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

Condensed Gas Calorimetry. I. Heat Capacities, Latent Heats and Entropies of Pure Para-Hydrogen from 12.7 to 20.3°K. Description of the Condensed Gas Calorimeter in Use in the Cryogenic Laboratory of the Ohio State University[1,2]

BY HERRICK L. JOHNSTON, JOHN T. CLARKE, ELLIS B. RIFKIN AND EUGENE C. KERR

Introduction

Measurements of the calorimetric properties of solid and liquid hydrogen have been carried out by several investigators. Eucken[3] made the first measurements in 1916, but limited his data to a few points in the temperature range 17–21°K. Work on the solid was first done at Leiden by Keesom and Onnes[4] in 1917. Measurements of somewhat higher accuracy were later carried out by Simon and Lange.[5] None of these investigators were aware of the existence of the ortho and para forms of hydrogen, which were discovered in 1928[6] following predictions from quantum theory,[7] and their samples of liquid and solid hydrogen undoubtedly contained a para hydrogen content somewhere intermediate between 25%, typical of the normal mixture, and 99.8%, corresponding to the equilibrium mixture at the boiling point of hydrogen. Following the discovery of the ortho and para forms of hydrogen and the discovery by Bonhoeffer and Harteck[6] of a means of catalyzing the conversion, Clusius and Hiller[8] measured the heat capacities and heat of fusion of 95% para hydrogen. Their data fitted the curves obtained by Simon and Lange for the approximately normal mixture.

In our desire to check the heat of vaporization of liquid hydrogen, and as a preliminary to measurements with liquid and solid deuterium, we have redetermined heat capacities and latent heats of solid and liquid hydrogen. We have employed for the purpose para hydrogen of 99.8% purity, prepared by equilibration over charcoal at 20.3°K.

We have computed entropies of the pure para form from the calorimetric data, and compared the entropy of the gas at the normal boiling point with that computed statistically.

Apparatus and Procedure

(1) Calorimeter and Cryostat.—A general diagram of the condensed gas calorimeter used in this work is shown in Fig. 1. It is an improved form of the condensed gas calorimeter developed at Berkeley[9] and used by Giauque and Johnston, for oxygen. The calorimeter proper is a cylindrical container of copper with a volume of 119.2 ml. It is approximately 9.5 cm. long and 3.8 cm. in diameter with a wall thickness of 0.079 cm. Twelve radial fins of 0.013-cm. copper sheet are soldered inside the calorimeter to aid in establishing thermal equilibrium. Copper caps 0.046 cm. thick overlap the cylinder and are soldered to its top and bottom. The gas inlet tube is made of 0.011 cm. i. d. × 0.0157 cm. o. d. monel tubing and is connected to the top of the calorimeter through a soldered sleeve. The calorimeter wall is coated with a

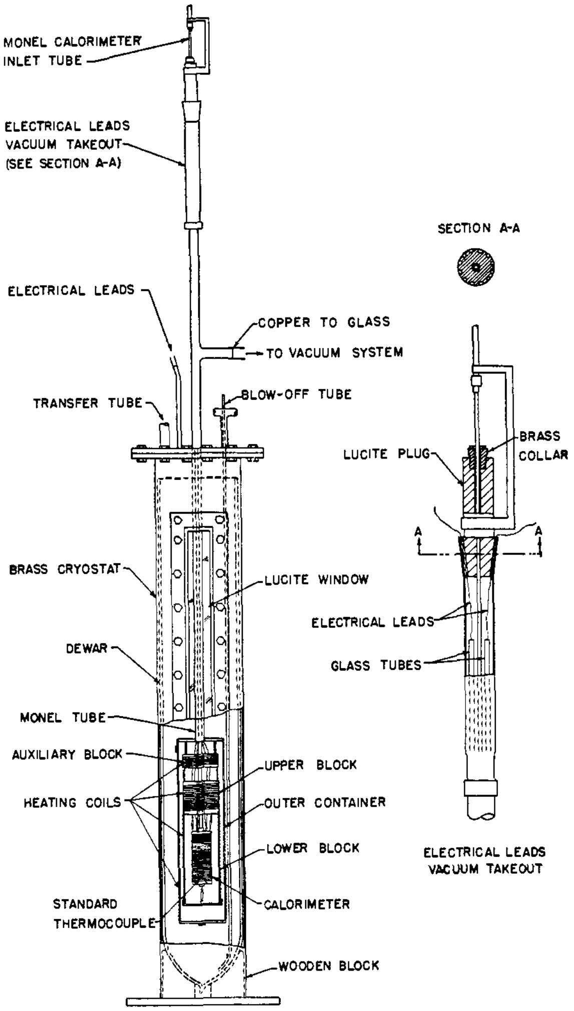

Fig. 1.—Calorimeter and cryostat.

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] Presented before the Division of Physical and Inorganic Chemistry at the Atlantic City Meeting of the American Chemical Society, held September 20 to 24, 1949.

[3] A. Eucken, *Verh. d. D. Physik Ges.*, **18**, 4 (1916).

[4] W. Keesom and K. Onnes, *Leiden Comm.*, 153a (1917).

[5] Simon and Lange, *Z. Physik*, **15**, 307 (1923).

[6] (a) W. F. Giauque and H. L. Johnston, THIS JOURNAL, **50**, 3221 (1928); (b) G. C. McLennan and G. H. McLeod, *Nature*, **123**, 160 (1929); (c) K. F. Bonhoeffer and P. Harteck, *Naturwiss*, **17**, 182 (1929).

[7] (a) W. Heisenberg, *Z. Physik*, **38**, 411 (1926); (b) Hund, *ibid.*, **42**, 93 (1927); (c) D. M. Dennison, *Proc. Roy. Soc.*, **A115**, 483 (1927).

[8] K. Clusius and K. Hiller, *Z. physik. Chem.*, **B4**, 158 (1929).

[9] (a) W. F. Giauque and R. Wiebe, THIS JOURNAL, **50**, 101 (1928); (b) W. F. Giauque and H. L. Johnston, *ibid.*, **51**, 2300 (1929); (c) W. F. Giauque and C. J. Egan, *J. Chem. Phys.*, **5**, 45 (1937).

solution of General Electric Adhesive No. 7031 in ethyl alcohol and toluene, air-dried. The calorimeter is wound with 320 ohms of nylon-covered No. 40 (gold + 0.15% silver) wire which serves as a combination resistance thermometer–heater, and thoroughly coated with G. E. Adhesive No. 7031. The winding on the calorimeter is covered with gold leaf to reduce the heat leak from radiation. In addition to end leads a gold wire lead is taken off the coil at the mid-point so that energy can be supplied separately to the lower half of the calorimeter during heat of vaporization measurements. These three gold leads are soldered to the lower ends of thick copper rivets that pierce the "upper block." These rivets make good thermal contact with the block but are insulated from it electrically by means of Bakelite insulators. Current and potential leads of No. 30 B and S gage double nylon covered copper, soaked in G. E. Adhesive No. 7031, are soldered to the upper ends of the copper rivets. A copper-constantan thermocouple is also soldered, by means of low melting cerrobend alloy, to the tinned interior of a small copper tube silver soldered to the bottom of the calorimeter. This thermocouple is wrapped tightly around the calorimeter, for several turns, to give good thermal contact, and taken out through a hole drilled through the upper block. The hole surrounding the thermocouple is filled with paraffin to give good thermal contact with the upper block.

The calorimeter and blocks are mounted as shown in Fig. 1. The upper block which is a lead-filled copper cylinder wrapped with a nylon insulated B. and S. gage no. 30 manganin heater, is just above the calorimeter and has an o. d. of 6.8 cm. and a height of 6.3 cm. The "lower block," shown to the right, is a copper cylinder 20 cm. high by 6.8 cm. o. d. with a 1-cm. wall thickness. It is wrapped with a heater of nylon-insulated B. and S. gage no. 30 manganin wire. When in position, it surrounds the calorimeter as a combination heat sink and radiation shield and is fastened to the tapered bottom of the upper block by means of small screws. Good thermal contact between the two blocks is attained by the use of a thin film of stopcock grease on the tapered joint.

The upper block is suspended by nylon fish cord from an "auxiliary block" which, in turn is held tight against the shoulders of three brass studs attached to the underside of the "container" lid. The small monel tube passes upward through holes in the upper and the auxiliary blocks with which it is brought into good thermal contact by means of cerrobend alloy. Thermocouples and thermometer leads pass through holes drilled in the auxiliary block. The holes are filled with paraffin.

As shown in Fig. 1, a brass container surrounds the block assembly and is connected to a vacuum system by means of an 18 mm. o.d. monel tube which also serves as a support. The brass container is suspended in a 36 by 5.5 inch glass dewar which is set in a brass cryostat[11] whose windows coincide with unsilvered strips in the dewar. The cryostat is vacuum tight and can be connected either to the hydrogen return line or to the Kinney vacuum pump; the latter is used for reducing the temperature in the dewar by adiabatic evaporation.

The monel inlet is wound to within 0.5 inch of the calorimeter with a heater of no. 36 constantan wire. The tube is taken out of the outer container vacuum system through a lucite plug in a standard taper joint[10] and a vacuum tight seal made by means of DeKhotinsky cement. The thermocouples and lead wires are taken out of the outer container vacuum system by inserting them in slots around the periphery of the lucite plug, sealed by DeKhotinsky cement. The monel tube is connected to the glass system by means of a kovar to Pyrex seal. The glass tube connects through a mercury trap of gold foil to the gas metering system, the constant volume manometer and the gas purification train.

The brass cryostat vessel, with lucite windows, is standard equipment in the Ohio State Cryogenic Laboratory and is described elsewhere.[11]

(2) **Gas Measuring System.**—The gas measuring system is in every respect similar to that employed by Giauque and Johnston,[9b] with oxygen and nitric oxide. It consists of a 5-liter mercury buret immersed in a constant temperature bath in which the quantity of material in the calorimeter is determined volumetrically when it is evaporated out at the end of a series of runs. The pressure in the 5-liter buret is kept constant, by automatic regulation, in the manner described by Giauque and Johnston, during heat of vaporization runs.

Accurate pressure readings on the gas in the buret are made by means of a large bore mercury manometer with the aid of a standard meter bar and a Gaertner M-904 cathetometer. The manometer itself is similar to the one described by Giauque and Johnston.[9b] However, we have added some new features that will be described in detail in a future publication[12] from this Laboratory.

Variable reflection from the surface of the mercury is minimized by employment of back lighting from a fluorescent lamp through 2-mm. slits cut at 2.5-cm. intervals in a long strip of Bakelite. The slits are cut horizontally and since the Bakelite strip on the vacuum arm of the manometer moves vertically, by means of a rack and pinion, through an amplitude of about 4 cm., one of the slits can be lined up behind the meniscus for any position of the mercury. This provides parallel lighting. The travel of the Bakelite strip is also controlled from the operators position by means of a flexible shaft. A single slit that may be adjusted manually so as to stand either directly back of the fiduciary point or at a level close to it gives parallel lighting for the lower meniscus.

Corrections were applied, as given in the "International Critical Tables," for temperature of mercury and of the standard meter scale and for capillary depression as measured by meniscus height. The gravitational correction was taken as 980.101 for this locality.

In determining the quantity of gas that collected in the buret, correction was made for gas imperfection by means of the virial equation

$$PV_m = RT + BP \qquad (1)$$

The second virial coefficient, B, for hydrogen was taken as +15.0 cc./mole at 25°.[13]

(3) **Electrical Circuits.**—The general plan of electrical circuits for energy supply and for resistance thermometer and thermocouple measurements is similar to that described by Gibson and Giauque.[14] A 50,000-ohm voltage divider is used in the energy circuit.

A White double potentiometer is used for energy and resistance measurements and a Wenner potentiometer for thermocouple readings.

The resistance thermometer has a (dR/dT) of 1 ohm per degree at 40°K. and can be read with a precision of better than 0.001 ohm. Thermocouple readings are reproducible to within about 0.01° above 50°K., but the sensitivity is reduced in the liquid and solid hydrogen range.

(4) **Timing.**—The timer is a slightly modified form of the one designed by Johnston,[15] its basic feature is that the same switching action is used in closing and breaking the circuit. The timer is electrically driven by a photoelectric relay activated by light reflected from a mirror on a pendulum clock. This is a modified version of the regulator clock with photoelectric contact obtained from the Gaertner Scientific Corporation; the photoelectric circuit is entirely new. Time intervals are measured to within ±0.001 second.

(5) **Temperature Scale.**—Vapor pressures of the pure liquid para hydrogen were used to establish the tempera-

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[10] A description of the lucite plug seal will appear in a paper on the heat capacity of boric oxide from this Laboratory.

[11] H. L. Johnston, *Rev. Sci. Inst.*, to be published.

[12] T. R. Rubin and L. E. Cox, submitted to *Rev. Sci. Inst.*

[13] D. White, A. S. Friedman and H. L. Johnston, THIS JOURNAL, **72**, 3565 (1950).

[14] G. E. Gibson and W. F. Giauque, *ibid.*, **45**, 93 (1923).

[15] H. L. Johnston, *J. Opt. Soc. Am.*, **17**, 381 (1928).

ture scale between 13.8 and 20.9°K. Measurements were made with the calorimeter only half full and with the monel capillary heated to a temperature a little above that of the calorimeter, to avoid condensation. Pressures were read on the accurate manometer and both thermocouple and resistance thermometer readings were taken. Readings were made at fifteen temperatures and the pressures converted to temperature by an equation that represents the results of vapor pressure measurements made at Leiden.[16]

The Leiden equation, which originally read

$$t,\ ^\circ\mathrm{C.} = -260.937 + 1.0270 \log P + 1.7303 \log {}^2P \quad (2)$$

where P equals pressure in centimeters of mercury, was adjusted so that the gas thermometer constants used in the original determinations were replaced by others more acceptable at the present time. The new constants that we employed are: the fundamental pressure coefficient for helium at constant volume, 36605.8×10^{-3}; the fundamental pressure coefficient for a perfect gas at constant volume, 36607.9×10^{-7}; the second virial coefficient for helium at the ice-point, 2.9306 cc./g.

These changes yield this new equation

$$T = (1 - 2.13 \times 10^{-4})t + 273.082 \quad (3)$$

in which t is the centigrade temperature given by equation (2) and T is the temperature in °K., with the new constants. Equation (3) yields a temperature scale in agreement with one recently established in this Laboratory by a constant volume helium thermometer.

It should be noted that the boiling point of normal hydrogen on this scale is then 20.382°K. which agrees well with the generally accepted value of 20.38°K. The absolute temperature of the ice-point on this scale is 273.16.

Tables of both resistance and thermocouple voltage were prepared as functions of the computed temperatures and the data smoothed by graphical and analytical means. The smoothed values were employed to extrapolate the scale below 13.8°, as well as to read off temperatures within the experimental range.

The smoothed resistance readings were the ones actually used in the computation of the heat capacities. Since resistance thermometer windings, of the present type, may change their calibration with time, it was necessary to ascertain whether or not a change in calibration may have occurred during the period of use. Three readings of the resistance at the triple point of para hydrogen agreed to within 0.002°. These triple point readings were made over a period of three months. Comparisons of the resistance thermometer and the less sensitive thermocouple, over a period of fifteen months, have also indicated that this calibration of the resistance thermometer remained unchanged. During this fifteen-month period hydrogen, deuterium, oxygen, neon, diborane and pentaborane have all been condensed in the calorimeter.

(6) Procedures and Treatment of Data.—Experimental procedures, and treatment of data, were carried out in the same manner as those discussed in some detail by Giauque and Johnston.[8b]

Preparation and Purification of Hydrogen.—The hydrogen used in this investigation was originally prepared by the electrolysis of an aqueous potassium hydroxide solution. Traces of oxygen were removed catalytically; the gas was dried over stick potassium hydroxide and was subsequently liquefied. The liquid was filtered to remove solid particles of condensable impurity and was then evaporated and subjected to a second liquefaction and distillation. After compression in a standard high pressure storage cylinder, the gas was analyzed and found to contain less than 0.01 mole per cent. of impurity.

Finally, gas from the cylinder was placed in contact with active charcoal for three hours and then condensed in a special Pyrex vessel, surrounded by a bath of liquid hydrogen. The special Pyrex vessel was constructed in such a way that the liquid hydrogen had to pass through a glass wool filter after contact with the charcoal as it was slowly evaporated and recondensed in the calorimeter. A period of ten hours was taken for the slow evaporation from the charcoal to fill the calorimeter of 119.2 cc. volume. The hydrogen that entered the calorimeter was thus in contact with the charcoal for from three to thirteen hours. Conversion to 99.8% para composition should be complete.

A thermostated mercury buret was used as a mercury piston to assist in condensing hydrogen in the calorimeter during the filling process; the vacuum space surrounding the calorimeter was filled with helium as an exchange gas. Hydrogen was admitted to the calorimeter until response to the tube heater indicated that the liquid level extended a short distance into the monel capillary. Sufficient hydrogen was then withdrawn into the thermostated buret to leave 0.5 cc. of gas-filled space in the top of the calorimeter (at the boiling point of hydrogen). The calorimeter and contents were then cooled to about 11.5°K., where measurements were begun after a good vacuum was obtained.

Three successful series of runs were made, with three different fillings of hydrogen in the course of this investigation. The method of purification and of ortho to para conversion outlined above was followed in each case.

Experimental Results

(1) Heat Capacities of Solid and Liquid.—The heat capacity data obtained in the three series of runs are presented in Table I.

TABLE I

HEAT CAPACITY OF 99.8% PARA HYDROGEN

MOLECULAR WEIGHT 2.0161

Series II, 4.051 moles; Series III, 4.102 moles

Series	T_{av}, °K.	ΔT, °K	C_{p}, cal./mole/degree
II	12.71	0.120	1.00
II	12.89	.156	1.13
II	13.20	.209	1.25
II	13.45	.199	1.28
III	12.85	.276	1.12
III	13.16	.250	1.25
Melting point at	13.84		
III	15.15	0.901	3.52
II	15.30	.935	3.54
III	16.05	.859	3.67
II	16.26	.897	3.66
III	17.03	.956	3.81
II	17.31	1.134	3.85
III	17.98	0.898	4.03
II	18.27	.656	4.10
III	18.89	.855	4.24
II	18.99	.747	4.32

(2) Triple Point Pressure and Temperature.—Three determinations of the triple point pressure were made, with the calorimeter only half filled in order to avoid superheating of the surface by heat leak down the monel tube which was purposely kept warmer than the calorimeter. All determinations were made with Preparation III. Fifteen minutes to a half-hour was allowed for attainment of thermal equilibrium with the solid in the calorimeter less than half melted. The three determinations yielded the respective values 5.278, 5.274 and 5.276 cm. of mercury. We have therefore adopted the value 5.276 ± 0.01 cm. of mercury as the triple point of pure para hydrogen. This result compares with

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(16) P. Keesom, A. Bijl and H. Van der Horst, *Leiden Comm.*, 217a (1931).

the values 5.38 ± 0.01 for the triple point of normal hydrogen (25% para) and of 5.34 ± 0.01 for hydrogen equilibrated at liquid air temperature (50% para) as reported by Giauque and Johnston.[6a]

By substituting 5.28 for P in equation (2), and solving both equation (2) and (3), we obtain 13.845 for the triple point temperature of pure para hydrogen.

(3) **Heat of Fusion.**—Two measurements of the heat of fusion were carried out, in Series II and Series III, respectively. These were carried out in the usual manner by beginning heat input a little below the melting point and ending a little above. Corrections were then applied for the $C_p dT$ integrals as well as for the heat absorbed by a small amount of sublimation and evaporation. The results are summarized in Table II and give an average value of 28.08 calories per mole, which is believed accurate to within about 0.5 of 1%.

TABLE II

HEAT OF FUSION OF PARA HYDROGEN

Series	Temp. interval, °K.	Corrected total heat input, cal.	$\int C_p dT$, total	ΔH, cal./mole
II	13.711–14.714	126.52	12.80	28.07
III	13.436–14.616	128.43	13.10	28.09
		Average		28.08 ± 0.15

(4) **Heat of Vaporization.**—Six determinations of the heat of vaporization were carried out at the close of Series III heat capacity runs. The vaporization was carried out at the normal boiling point using the procedure employed by Giauque and Johnston.[9b] Because (dP/dT) for hydrogen at its boiling point is quite large (over 22 cm. per degree), the temperature remained very constant during the half-hour of heat input necessary to volatilize approximately 0.2 of a mole of liquid hydrogen into the 5-liter mercury buret. However, small temperature changes occurred after the stopcock was opened at the beginning of the run and after it was closed, at the conclusion of the run, during approach to thermal equilibrium. We therefore made small corrections for the $C_p dT$ integrals in these runs and applied corrections for the increased vapor in the calorimeter due to the increase in vapor space and to small pressure changes. Correction was also made for heat transfer between the calorimeter and its surroundings, with proper account taken of the temperature rise of the heater wires during the heating period. The heat transfer constant was determined in preliminary experiments with the block at a temperature somewhat different from that of the calorimeter. The rate of temperature rise was determined by the rate of change of vapor pressure, which is more sensitive than (dR/dT).

Electrical energy was applied only to the lower half of the calorimeter heater winding to avoid superheating of the surface of the liquid.

Runs were discontinued when the liquid level dropped to about 70% of the height of the calorimeter.

Preliminary computations indicated that the monel capillary was sufficiently large to prevent sensible pressure gradients from developing.

The results are summarized in Table III and lead to an average value of 214.8 ± 0.2 calories per mole.

TABLE III

HEAT OF VAPORIZATION OF PARA HYDROGEN AT ITS NORMAL BOILING POINT (20.261°K.)

Run	Mole vaporized	ΔH, cal./mole
1	0.20426	214.8
2	.20187	214.6
3	.20238	214.65
4	.16776	215.0
5	.19218	216.3[a]
6	.19796	214.9
	Average	214.8 ± 0.4

[a] Assumed to be in error through a mistake in recording data. Not counted in obtaining the average.

(5) **The Heat of Vaporization of Normal Hydrogen.**—The *differences* in the heats of vaporization of normal and of para hydrogen at a common temperature can be computed by use of the accurate Clapeyron equation in the form

$$\Delta H_n - \Delta H_p = T(V_G - V_L)_n \left(\frac{dp}{dT}\right)_n - (V_G - V_L)_p \left(\frac{dp}{dT}\right)_p \quad (4)$$

The differences in the heats of vaporization were calculated at the boiling point of pure para hydrogen (20.261°K.). The heat of vaporization thus obtained for n-H_2 at this temperature was corrected to its own boiling point by applying a correction for $\int C_p dT$. Using the vapor pressure equations of Keesom, Bijl and von der Horst,[16] the liquid density equations of Scott and Brickwedde,[17] and the virial coefficient data of Schaefer,[18] we obtain a value of 4.49 calories/mole for $\Delta H_m - \Delta H_p$. Correcting to the boiling point of n-H_2 and adding to our value for the heat of vaporization of p-H_2, we obtain 219.3 cal./mole for the heat of vaporization of n-H_2.

(6) **Energy and Density Adoptions.**—The energy unit in which our data are expressed is the "thermochemical calorie,"[19] defined by the relationship: 1 calorie = 4.1833 international joules.

In estimating the amounts of gas present in the calorimeter during heat capacity and vaporization runs, we employed the density data of Scott and Brickwedde[17] for liquid para hydrogen and the second virial coefficients given by Schaefer[18] and by van Agt[20] for gaseous hydrogen.

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(17) R. B. Scott and F. A. Brickwedde, *J. Chem. Phys.*, **5**, 736 (1934).

(18) Klaus Schaefer, *Z. physik. Chem.*, **B36**, 85 (1937).

(19) First report of the Permanent Commission on Thermochemistry of the International Union of Chemistry, 1934.

(20) F. P. G. A. J. van Agt and H. Kammerlingh Onnes, *Leiden Comm.*, 176b (1925).

(7) **Accuracy.**—Our accuracy on heat capacity measurements in the solid range was limited by our desire to obtain several points over the region 12.5 to 13.8°, and therefore we were required to use small increments of temperature, ΔT. Since dR/dT for our resistance thermometer is only 0.137 ohm per degree at 13.0°K., and resistance values were real to within 0.001 ohm it follows that the evaluation of ΔT imposes an inaccuracy of approximately 5% for a 0.20° run at 13.0°K. In general, it may be said that the data recorded for the solid heat capacities entered in Table I may be in error by amounts ranging from 2 to 5%.

Because we employed larger ΔT's in the liquid range and because dR/dT was considerably larger (0.45 ohm per degree at the boiling point), less inaccuracy (0.2 to 0.5%) was introduced into the liquid heat capacities due to measurements of temperature. With allowance made for smaller uncertainties introduced by such factors as the heat leak correction we estimate that the liquid heat capacities entered in Table I should be accurate to within 0.4 to 0.5 of 1%. Actually a smooth curve fits these ten points for liquid hydrogen to within 0.3 of 1%.

The heat added in the measurements of heats of fusion and of vaporization can be measured with an inaccuracy no higher than about 0.07 of 1%.[9b] The principal error in the heat of fusion measurements enters through the evaluation of the $C_p dT$ integral corrections since the heat capacity of solid hydrogen is known to no better than about 2 or 3% and the liquid heat capacity to about 0.5%, and since the $C_p dT$ correction amounts to about 10% of the total heat, we estimate that this factor alone introduces about 0.2 of 1% into the heats of fusion. The over-all accuracy, with additional factors such as the heat leak correction (evaluated graphically) taken into account, should give values for the heat of fusion accurate to within 0.5 of 1%.

Since the $C_p dT$ correction is practically zero for the vaporization runs the principal sources of inaccuracy must be in the heat leak correction (amounting to only 1 or 2% of the total heat) and in small errors incident to the measurement of gas removed from the calorimeter. We estimate an over-all uncertainty of no more than about 0.2 of 1% in these data.

(8) **Comparisons with Other Authors.**—Comparison of our heat capacity data with those of Clusius and Hiller[6] is shown in Fig. 2. The agreement is good. The curve drawn through the points in the solid range fits the Debye equation with $\theta = 91$. We have therefore used the Debye equation to obtain the entropy of solid at the melting point.

TABLE IV

THE HEAT OF FUSION OF HYDROGEN

Year	Investigators	Heat of fusion, cal./mole	Material
1917	Keesom and Onnes[4]	26.6 32.8	n-H_2
1923	Simon and Lange[5]	28.0 ± 0.15	n-H_2
1929	Clusius and Hiller[8]	28.03 ± 0.4	94% p-H_2
1949	This Research	28.08 ± 0.15	99.8% p-H_2

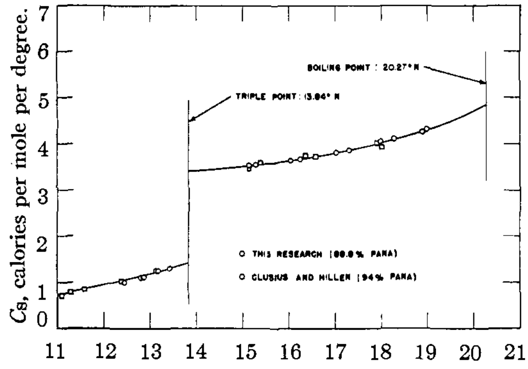

Fig. 2.—Heat capacity of saturated solid and liquid para hydrogen.

Comparison of our value for the heat of fusion with values obtained by other observers is made in Table IV.

Our value for the heat of vaporization is compared with other values in the literature in Table V.

TABLE V

THE HEAT OF VAPORIZATION OF HYDROGEN

Year	Investigator	H at b. p., cal./mole	Material
1905	Dewar[21]	246	n-H_2
1911	Keesom[22]	218	n-H_2
1923	Simon and Lange[5]	215.9	n-H_2
1949	This research	214.8 ± 0.4	p-H_2
1949	This research	219.3	n-H_2[23]

Entropy of Hydrogen.—The calculation of the statistical entropy of normal hydrogen gas was first correctly carried out by Giauque and Johnston[6a,24] who found good agreement with the experimental value, from the Third Law of Thermodynamics, when proper account was taken of the entropy of mixing due to the frozen in distribution between ortho and para forms in solid hydrogen.

In view of the uncertain ortho–para distribution while heat capacity measurements were made on the "normal" mixture due to some conversion in the solid and liquid states, possibly catalyzed by traces of air or other impurity, it is evident that comparison of the calorimetric and statistical entropies for 99.8% pure para hydrogen at its own

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[21] James Dewar, *Proc. Roy. Soc.* (*London*), **A76**, 325 (1905).

[22] P. Keesom, *Leiden Comm.*, 137e (1911).

[23] Computed from our measured value for p-H_2 by use of vapor pressure and density data, as discussed in an earlier section. The considerably lower value obtained by Simon and Lange may indicate that their hydrogen had undergone considerable conversion to the para form before heat of vaporization runs were made.

[24] *Cf.* also W. F. Giauque and H. L. Johnston, *Phys. Rev.*, **36**, 1592 (1930).

b. p. should provide an even closer Third Law check.

The equilibrium composition of hydrogen at 20.38° (the boiling point of normal hydrogen), produced by equilibration over charcoal, corresponds to 99.79% para[25] with the para molecules in the rotational quantum state ($J = 0$) with statistical weight of unity and the ortho molecules in the ($J = 1$) rotational state with a statistical weight of 9 (a weight factor of 3 from a rotational angular momentum of 1 and a second weight factor of 3 from a total nuclear spin of 1). The "frozen in" entropy of this mixture is given by the expression

$$S(\text{mixing}) = R(0.9979 \ln 0.9979 + 0.0021 \ln 0.000233) = 0.039$$

The experimental entropy of para hydrogen, with addition of the small contribution from frozen in entropy is summarized in Table VI.

TABLE VI

EXPERIMENTAL ENTROPY OF PARA HYDROGEN

Solid 0–13.84° ($\theta = 91$)	0.499 ± 0.05
Fusion at 13.845° (28.08/13.845)	2.028 ± 0.01
Liquid 13.84–20.261°	1.468 ± 0.01
Vaporization at 20.261° (214.8/20.261)	10.602 ± 0.02
Total calorimetric entropy	14.597 ± 0.09
Correction to the ideal gaseous state	0.195 ± 0.01
Frozen in entropy of mixing	0.039 ± 0.00
Total entropy of ideal gas at 20.26° K. and 1 atmosphere	14.83 ± 0.1 e. u.

The correction to the ideal gaseous state was made by use of the virial relationship

$$S(\text{ideal}) - S(\text{real}) = (\mathrm{d}B/\mathrm{d}T)P \qquad (5)$$

using values of the virial coefficient recently determined in this Laboratory,[26] ($\mathrm{d}B/\mathrm{d}T$) for hydrogen at its boiling point is 8.0 cc. per mole per degree.

The statistical computation of the entropy of hydrogen, as an ideal gas, at 1 atmosphere and 20.26°K. follows the equation

$$S^0 = 1.5\,R \ln M + 2.5\,R \ln T - 2.315 + S_{\text{int}} \qquad (6)$$

in which the first three terms represent the contribution from translational degrees of freedom and the last term, which represents the contribution from internal degrees of freedom, is identical with the entropy of the frozen in entropy of mixing term in the present instance. With R set equal to 1.9872, M equal to 2.016, T equal to 20.261, and S_{int} assigned its previous value, Equation 6 yields an S^0 of 14.76 e. u.

The calorimetric value of 14.83 e. u. is in excellent agreement with the statistical value and confirms our estimate of the reliability of the calorimetric data.

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Summary

We have measured heat capacities and latent heats of solid and liquid para hydrogen over the temperature range 11.5 to 20.3°K.

The pressure and temperature at the triple point are 52.76 mm. and 13.84°K., respectively.

The heats of fusion and of vaporization are, respectively, 28.08 ± 0.15 and 214.8 ± 0.4 cal. per mole.

The entropy of the gas at the normal boiling point, computed from the calorimetric data, with the aid of the Third Law of Thermodynamics, and corrected for both gas imperfection and "frozen in entropy," due to the presence of 0.2 of 1% of ortho hydrogen, is 14.83 ± 0.1 entropy units. This compares quite accurately with the statistically calculated value of 14.76 e. u.

The heat of vaporization of normal hydrogen at its boiling point (20.38°K.) is 219.3 cal. per mole, based on the data of this investigation for para hydrogen and on the vapor pressure data and density data for normal and for para hydrogen. Possibly the somewhat lower value (1.5%) obtained by Simon and Lange was considerably influenced by conversion of their normal hydrogen to the para enriched form prior to their vaporization runs.

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[25] W. F. Giauque, THIS JOURNAL, **52**, 4816 (1930).

[26] White, Johnston and Friedman, unpublished data.