

content and entropy increments above 298.16°K. The latter were calculated by the method of Kelley.⁷

The following equations represent the heat content results within the average limits and for the temperature intervals indicated in parentheses.

$$\text{CaFe}_2\text{O}_4(\text{c}): H_T - H_{298.16} = 39.42T + 2.38 \times 10^{-3}T^2 + 3.66 \times 10^{-5}T^{-1} - 13,194; (0.3\%; 298-1510^\circ\text{K}.)$$

$$\text{CaFe}_2\text{O}_4(\text{l}): H_T - H_{298.16} = 54.90T - 5030; (0.1\%; 1510-1800^\circ\text{K}.)$$

$$\text{Ca}_2\text{Fe}_2\text{O}_5(\text{c}): H_T - H_{298.16} = 59.24T + 11.68 \times 10^5T^{-1} - 21,580; (0.5\%; 298-1750^\circ\text{K}.)$$

$$\text{CaFe}_2\text{O}_5(\text{l}): H_T - H_{298.16} = 74.20T - 10,980 (0.1\%; 1750-1850 \text{ K}.)$$

$$\text{MgFe}_2\text{O}_4(\alpha): H_T - H_{298.16} = 21.06T + 22.29 \times 10^{-3}T^2 - 8261; (1.2\%; 298-665^\circ\text{K}.)$$

$$\text{MgFe}_2\text{O}_4(\beta): H_T - H_{298.16} = 45.40T - 14,590; (0.1\%; 665-1230^\circ\text{K}.)$$

$$\text{MgFe}_2\text{O}_4(\gamma): H_T - H_{298.16} = 25.67T + 6.79 \times 10^{-3}T^2 - 247; (0.1\%; 1230-1800^\circ\text{K}.)$$

(7) K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

BERKELEY 4, CALIFORNIA

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Compressibility of Liquid Normal Hydrogen from the Boiling Point to the Critical Point at Pressures up to 100 Atmospheres¹

BY HERRICK L. JOHNSTON, WILLIAM E. KELLER AND ABRAHAM SOLOMON FRIEDMAN

RECEIVED SEPTEMBER 14, 1953

A description is given for an apparatus used to determine equation of state data for liquids at low temperature. Measured values of \bar{P} vs. V isotherms of normal liquid H_2 are tabulated for seven temperatures between 20.38 and 32.58°K. The data have been replotted as isochores, the straight-line character of which can be adequately described by $P = A_v + B_v T$ with $B_v = -7.11 + 437(1/V)$; values of A_v and B_v are given at integral values of the specific volume. Comparison of experimental results with calculations based on two proposed models for liquids are made and the agreement is found to be unsatisfactory.

Introduction

No comprehensive investigation of the P - V - T properties of liquid hydrogen² has heretofore been undertaken. The most accurate information available has been that derived from Bartholomé's measurements³ of the compressibility of liquid normal hydrogen at the boiling point (20.39°K.), at 18.24°K. and at 16.43°K., and from liquid-vapor density determinations of Mathias, Crommelin and Onnes.⁴ The regions of temperatures above the boiling point and pressures above saturation have not been mapped. As part of this Laboratory's program for the determination of the properties of hydrogen, we have measured P vs. V isotherms for the liquid in that region. It is the purpose of this communication to describe the apparatus employed and to report experimental results.

Apparatus.—The general plan of the experiment includes the following measurements: (1) the temperature of a bomb containing a known volume of liquid hydrogen; (2) the pressure exerted on the liquid by gaseous hydrogen; and (3) the number of moles of liquid in the bomb corresponding to each pressure determination along each isotherm. An isotherm is determined by first filling the pipet to the highest pressure and then decreasing the pressure in stepwise fashion, measuring the number of moles of each decrement.

Figure 1 illustrates the cryostat assembly. The liquid under investigation is contained in the copper bomb, or pipet (A). Tests indicated that 200 atm. of internal pressure does not significantly deform the pipet. Within the pipet are four snug-fitting fins made from $1/32$ in. sheet copper to ensure rapid thermal equilibration. The threaded

plug (B) and monel capillary (C) (0.012 in. inside diameter, 0.025 in. wall) were silver-soldered to the pipet in a helium atmosphere in order to prevent oxidation of the internal copper surfaces. D is a well for the junction of a copper-constantan thermocouple embedded 2 in. into the pipet wall. This well is filled with Wood's metal to maintain good thermal contact between couple and pipet.

In order to determine the level of liquid hydrogen and the thermal gradient along the capillary, control thermocouples are situated at 8-in. intervals along the length of the capillary. To make certain that the meniscus will never be far above the neck of the pipet a small, 4-watt heater-station is placed on the capillary 1 in. above the bomb. During the course of the experiments, however, the temperature of the capillary an inch or two above the pipet was always above the critical temperature of hydrogen, so that it was never necessary to use the heater.

Surrounding the pipet is a heavy-walled copper container (I) for the liquid hydrogen refrigerant. The vapor pressure of the refrigerant is so regulated between the normal boiling and critical pressures that the temperature of the bath determines the temperature of the isotherm being run. Control of the temperature is effected by manual adjustment of a set of four needle valves in parallel with the hydrogen gas outlet line (E). Vapor pressures of the coolant are read on a 300-lb. test gage having 1-lb. subdivisions, and pressures can be maintained within 0.25 p.s.i. of any desired value in the working range. This results in temperature control to within 0.02° under the most unfavorable conditions, and usually to within 0.01°. A 240-ohm, 60-watt manganin wire heater coiled around the outside of the copper container is used to raise the bath temperature.

The top of the refrigerant container, which is threaded and soft-soldered in place, is fitted with 12.5 mm. o.d. monel tubes to allow for the introduction of liquid hydrogen coolant and the escape of vapor. The inlet tube just above the container passes through a high pressure valve (F) operated from outside the cryostat; the outlet tube leads directly into the temperature control system. The pipet thermocouple is surrounded by a monel tube (H) so that the couple makes no direct contact with liquid hydrogen. The pipet itself is suspended in the container by a thick-walled monel tube (G), which also serves as a vacuum jacket around the capillary.

The outer vessel of this apparatus is a vacuum-tight copper cylinder (J) constructed so as to allow all the tubes leading to the refrigerant container to be vacuum-jacketed

(1) The essentials of the present report were presented at the Proceedings of the NBS Semicentennial Symposium on Low Temperature Physics, March, 1951.

(2) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948).

(3) F. Bartholomé, *Z. physik. Chem.*, **B33**, 387 (1936).

(4) F. Mathias, C. A. Crommelin and H. K. Onnes, *Communs. Phys. Lab. Univ. Leiden*, No. 154b (1921).

from their respective points of entrance to the cryostat. The complete assembly is suspended in a glass dewar within a brass cryostat of the type generally used in this Laboratory. Provision is made for the introduction, when necessary, of exchange gas into the vacuum chamber.

The capillary leads into a high pressure manifold at room temperature. This manifold connects with (1) a 200-lb. Bourdon gage, (2) a vacuum pump, (3) a source of pure hydrogen gas, (4) an M.I.T.-type dead-weight gage for accurate pressure measurements, and (5) a system of four expansion tanks in a constant temperature (25°) water-bath (the nominal capacities of the expansion tanks are 1, 2, 6 and 16 liters).

Calibration of Apparatus.—The pipet volume was determined from the weight of water it contained at 25.00°C. Once refinements were made on the calibration system, five successive runs showed an average deviation of 1 part in 22,000. The volume of the pipet at 25.00°C. was determined to be 92.172 ± 0.006 cm.³, and the volume as a function of temperature from 300 to 20°K. was computed from the thermal coefficient of expansion of copper.^{5,6}

The volume of the high pressure lines was determined by procedures duplicating conditions of the actual runs, that is, by expanding hydrogen gas in the lines, at high pressure, into the previously calibrated expansion tanks. This dead space, which includes the high pressure manifolds and the lines up to the gas-mercury interface of the dead-weight gage, was found to be 87.85 ± 0.17 cm.³. The number of moles of liquid in the pipet (*i.e.*, the total moles in the system minus the moles in the lines) can be determined with a precision of 1 part in 6000 at the highest pressures measured; the error at lower pressures is less.

The pipet thermocouple was calibrated against the vapor pressure of liquid normal hydrogen⁷ to a precision of 0.02°.

Experimental Procedure.—The apparatus was precooled with liquid nitrogen in the glass dewar and the exchange gas (helium) in the vacuum vessel. The exchange gas was then removed, and liquid hydrogen was transferred to the refrigerant container. When the container was full, the thermocouple showed a pipet temperature of 20°K. and liquid air dripped copiously from the outlet line. Pure H₂ gas to a pressure of about 100 atm. was then admitted to the pipet. The refrigerant was raised to the desired temperature and maintained there with little further adjustment of the needle-valves on the outlet line. At this point, the dead-weight gage was put into operation. By an alternate slight raising and lowering of the vapor pressure in the refrigerant container, it was determined that the thermocouple reading lagged behind the dead-weight gage reading by less than a minute. Consequently, an equilibrium condition was easily established.

Once the pressure in the pipet was steady, the thermocouples on the capillary were read. Then simultaneous readings of the pipet thermocouple and dead-weight gage were taken at 2-min. intervals for a period of 6 min. During the first few runs the capillary thermocouples were re-read after the 6-min. period; but since no significant difference from the initial values was noted, this practice was abandoned in later runs. For each run, the temperature of the high pressure lines outside the cryostat was read to 0.1° on a mercury thermometer and the barometric pressure was observed.

The pressure on the liquid hydrogen was then decreased by expanding gas to the thermostated tanks. After equilibration for 15 minutes, the pressure in the tanks was read to 0.02 mm. on a constant volume mercury manometer, using a cathetometer, in conjunction with a standard meter bar. Very little time was required to re-establish equilibrium in the pipet, so that immediately after the pressure in the expansion system was determined, readings were begun on the next lower pressure point on the isotherm. The process of reading temperature and pressure and then expanding some gas was repeated until the lowest pressure point on the isotherm, always above saturation pressures, was measured. Then the hydrogen remaining in the pipet was expanded into the tank system. At no time did the

(5) W. H. Keesom, F. P. G. A. J. von Agt and A. F. J. Jansen, *Com-muns. Phys. Lab. Univ. Leiden*, No. 182a (1926).

(6) T. Rubin, H. Altman and H. L. Johnston, this Laboratory, unpublished results.

(7) D. White, A. S. Friedman and H. L. Johnston, *THIS JOURNAL*, **72**, 3927 (1950).

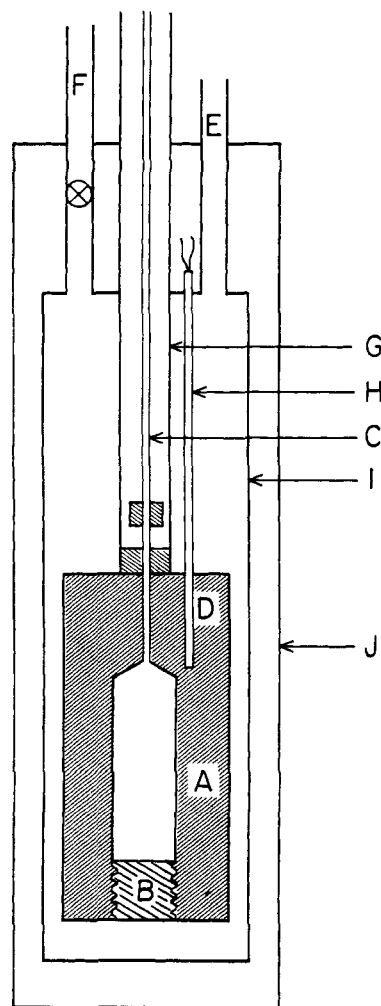


Fig. 1.—Apparatus (schematic) for measuring P - V - T properties of liquids at low temperature.

liquid H₂ remain in the pipet more than 6 hr., so that conversion of the ortho form to the para had negligible effect on results. One filling of the refrigerant container was sufficient for each isotherm.

Results

Data for the P - V isotherms determined in this investigation are listed in Table I and plotted in Fig. 2. Isotherms for both the highest and the lowest temperature were each repeated once in order to test the reproducibility of the experiments. Satisfactory reproducibility is demonstrated in Fig. 3, which presents on an expanded volume scale two boiling point isotherms run on separate days when the difference in atmospheric pressure caused the boiling temperatures of hydrogen to change by 0.04°. Also shown in Fig. 3 are the points below 110 atm. obtained by Bartholomé³ for the 20.39°K. isotherm. At lower pressures there is essential agreement between the two sources of data, but at higher pressures there is considerable divergence, greater than the estimated experimental errors.

Since no data below 9 atm. were obtained in this present work, the isotherms were extrapolated to meet the curve of Mathias, Crommelin and Onnes⁴

TABLE I

DATA OF STATE FOR COMPRESSED LIQUID HYDROGEN

P , atm.	V , cm. ³ /mole	PV/RT
$T = 20.34^\circ\text{K.}$		
67.584	25.970	1.05160
59.111	26.187	0.92745
47.624	26.524	.75688
35.252	26.921	.56860
23.529	27.349	.38555
13.937	27.754	.23176
$T = 20.38^\circ\text{K.}$		
106.179	25.133	1.59575
89.422	25.472	1.36204
74.627	25.808	1.15168
54.064	26.352	0.85193
41.623	26.724	.66515
24.733	27.323	.40410
9.969	27.960	.16668
$T = 22.96^\circ\text{K.}$		
104.199	25.689	1.42077
82.091	26.223	1.14260
62.410	26.805	0.88794
45.446	27.376	.66036
32.700	27.890	.48407
22.698	28.360	.34167
16.302	28.732	.24861
9.285	29.187	.14384
$T = 25.81^\circ\text{K.}$		
106.708	26.318	1.32602
81.007	27.051	1.03468
63.226	27.676	0.82622
48.889	28.282	.65286
37.153	28.887	.50675
23.500	29.774	.33037
16.371	30.340	.23452
9.629	30.988	.14089
$T = 28.17^\circ\text{K.}$		
97.983	27.192	1.15263
75.792	27.981	0.91746
54.962	28.942	.68816
41.805	29.751	.53806
31.527	30.508	.41610
22.033	31.430	.29958
14.789	32.322	.20679
9.102	33.271	.13101
$T = 30.11^\circ\text{K.}$		
100.125	27.724	1.12350
76.737	28.669	0.89041
55.453	29.823	.66935
41.779	30.846	.52159
32.108	31.775	.41293
23.345	32.903	.31089
15.341	34.415	.21369
9.729	36.203	.14256
$T = 31.62^\circ\text{K.}$		
117.062	27.587	1.24464
92.264	28.527	1.01441
68.598	29.720	0.78575
51.724	30.910	.61619
37.237	32.323	.46388
25.853	34.027	.33905
20.054	35.327	.27304
13.641	37.774	.19859

 $T = 32.58^\circ\text{K.}$

45.249	32.030	0.54213
18.695	37.320	.26098
13.912	40.377	.21012
11.519	46.623	.20088
$T = 32.58^\circ\text{K.}$		
116.474	27.887	1.21497
81.558	29.397	0.89682
55.426	31.134	.64548
37.197	33.090	.46040
29.935	34.269	.38372
23.672	35.734	.31641

for the volume of the liquid under saturation pressure shown in Fig. 2. Values obtained for the smoothed isotherms were then replotted as isochores, shown in Fig. 4, in which the dashed line represents the vapor pressure curve obtained in this Laboratory.⁷ The isochore plot shows only curves in the region $V/n = 26-39$ cm.³/mole; for values of V/n greater than 39 the experimental data yielded but one point for each isochore. However, it was determined that for $26 \leq V/n \leq 39$, the isochores could be represented within the experimental error by straight lines terminating at the vapor pressure curve and, furthermore, that the slope of the isochores is a linear function of the density. That is

$$P = A_v + B_v T \quad (1)$$

$$B_v = (\partial P / \partial T)_v = m + n(1/V) \quad (2)$$

with $m = -7.11$ and $n = 437$. The adequacy of equation 2 is shown by the fact that B_v approximates the slope of the vapor pressure curve at the critical point.

Comparing the relation 1 with a so-called thermodynamic equation of state

$$P = -(\partial E / \partial V)_T + T(\partial P / \partial T)_v \quad (3)$$

we see that A_v is identical with $-(\partial E / \partial V)_T$. Values of B_v and A_v at integral values of the molar volume are shown in Table II, the numbers for A_v having been determined from the P - T plot (Fig. 4) and the smoothed values for B_v . It is seen that A_v approaches zero at both high and low volumes. This is as expected from the shape of the curve relating potential energy $E(r)$ to separation r for the interaction of two H_2 molecules, the slope of the curve becoming zero at $r = \infty$ and $r = r_0$, where the interaction energy is at a minimum. Because of insufficient data it has not been possible to extrapolate the low-volume end of the curve A_v vs. V and thereby obtain the volume corresponding to r_0 .

TABLE II

VALUES OF A_v AND OF B_v FOR INTEGRAL VALUES OF V

V , cc./mole	B_v , atm./deg.	$-A_v$, atm.	V , cc./mole	B_v , atm./deg.	$-A_v$, atm.
26	9.69	131	33	6.12	162
27	9.07	152	34	5.74	155
28	8.50	164	35	5.37	149
29	7.96	170	36	5.03	141
30	7.46	172	37	4.70	133
31	6.99	171	38	4.39	125
32	6.55	167	39	4.10	118

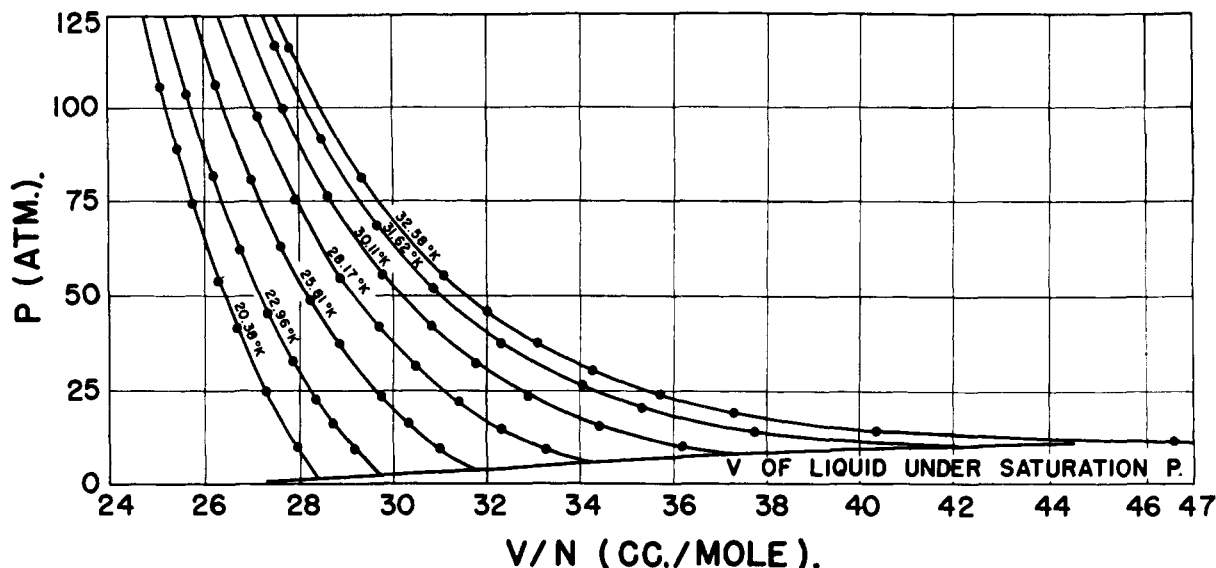


Fig. 2.— P - V isotherms for compressed liquid hydrogen. The solid line with no points represents the volume of the liquid under saturation pressure as given in reference 3.

P. W. Bridgman⁸ notes that for most liquids the relation $(\partial P/\partial T)_V = B_V$ does not hold at very high pressures.

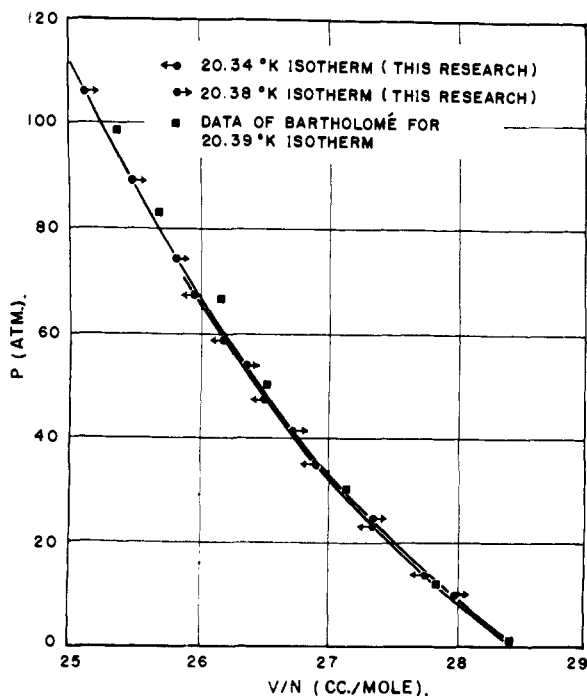


Fig. 3.—Two isotherms for compressed liquid hydrogen near the boiling point compared with the data of Bartholomé: \leftarrow , 20.34°K. isotherm (this research); \rightarrow , 20.38°K. isotherm (this research); \blacksquare , 20.39°K. isotherm (Bartholomé).

An attempt has been made to fit the compressibility data of this research to the Lennard-Jones and Devonshire (LJD) equation of state for compressed fluids. Wentorf, Buehler, Hirschfelder

(8) P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons. Ltd., London, 1949, pp. 137-140.

and Curtiss⁹ have computed tables of compressibilities from the LJD model, improved to the extent of including the second and third shells of molecules surrounding the encaged molecules. Peek and Hill¹⁰ modified the LJD theory by considering holes in the liquid and an expansible lattice. The comparisons were, however, unsatisfactory for the

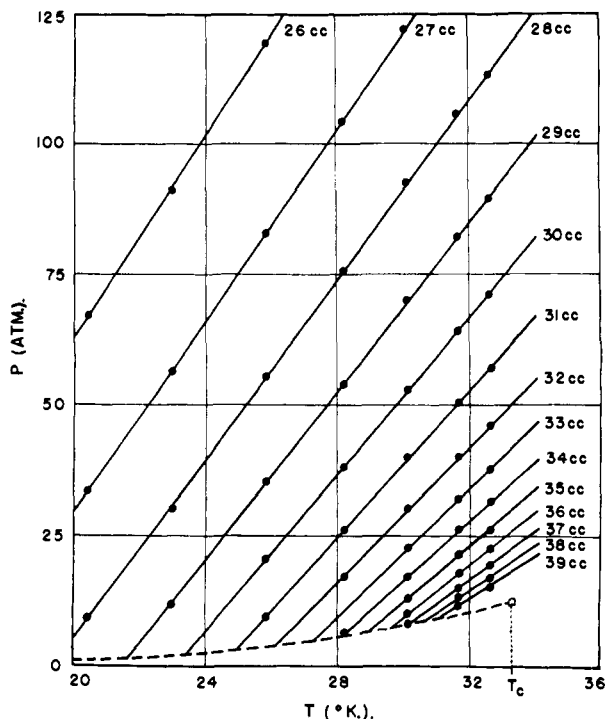


Fig. 4.— P - T isochores replotted from the isotherms given in Fig. 3. The large dashed line represents the vapor pressure curve.

(9) R. H. Wentorf, Jr., R. J. Buehler, J. C. Hirschfelder and C. F. Curtiss, *J. Chem. Phys.*, **18**, 1484 (1950).

(10) H. M. Peek and T. L. Hill, *ibid.*, **18**, 1254 (1950).

range of densities investigated. This can be seen in Fig. 5, where the data of an isotherm (curve c) less than a degree below the critical temperature are compared to the LJD curve as computed by Wentorf, *et al.*⁹ In curve a the force constants used in the LJD model are those obtained by

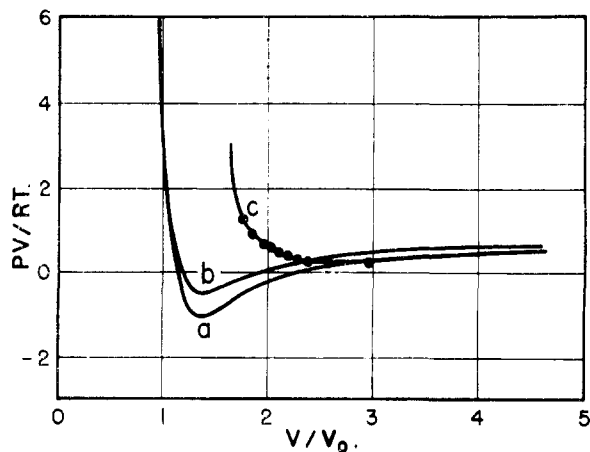


Fig. 5.—Data for an isotherm near the critical temperature (c) as compared with two computations of the LJD model (a, b).

Hirschfelder, Bird and Spatz¹¹ from the viscosity data of Johnston and McCloskey.¹² The force constants used in curve b were obtained from second virial coefficients recently determined in this Laboratory.¹³ The lower temperature isotherms deviate from the LJD theory even more. The deviation of the hydrogen isotherms from the theory may be accounted for by the non-spherical symmetry of the H₂ molecule and by quantum effects. Evidence of the importance of this orientation effect in the H₂ molecule is the marked discrepancy between the third virial coefficients obtained experimentally in this Laboratory and those computed by Bird, Spatz and Hirschfelder.¹⁴

Acknowledgment.—We wish to acknowledge the assistance of Dr. Frederick J. Martin in the early stages of design, and that of Mr. L. E. Cox, Shop Foreman of the Cryogenic Laboratory, in features of shop construction. We also wish to acknowledge helpful suggestions given by Dr. David White.

(11) J. O. Hirschfelder, R. B. Bird and E. L. Spatz, *J. Chem. Phys.*, **16**, 968 (1948).

(12) H. L. Johnston and K. E. McCloskey, *J. Phys. Chem.*, **44**, 1038 (1940).

(13) D. White, A. S. Friedman and H. L. Johnston, *Phys. Rev.*, **79**, 235 (1950).

(14) R. B. Bird, E. L. Spatz and J. O. Hirschfelder, *J. Chem. Phys.*, **18**, 1395 (1950).

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Condensed Gas Calorimetry. VI. The Heat Capacity of Liquid Parahydrogen from the Boiling Point to the Critical Point

BY A. LEE SMITH, NATHAN C. HALLETT AND HERRICK L. JOHNSTON

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Previous measurements of the heat capacity of liquid parahydrogen below its boiling point have been extended to the critical temperature for hydrogen. The computed calorimetric entropy at the critical point is 17.2 e.u., and agrees well with the statistical entropy, 17.208 e.u.

Introduction

As part of a general study in this Laboratory on the thermodynamic properties of hydrogen, previous measurements¹ of the heat capacity of liquid parahydrogen below its boiling point have now been extended to the critical temperature for hydrogen (33.24°K.). The calorimetric entropy at the critical point has been computed and compared with the statistical entropy.

Experimental Procedure

Pure hydrogen gas was condensed into an ortho-para converter containing chromic oxide gel, and allowed to stand for two hours at the boiling point of liquid hydrogen. Conversion is extremely rapid and the equilibrium mixture of 99.79% para- and 0.21% orthohydrogen may be expected in a few minutes.² The gas was then metered into the calorimeter using a 5-liter constant-temperature buret.¹

The high-pressure calorimeter used in this work has been described.³ It consists of a copper bomb with an inconel

gas inlet capillary. A re-entrant well in the bottom of the calorimeter contains a combination heater-resistance thermometer. An atmosphere of helium gas was used to establish thermal contact. The calorimeter is mounted in the usual manner.¹ The electrical circuits, procedure and treatment of data were the same as described in the previous research on parahydrogen.¹ The temperature scale was established by a thermocouple calibrated against our standard No. 80 which was in turn calibrated by comparison with the Cryogenic Laboratory helium thermometer.⁴ Temperature intervals were computed, using resistance values, by reference to a smoothed table in which resistance was expressed as a function of temperature.

Experimental Results

Saturated Heat Capacities of the Liquid.—Results of the measurements are given in Table I, and are shown plotted in Fig. 1 along with the data of Johnston and co-workers.¹ It is seen that near the critical temperature, the heat capacity rises sharply to very high values. From a plot of $\log C_s$ vs. T we estimate the heat capacity to be over 50 cal. per mole at 33.24°K.

(4) T. Rubin, H. L. Johnston and H. Altman, *ibid.*, **73**, 340i (1951).

(1) H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, *THIS JOURNAL*, **72**, 3933 (1950).

(2) Unpublished data, this Laboratory.

(3) E. B. Rifkin, E. C. Kerr and H. L. Johnston, *THIS JOURNAL*, **75**, 785 (1953).