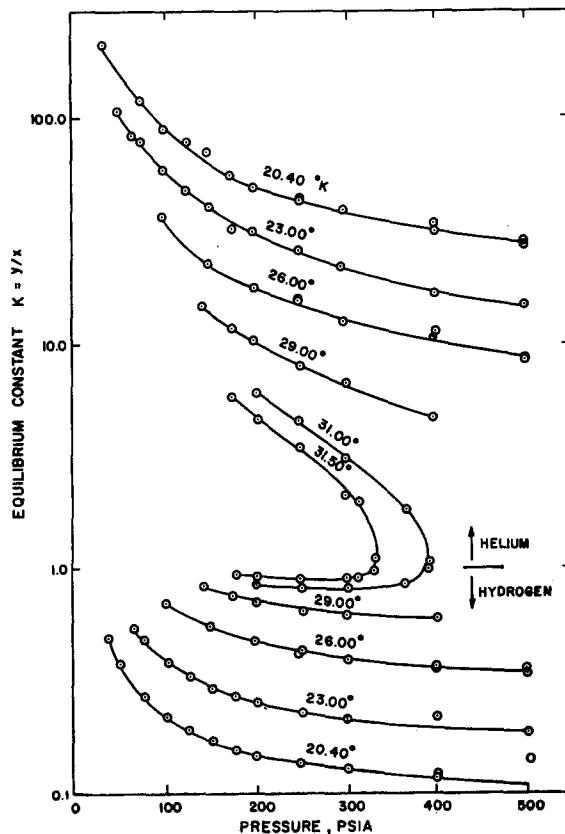


FIG. 3. Equilibrium  $K$  values.

TABLE I. Equilibrium hydrogen-helium summary of experimental data.

Temperature (°K)	Liquid		Vapor		
	Pressure (psia)	Mole % He	Mole % H <sub>2</sub>	Mole % He	Mole % H <sub>2</sub>
20.40	34.7	0.23	99.77	49.40	50.60
	50.5	0.58	99.42	62.79	37.21
	75.0	0.60	99.40	72.80	27.20
	100.0	0.87	99.13	78.21	21.79
	125.0	1.02	98.98	80.83	19.17
	150.0	1.17	98.83	83.00	17.00
	175.0	1.55	98.45	84.71	15.29
	200.0	1.77	98.23	85.79	14.21
	250.0	1.92	98.08	...	...
		2.04	97.96	86.64	13.36
	300.0	2.25	97.75	86.80	12.20
	400.0	2.66	97.34	88.72	11.28
		2.94	97.06	88.56	11.44
	500.0	3.08	96.92	...	...
		3.16	96.84	85.99	14.01
23.00	64.5	0.54	99.46	45.60	54.40
	75.0	0.65	99.35	52.20	47.80
	101.0	1.05	98.95	61.70	38.30
	125.0	1.38	98.62	67.00	33.00
	150.5	1.75	98.25	70.90	29.10
	175.0	2.27	97.73	73.50	26.50
	200.0	2.40	97.60	75.35	24.65
	250.0	3.00	97.00	77.90	22.10
	300.0	3.65	96.35	79.50	20.50
	400.0	4.73	95.27	79.10	20.90
500.0	5.62	94.38	82.50	17.50	
26.00	100.0	0.79	99.21	29.66	70.34
	150.0	2.00	98.00	45.57	54.43
	200.0	3.03	96.97	53.55	46.45
	250.0	3.67	96.33	58.77	41.23
		3.90	96.10	59.52	40.48
	300.0	5.08	94.92	63.00	37.00
	400.0	5.95	94.05	66.51	33.49
		6.37	93.63	65.05	34.95
500.0	7.82	92.18	67.15	32.85	
		8.10	91.90	68.04	31.96
29.00	142.0	1.19	98.81	17.60	82.40
	174.5	2.22	97.78	26.15	73.85
	200.0	3.05	96.95	31.15	68.85
	251.5	4.78	95.22	37.90	62.10
	300.5	6.33	93.67	41.90	58.10
	400.5	10.06	89.94	46.00	54.00
	501.0	...	...	47.00	3.00
31.00	200.0	2.17	97.83	13.17	86.83
	248.5	4.40	95.60	20.10	79.90
	250.0	4.55	95.45	...	...
	300.0	7.52	92.48	23.14	76.86
	324.0	9.08	90.92	...	...
	332.0	...	...	23.68	76.32
	350.0	...	...	23.94	76.06
	366.5	12.55	87.45	23.53	76.47
390.5	18.12	81.88	18.44	81.56	
31.50	176.5	1.07	98.93	6.34	93.66
	203.0	2.39	97.61	10.99	89.01
	225.0	...	...	14.02	85.98
	250.0	4.55	95.45	15.68	84.32
	275.0	...	...	16.97	83.03
	300.0	8.08	91.92	17.13	82.87
	315.0	9.28	90.72	18.70	81.30
332.0	14.90	85.10	16.57	83.43	

be greatly magnified. The few data points showing any noticeable scatter are vapor-phase samples, and are probably the result of poor sampling at these particular points. A plot of the data on  $T-x$  coordinates also indicates that the low-pressure vapor-phase helium mole fractions at 26.00°K are slightly low.

#### IV. COMPARISON WITH THE SYSTEM NORMAL HYDROGEN-HELIUM

Comparison of the results obtained in this system with those reported previously<sup>1</sup> are shown on  $P-x$  coordinates in Figs. 4 and 5 for the two isotherms 20.40° and 31.00°K. If the systems behaved ideally, then it would be possible to describe their behavior in terms of Raoult's law—ideal gas. The differences in composition between the two systems investigated would then be a result of the differences in the vapor pressures of pure equilibrium and normal hydrogen at the temperature of interest. Since equilibrium hydrogen has a somewhat higher vapor pressure, the isotherm on a  $P-x$  plot for equilibrium hydrogen-helium should be shifted from that for normal hydrogen-helium in the direction of increasing temperature. It is known from the experimental results, however, that these systems do not behave ideally. Therefore, the behavior of these systems will also be influenced to some extent by their pressure-volume-temperature ( $PVT$ ) behavior in both the liquid and vapor phases. Nevertheless, the principal factor contributing to differences between the two systems is no doubt that of the vapor pressure of the two forms of hydrogen, since  $PVT$  behaviors of normal and equilibrium hydrogen are nearly the same.

From Fig. 4 it is seen that at 20.40° the vapor-phase mole fractions of helium with equilibrium hydrogen are shifted slightly in the direction of higher temperature as expected, while no such shift is indicated by the liquid data. Similar plots of the isotherms 23.00°, 26.00°, and 29.00°K show the same results. It is felt that differences in the liquid-phase compositions do exist in this range of temperature, but are smaller than the scatter in the experimental data.

A comparison of the results at 31.00°K, where vapor-pressure differences become significant, is shown in Fig. 5, and does indicate such a shift in liquid-phase results. It is further noted that vapor-phase differences become quite significant at this temperature. The same trend is also observed from a similar comparison of the two systems at 31.50°K.

From the comparisons of the two systems at the six isotherms investigated using equilibrium hydrogen, it can be concluded that for temperatures less than 20.40°K, the liquid-phase compositions in this system would be the same as those for normal hydrogen-helium, at least within the experimental accuracy of these studies, while differences in vapor-phase composition for the two systems would be very small.

In both of these investigations the question arises as to the exact composition of the hydrogen at the time

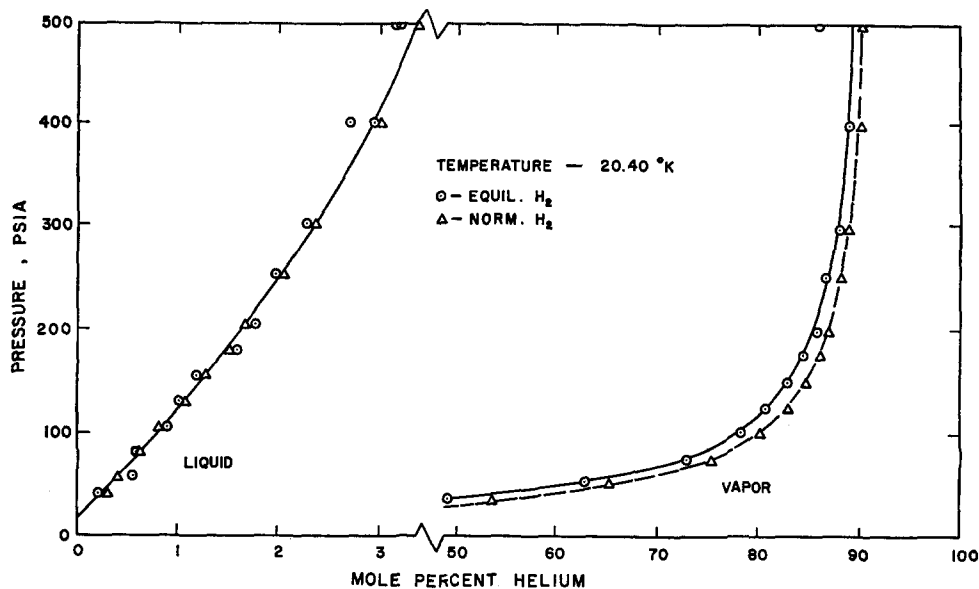


FIG. 4. Comparison of the two systems at 20.4°K.

the measurements were made. This is due to the spontaneous conversion of the hydrogen towards its new equilibrium composition as the temperature of the hydrogen is changed. In the previous study involving

normal  $H_2$ , the maximum elapsed time for initial cooling of the room-temperature hydrogen supply until sampling the equilibrium phases was less than four hours. It is estimated that during this time the hydrogen ortho content dropped from 75% to about 72% as a result of spontaneous conversion. From Figs. 4 and 5 it is evident that this change in composition would not have significantly influenced the experimental results. For the present investigation, assumed to involve 20.40°K equilibrium hydrogen, samples were collected within 1–3 h after charging the cell. Thus, it is felt that spontaneous conversion from 0.21% ortho- $H_2$  toward the different equilibrium composition at the higher temperatures (about 1.2% ortho- $H_2$  at 26K, 3.8% ortho- $H_2$  at 31.5K) was negligible, and did not influence the experimental results.

Analytical predictions and correlations of the experimental data for the two systems studied have not as yet been carried out. Such calculations require information regarding  $PVT$  behavior of the liquid solutions, which is not available. This aspect of the problem is being investigated at the present time.

#### ACKNOWLEDGMENTS

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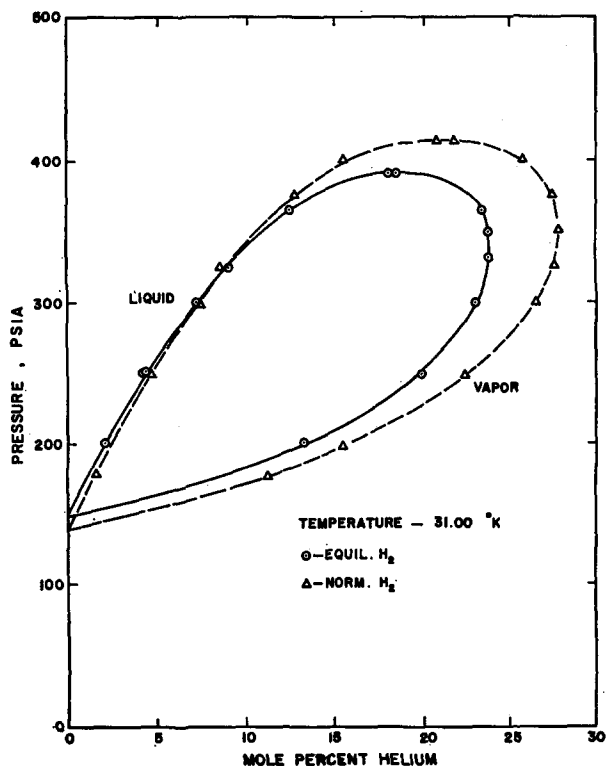


FIG. 5. Comparison of the two systems at 31.0°K.