

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

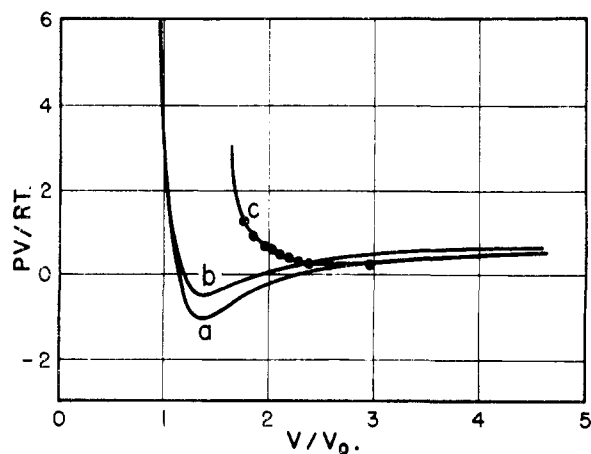


Fig. 5.—Data for an isotherm near the critical temperature (c) as compared with two computations of the LJD model (a, b).

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

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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.

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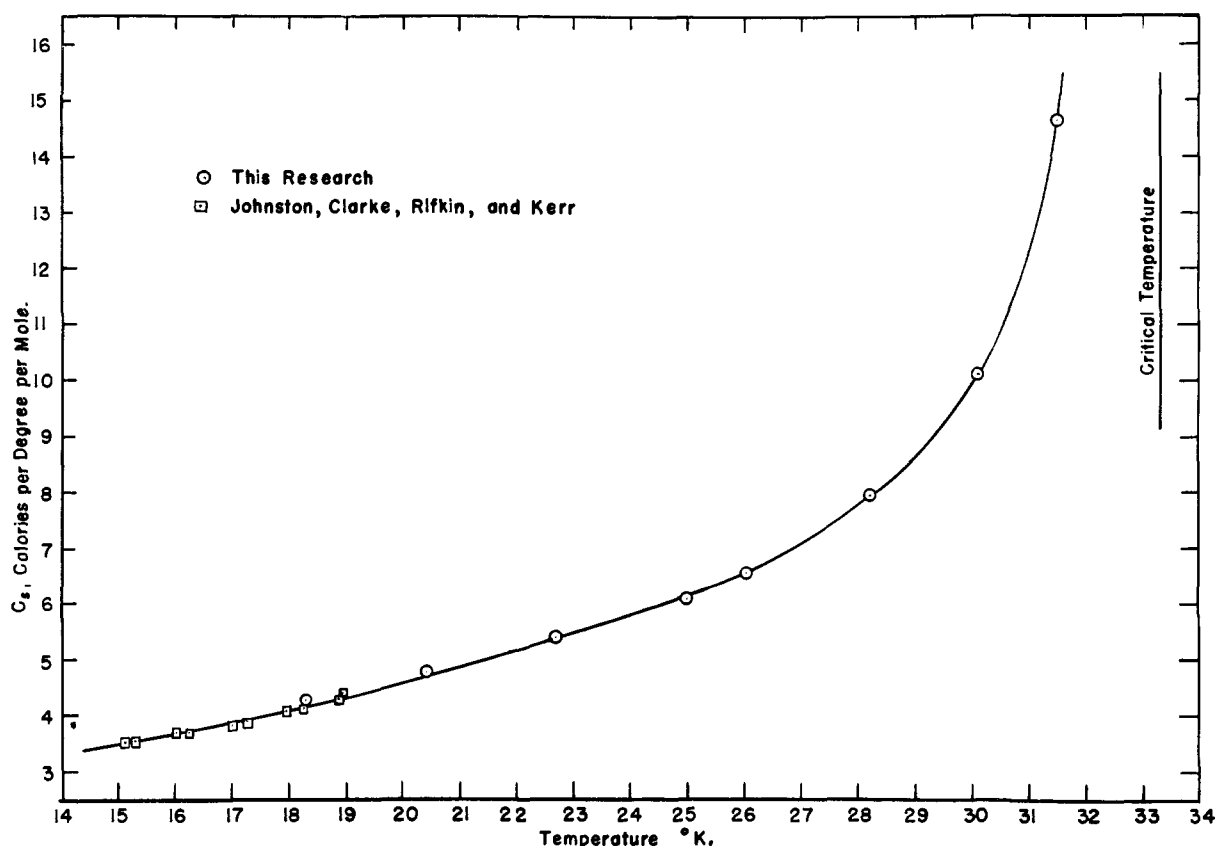


Fig. 1.—Heat capacity of liquid parahydrogen.

Run	T_{av} , °K.	ΔT , °K.	Moles	C_s , cal./mole/deg.
2	18.28	2.009	3.519	4.18
3	20.45	2.165	3.519	4.71
4	22.71	2.205	3.519	5.33
5	25.00	2.174	3.519	6.03
6	26.04	1.714	2.493	6.46
8	28.20	1.869	2.493	7.85
9	30.10	1.818	2.493	9.94
10	31.49	1.637	2.284	14.56

The number of moles of gas was measured during both the filling and the emptying of the calorimeter, and the two results agreed to within one part in 3000.

Correction for the heat of vaporization of hydrogen into the space above the liquid was made by the method of Osborne and VanDusen.⁵ In applying the correction we used the vapor pressure data of White, Friedman and Johnston,⁶ and liquid volumes as given by Mathias, Crommelin and Onnes,⁷ and Johnston, Keller and Friedman.⁸

Evaluation of Errors.—Since for our resistance thermometer dR/dT is only 0.0415 ohm/degree at 20°K. and resistance may be determined to

(5) N. S. Osborne and M. S. VanDusen, *Bull. Bur. of Stand.*, **14**, 397 (1918).

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

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(8) H. L. Johnston, W. E. Keller and A. S. Friedman, *THIS JOURNAL*, **76**, 1482 (1954).

within 0.001 ohm, the uncertainty in a 2-degree temperature increment is about 2% at the lowest temperature. This uncertainty diminishes rapidly with increasing temperature and is less than 1% at 30°K. The input of electrical energy to the calorimeter is known to an accuracy better than 0.1 of 1%.

In condensed gas calorimetry, the vaporization correction may become quite large, and in two cases (runs 6 and 10) amounted to about 27% of the total heat capacity. Since the correction is uncertain to a maximum of 4%, a 1% uncertainty is introduced from this source. The fact that the data, even for these points, fits a smooth curve to

Liquid at 20.26°K. and 1 atm.	3.995 ± 0.07 ¹
Change for liquid in going from 1 atm. at 12.8 atm.	-0.144 ± 0.00
Liquid 20.26–33.24°K.	4.825 ± 0.30
Total calorimetric entropy at 33.24° ^a	8.676 ± 0.37
Correction to the ideal gaseous state	8.516 ± 0.05
Frozen in entropy of mixing	0.039 ± 0.00
Total entropy of 99.79% parahydrogen at 33.24°	17.23 ± 0.4 e.u.

^a The rather large uncertainty in the experimental value for the entropy of the liquid arises from the difficulty of extrapolating the heat capacity curve from 32 to 33.24°K., and not from errors in the measurements.

within 0.5 of 1% shows that the over-all error is somewhat reduced by compensation of component errors. The uncertainty of the extrapolation to the critical temperature accounts for the relatively large estimated limits of error in the entropy shown in Table II.

Entropy of Hydrogen at the Critical Point.—At the critical temperature a gas is indistinguishable from a liquid, and the entropies of the two phases are identical. The calorimetric entropy is evaluated in Table II.

Since the entropy is given by $\Delta S = \int C_p d \ln T$, the heat capacity at constant pressure rather than the saturation heat capacity must be used to evaluate the integral. The relation between C_p and C_s is given by

$$C_s = C_p - T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial P}{\partial T} \right)_p \quad (1)$$

and the corresponding entropy difference amounts to 0.499 e.u. between 20.26 and 33.24°K. C_p

was computed at 12.8 atm. (the critical pressure) with the use of P - V - T data, and a correction for the entropy change of the liquid in going from 1 to 12.8 atm. was applied. The entropy of mixing of the 0.21% orthohydrogen has been discussed elsewhere.¹ The entropy correction in going from a real gas to an ideal gas at 33.24°K. and 12.8 atm. was found by extrapolation from tables based on P - V - T data for hydrogen.^{2,9}

The entropy of a perfect gas at 33.24°K. including nuclear spin is 17.192 e.u. and the entropy of mixing is 0.016 e.u. The statistical entropy is thus 17.208 e.u. which is in satisfactory agreement with our experimental value of 17.2 e.u.

Acknowledgments.—We wish to thank Mr. Howard Altman and Mr. W. D. Wood, who helped with the runs and with calculations.

(9) H. W. Wooley, R. S. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948), RP 1932.

COLUMBUS, OHIO

[CONTRIBUTION NO. 42 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thermodynamic Functions and Heat of Formation of $S_8(\text{Gas})^1$

BY G. B. GUTHRIE, JR., D. W. SCOTT AND GUY WADDINGTON

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The thermodynamic functions ($F^\circ - H_0^\circ$)/ T , $(H^\circ - H_0^\circ)$ / T , $H^\circ - H_0^\circ$, S° , and C_p° , for $S_8(\text{gas})$ at selected temperatures to 1000°K. were calculated from spectroscopic and molecular structure data. Values of the heat of formation of $S_8(\text{gas})$ from rhombic sulfur were computed from published experimental data. The value $\Delta H_{10}^\circ = 25.23 \pm 0.05$ kcal. mole⁻¹ was selected as the most probable. The heat, free energy and equilibrium constant at selected temperatures were calculated for the reaction $4S_2(\text{gas}) = S_8(\text{gas})$. A vibrational assignment previously proposed for S_8 was found to be inconsistent with the vapor pressure and thermal data for rhombic sulfur and was revised to remove the inconsistency. Consideration of tautomers of the cyclic S_8 molecule other than the one of D_{4d} symmetry made it seem unlikely that these make significant contributions to the thermodynamic properties at temperatures below 1000°K.

In order to utilize fully the thermodynamic data that are being obtained for organic sulfur compounds in this Laboratory and elsewhere, it is necessary to have thermodynamic data of equal quality for elemental sulfur. Because elemental sulfur occurs in some petroleum crudes and refinery processes, accurate values of its thermodynamic properties are pertinent to petroleum technology. Only two comprehensive correlations of the thermodynamic properties of elemental sulfur have been published. The earlier one, that of Lewis and Randall,² antedates their book published in 1923. The more recent one, published by Kelley³ in 1937, took advantage of newer data that had been obtained since the time of Lewis and Randall's work.

Additional and more accurate data that have become available for elemental sulfur since 1937 make an up-to-date correlation of its thermodynamic properties desirable, and such a correlation has

been undertaken in this Laboratory. This paper presents values of the chemical thermodynamic properties of $S_8(\text{gas})$ that were computed from spectroscopic, molecular structure, vapor pressure and other data as a part of the over-all correlation. Values of the chemical thermodynamic properties of two simpler sulfur species, $S_2(\text{gas})$ and $S(\text{gas})$, are already available from the recent work of Evans and Wagman.⁴

Vibrational Assignment and Thermodynamic Functions

Vibrational Assignment.—Calculation of thermodynamic functions for S_8 required a complete assignment of the fundamental vibrational frequencies of the molecule. Bernstein and Powling⁵ recently reviewed and added to the available spectroscopic data for S_8 and proposed a vibrational assignment that is essentially an extension of the earlier incomplete assignment of Bhagavantam and Venkatarayudu.⁶ When thermodynamic functions computed from Bernstein and Powling's assignment were used with vapor pressure data for rhombic sulfur to compute ΔH_{10}° for the reaction $8S(\text{rhombic}) =$

(1) This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) G. N. Lewis and M. Randall, (a) *THIS JOURNAL*, **33**, 476 (1911); (b) *ibid.*, **36**, 2468 (1914); (c) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 534-535.

(3) K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. VII. The Thermodynamic Properties of Sulfur and its Inorganic Compounds," Bureau of Mines Bulletin 406, U. S. Govt. Printing Office, Washington, D. C., 1937, pp. 2-11.

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(5) H. J. Bernstein and J. Powling, *J. Chem. Phys.*, **18**, 1018 (1950); *ibid.*, **19**, 139 (1951).

(6) S. Bhagavantam and T. Venkatarayudu, *Proc. Indian Acad. Sci.*, **8A**, 115 (1938).