

cantly since they are on the order of the experimental uncertainty (≈ 0.2 MHz).

In determining the molecular structure and internal rotation barrier of acetone, Nelson and Pierce¹¹ found that the methyl-group axis was not directed along the C-C bond but was tilted 1.3° toward the double bond. Similar results were noted in other compounds in which methyl groups are attached to an unsaturated carbon. Since the ring carbon in dimethyldiazirine exhibits some characteristics of an sp^2 hybridized carbon, it might be expected that a methyl-group tilt also exists. However, the internal-rotation analysis yielded an angle between the symmetry axes of the methyl groups (2θ in Table III) which differs by only 0.7° (corresponding to a nominal methyl group tilt of 0.35°) from the C-C-C angle. Since this difference is of the order of the experimental uncertainty, no definite conclusion concerning the existence of a tilt can be made except that it is less than the value found in acetone.

DIPOLE MOMENT

A dipole moment for $(\text{CH}_3)_2\text{CN}_2$ of 2.19 ± 0.07 D was obtained from the Stark shift observed on the $0_{00} \rightarrow 1_{01}$ transition.²¹ The relatively large uncertainty

²¹ Electrode plate spacing was determined using an OCS dipole moment of 0.7152 D. J. S. Muenter, *J. Chem. Phys.* **48**, 4544 (1968).

is again attributed to unresolved quadrupole and internal-rotation splittings. This value may be compared with 1.59 ± 0.06 D obtained for diazirine.¹ An increase of about 0.6 D with the substitution of two methyl groups might be anticipated from a consideration of the dipole moments in formaldehyde²² (2.34 D) and acetone²³ (2.93 D). Although the dipole moments of ethylene (zero because of symmetry) and isobutylene²⁴ (0.503 ± 0.009 D) lead to the same conclusion, caution must be exercised in extending any bond moment comparisons. This is illustrated by a comparison of H_2O (1.884 ± 0.012 D)²⁵ and $(\text{CH}_3)_2\text{O}$ (1.31 ± 0.01 D)¹⁴ where the effect is again about 0.6 D but in the opposite direction.

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²³ R. Peter and H. Dreizler, *Z. Naturforsch.* **20A**, 301 (1965).

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²⁵ M. Lichtenstein, V. E. Derr, and J. J. Gallagher, *J. Mol. Spectry.* **20**, 391 (1966).

Helium-Hydrogen Liquid-Vapor Equilibrium to 100 atm

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Liquid-vapor phase compositions are given for 11 isotherms of the system normal-hydrogen-helium over the range 15.5° to 29.8°K at pressures to 1500 lb/in.² In this range, the mixture critical curve is located, the freezing points are shown, and the locus is determined for the barotropic phenomenon (gravitational phase inversion). Two isotherms are duplicated with the substitution of parahydrogen.

INTRODUCTION

The binary system helium-hydrogen exhibits, over a portion of the liquid-vapor equilibrium region, a barotropic phenomenon wherein a condition of gravitational phase inversion occurs. This is due to the fact that the liquid phase, which is largely hydrogen, may, upon compression, become less dense than the vapor phase which is composed principally of helium having twice the molecular weight of hydrogen. As a result, the liquid phase will rise and float on top of the vapor.

Knowledge of the phenomenon for this system is necessary if helium-pressurized liquid-hydrogen tanks are to dependably supply rocket engines.

Another matter of interest is whether this system exhibits limited fluid-fluid solubility at high pressure in the neighborhood of the critical temperature of the less-volatile component. The results indicate that this is very probable.

This experimental work¹ reports 11 isotherms of liquid-vapor equilibrium for helium-normal-hydrogen

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¹ C. M. Sneed, Ph.D. thesis, University of Michigan, Ann Arbor, Mich., 1966.

in the range 15.5° to 29.8°K with pressures of 500 to 1500 lb/in.² The gravimetric inversion locus is determined in this region by the use of carbon-resistance sensors to indicate the liquid location. The freezing points are also given as determined by flow blockage and the locus of mixture critical points as found graphically. Three isotherms are also given for the system helium-parahydrogen.

EXPERIMENTAL EQUIPMENT

The apparatus is a vapor-recirculating equilibrium system of the type developed by B. F. Dodge and uses some components designed and used previously by Streett.² The equilibrium cell, shown in Fig. 1, is immersed in boiling liquid hydrogen with temperature control by semiautomatic vapor-pressure control on the bath. Equilibrating heat-exchange coils are located in the vapor tubing adjacent to the cell. A counterflow heat exchanger is located at the neck of the cryostat in the path of the boiloff vapor. The vapor loop continues through coils in the open liquid-nitrogen pool atop the cryostat which absorbs most of the operating heat load on the system. A vapor crossover is provided to reverse the vapor circulation to the cell under inversion operation. An armored rotameter is used to observe the vapor circulation; the metering tube is externally pressurized by internal gas through a vent; the dead-space volume is minimized by a clear epoxy potting resin.

Vapor-phase sampling is done from a small section of the loop through a cross-flow valve located between

two isolating valves. The sample is expanded into glass bottles for analysis on a mass spectrometer.

An enclosed water-cooled magnetic circulation pump provides prompt equilibration by providing a cell circulation exchange time of under 40 sec. The cell and loop volumes totaled 121 ml, about 51% of this at room temperature.

Sampling of the liquid phase is done through a 0.004-in. stainless-steel capillary tube with sensitive needle valves and bypass loops permitting controlled expansion to room conditions and a sample bottle bank similar to that for the vapor samples. Depending on the liquid position in the cell, the sample is drawn by a tube opening near the top or one opening near the bottom of the cell.

The presence of liquid in the cell is determined by selectively monitoring a bank of 0.4-W, 1000 Ω carbon resistors located in the cell. The indicating device was designed in accordance with a National Bureau of Standards publication³ with a 10-V dc voltmeter as the output indicator. The circuit is momentarily energized and the dynamic behavior of the voltmeter needle observed to determine which phase surrounds the sensor. Bridge balance settings are used such that in liquid the voltmeter indicates a steady value of about 4.3 after a moderate rate of needle rise. In vapor, however, the needle rises rapidly to about this value but falls quickly to about 2 V. Highly satisfactory results are obtained from this indicator even when the phases are of like density but dissimilar composition once some skill in its use has been obtained.

The system pressure was read on a 16-in. Heise gauge of range 0–1500 lb/in.² with an accuracy of ± 1.5 lb/in.². Various periodic checks gave assurance that this limit applies to the equilibrium pressures here reported.

Temperature was taken with a Leeds & Northrup type 8164 platinum resistance thermometer calibrated by the National Bureau of Standards and read on a type G-2 Mueller bridge. The thermometer was checked regularly against the vapor pressure of parahydrogen during the research. Temperatures are reported to 0.01°K and this value may be considered as an upper limit of uncertainty in temperature. Gold-cobalt thermocouples are used to check for gradients in the cell and adjacent bath. None were found within the limit of sensitivity of the Leeds & Northrup K3 potentiometer. The automatic temperature control by bath-pressure regulation functioned in a highly stable and satisfactory manner and yielded temperature control better than the above-mentioned temperature limit of 0.01°K. The steady-state heat gain to the hydrogen bath in the cryostat is below 3 W. To provide prompt approach to the upper isotherms, electrical heating of up to 25 W is provided in the bath near the bottom of

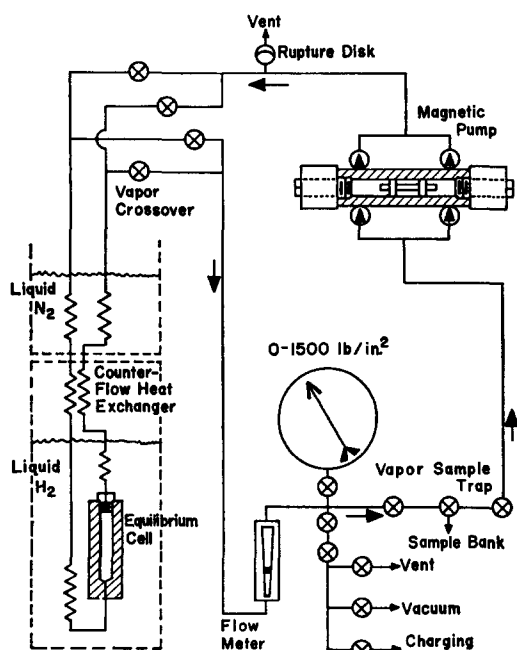


FIG. 1. Equilibrium cell and vapor loop.

² W. B. Streett, R. E. Sonntag, and G. J. Van Wylen, *J. Chem. Phys.* **40**, 1390 (1964).

³ R. C. Muhlenhaupt and P. Smelser, *Natl. Bur. Std. Tech. Note* **200** (1963).

TABLE I. Experimental results.

T (°K)	P (lb/in. ²)	Mole% liquid		Mole% vapor		T (°K)	P (lb/in. ²)	Mole% liquid		Mole% vapor	
		He	H ₂	He	H ₂			He	H ₂	He	H ₂
Helium and normal hydrogen											
15.50	386	0.95	99.1	97.1	2.9	28.20	850	21.2	78.8	52.1	47.9
	500	1.12	98.9	97.0	3.0		997	26.4	73.6	48.6	51.4
	601	1.13	98.9	97.3	2.7		1027	26.9	73.1	47.5	52.5
	751	1.18	98.8	97.5	2.5		1054	27.9	72.1	47.7	52.3
	761	1.20	98.8	97.4	2.6		1138	32.1	67.9	44.1	55.9
17.00	421	1.57	98.4	95.1	4.9	28.45	622	15.0	85.0	51.5	48.5
	599	1.66	98.3	95.7	4.3		750	19.1	80.9	49.6	50.4
	750	1.82	98.2	96.0	4.0		865	25.2	74.8	47.4	52.6
	949	1.89	98.1	96.2	3.8		916	27.6	72.4	44.1	55.9
	1201	1.96	98.0	96.6	3.4		941	29.7	70.3	41.6	58.4
20.40	500	3.35	96.7	89.7	10.3	29.00	432	9.8	90.2	45.7	54.3
	601	3.56	96.4	90.2	9.8		527	13.3	86.7	46.9	53.1
	751	4.05	96.0	90.3	9.7		601	16.5	83.5	46.5	53.5
	950	4.32	95.7	91.2	8.8		750	26.8	73.2	38.0	62.0
	1201	4.31	95.7	92.0	8.0		754	27.7	72.3	36.5	63.5
	1500	4.50	95.5	92.7	7.3		29.80	412	10.7	89.3	38.7
23.00	600	5.8	94.2	82.4	17.6	500		15.6	84.4	39.0	61.0
	749	6.5	93.5	82.8	17.2	560		19.5	80.5	35.8	64.2
	950	7.1	92.9	83.7	16.3	581		23.2	76.8	32.7	67.3
	1200	7.6	92.4	85.1	14.9	585		24.8	75.2	31.7	68.3
1499	7.8	92.2	86.7	13.3	Helium and parahydrogen						
26.00	599	9.2	90.8	68.8	31.2	20.40	841	4.61	95.4	90.3	9.7
	755	11.1	88.9	69.5	30.5		1062	4.59	95.4	90.8	9.2
	950	13.8	86.2	70.5	29.5		1258	4.42	95.6	91.4	8.6
	1202	15.7	84.3	71.6	28.4		1499	4.46	95.5	92.2	7.8
	1500	14.4	85.6	73.6	26.4		27.80	286	4.9	95.1	48.2
27.80	343	6.6	93.4	53.0	47.0	501		10.4	89.6	54.6	45.4
	501	10.2	89.8	55.8	44.2	750		17.0	83.0	54.8	45.2
	749	16.6	83.4	56.7	43.3	952		22.7	77.3	53.0	47.0
	950	20.5	79.5	55.6	44.4	1196		28.1	71.9	50.9	49.1
	1200	24.2	75.8	54.3	45.7	1296		29.3	70.7	49.3	50.7
	1278	25.3	74.7	54.9	45.1	1461		30.8	69.2	48.3	51.7
	1322	26.0	74.0	55.6	44.4	29.00		532	14.3	85.7	44.7
	1348	25.7	74.3	56.1	43.9		627	19.1	80.9	42.4	57.6
1502	26.4	73.6	57.6	42.4	687		24.9	75.1	38.2	61.8	
28.05	1020	25.5	74.5	50.4	49.6		696	26.1	73.9	35.9	64.1
	1307	29.7	70.3	49.7	50.3	705	30.5	69.5	30.5	69.5	
	1411	31.4	68.6	50.9	49.1						
	1500	32.8	67.2	51.7	48.3						

the cryostat. This is particularly effective in eliminating any gradient to lower temperature near the bottom of the cryostat upon approach to equilibrium.

The maximum precision was not always realized in the gas analyses of the Consolidated Electrodynamics

TABLE II. Mixture critical states.

T (°K)	P (lb/in. ²)	Mole% helium
33.18	191	0
32.50	255	7.6
31.90	311	13.4
31.50	352	17.1
31.00	414	21.4
30.60	470	23.9
29.80	595	28.1
29.00	764	32.0
28.45	968	36.3
28.20	1183	38.5
28.14	1500	40.4

21-103 mass spectrometer. Knowledge of the accuracy of the analyses must come through indirect evidence of checks with previous work with these gases, reruns of experimental points, and replication of gas-sample runs on the spectrometer. These comparisons show that some analyses of liquid samples may be in error by ± 0.3 and vapor samples ± 1.0 mole %. Most of the analyses are felt to be considerably better than these

TABLE III. Observed inversion points.

T (°K)	P (lb/in. ²)	Liquid mole % helium
15.50	369	1.0
17.04	415	1.5
20.40	529	3.5
23.00	626	5.9
26.00	742	10.8
27.80	818	17.9
28.45	844	24.2

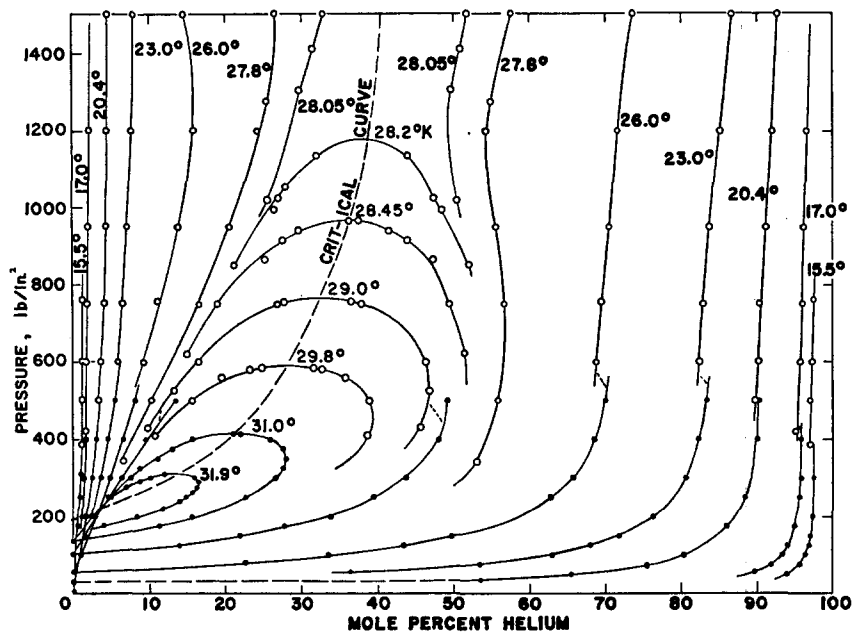


FIG. 2. Isothermal pressure-composition diagram.

limits. Operating problems in the mass spectrometer were considered to be a more significant limitation on the results than any questions of sampling, equilibration, stability, or phase separation.

The helium was high-purity analyzed gas supplied through the courtesy of the U. S. Bureau of Mines Helium Research Center. Matheson ultrapure hydrogen gas was used for the supply of normal hydrogen. Parahydrogen was obtained as the boiloff gas from a

supply of equilibrium liquid hydrogen which had been catalyzed and stored at a 10-lb/in.² gauge reading. Both initial charging and incremental charging of the cell are done by use of premixed gas of desired composition. This greatly facilitates the close location of the mixture critical on an isotherm. High pressures are obtained by use of a diaphragm compressor in the charging system.

EXPERIMENTAL RESULTS

The experimental results of this research are listed in Table I. All results are for the normal hydrogen in the mixture except for the last three isotherms listed which are for parahydrogen. The isotherms with normal hydrogen are shown in Fig. 2, which includes some data from Streett shown as blacked circles. The present work shows results for both liquid and vapor phases that are lower in helium composition than reported by Streett in the region of duplicated pressure from 300 to 500 lb/in.² absolute. This difference is

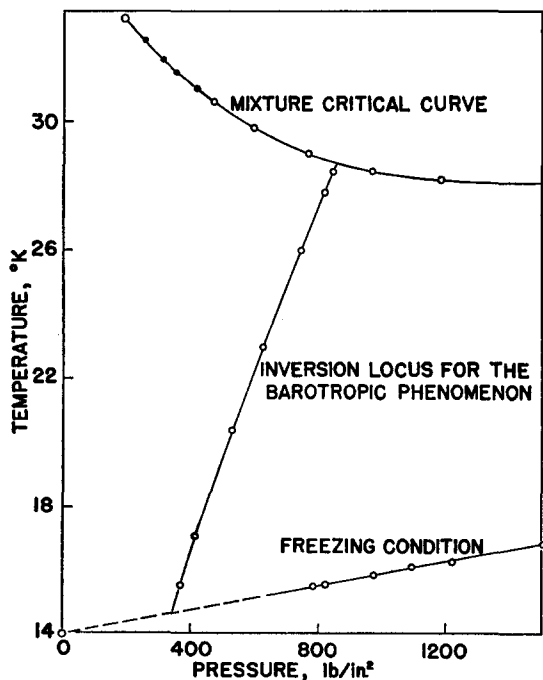


FIG. 3. Helium-normal-hydrogen behavior.

TABLE IV. Freezing states.

T (°K)	P (lb/in. ²)	Liquid mole % helium
16.82	1504	1.87
16.25	1221	1.58
16.09	1094	1.49
15.82	975	1.35
15.52	822	1.18
15.48	784	1.18

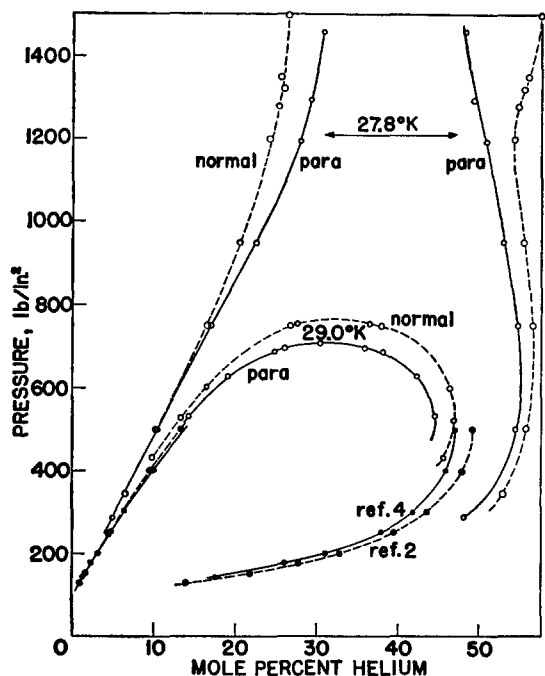


FIG. 4. Normal and para comparative isotherms.

negligible at the lowest temperatures but increases with temperature up to nearly a 1% difference in liquid and to about 2% in vapor at 29°K. Sneed¹ discusses factors of sampling system and techniques, dead-space volumes, charging, flow rate, and equilibration times and indicates that these factors probably account for this difference. It is felt that the present values are the more reliable in this region of overlap.

On Fig. 3 are shown the mixture critical locus as far as it has been determined, the boundary curve for the inversion (barotropic) phenomenon, and the curve of freezing for the helium-normal-hydrogen system.

The mixture critical loci are found by extrapolation of the dew- and bubble-point isotherms to a maximum pressure intersection. Values are given in Table II with the data of Streett used at 31° and higher. The value at 28.2° was only defined approximately and it is believed that there is a minimum critical temperature of approximately 28.14°. It seems very probable that there are minimum critical solution temperatures above this temperature and at pressures above 1500 lb/in.² such that the system may co-exist in two fluid states of differing composition. This is strongly indicated by construction of a pressure-temperature projection with lines of constant composition using only the isotherms of hour-glass shape in Fig. 2.

The inversion loci were observed by the switching

of liquid indication of the sensors as the pressure was slowly raised (or lowered) at constant temperature. Modest flow circulation was maintained in the correct direction of approach in each case. This is the reason that little hysteresis seemed to be present. Very near the inversion state, phase separation was sometimes too poor for meaningful sampling. There was no difficulty in defining the switching of the position of the phases and Table III lists the values observed. No attempt was made to define the pressures of inversion closer than $\pm 0.7\%$. It seems strange that the sensors could have so reliably indicated inversion as high as 28.45°, as here the phases are of essentially identical density and very similar composition. Certainly when the pressures were twice as much as here, the sensor indication was practically meaningless.

The points at which freezing occurred in the cell are listed in Table IV. This was observed by the blockage of circulation upon increasing pressure or decreasing temperature. Melting seemed to occur at values very close to those listed here, although observation of melting was somewhat uncertain. The presence of 1.2% to 1.9% helium in liquid hydrogen depresses the freezing point 0.17° to 0.25°K below published values for pure normal hydrogen. The freezing states observed here correlated very well with the three-phase locus for hydrogen-helium observed by Greene⁴ at lower temperature using a glass equilibrium cell.

A comparison between normal hydrogen and para-hydrogen as the less-volatile binary component is shown in Fig. 4. The isotherms shown are those most distinctive found here. A more complete comparison is given by Sonntag *et al.*⁵ at pressures up to 500 lb/in.². It seems that the ortho-para difference is a factor of minor significance in the phase equilibrium of this system.

This binary system may be unique since it appears capable of showing fluid-fluid states at little more than 100 atm due to the low critical pressures of the components.

ACKNOWLEDGMENTS

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⁴ N. E. Greene and R. E. Sonntag, *Advan. Cryog. Eng.* **13**, 357 (1968).

⁵ R. E. Sonntag, G. J. Van Wylene, and R. W. Crain, Jr., *J. Chem. Phys.* **41**, 2399 (1964).