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THE ANOMALOUS HEAT CAPACITY OF SOLID DEUTERIUM (33.1-87.2% PARA)

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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The Ohio State University
1963

Approved by

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Acknowledgments

I would like to thank James Eberhart for the para-ortho analysis and Charles Knobler for assistance in some of the measurements. Above all, I would like to thank my wife Barbara for enduring with me through my graduate tenure.
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Introduction

On the basis of quantum theory, it was postulated in 1927 that in molecular hydrogen two molecular species are present, (1) one with parallel nuclear spins of the two atoms, the other with opposing nuclear spins. The slow nuclear spin reversal does not normally permit the attainment of thermodynamic equilibrium, therefore, it is necessary to assume that hydrogen gas consists of a mixture of nuclear spin isomers to explain the experimental data. Additional confirmation came in 1929 when Bonhoeffer and Harteeck (2) succeeded in catalyzing the reversal of the spins. Following this experiment many investigators studied the properties of mixtures of the two as a function of composition and temperature, and after the discovery of the heavy isotope of hydrogen in 1931, the studies were extended to include the nuclear spin isomers of deuterium as well.

Since the quantum statistics which apply to hydrogen and deuterium are different, a brief review will avoid any subsequent confusion in the comparison of the experimental results for the two isotopes. The total wave function for a molecule is given, to a good approximation, as the product of individual wave functions, which are a function of the coordinates and spins. This separation of variables gives a set of wave functions associated with the translational, vibrational, electronic, rotational, and nuclear motions. The detailed form of the individual wave functions is of no importance to this discussion, but their symmetry properties with respect to exchange of a pair of identical nuclei are
important. For homonuclear hydrogens the sign of the translational, vibrational, and electronic wave functions are not affected by nuclear exchange. On nuclear exchange, the rotational wave function, is unchanged in sign or changes sign depending on whether the rotational quantum number $J$ is even or odd. That is, the rotational states are symmetric for even $J$ and antisymmetric for odd $J$.

The proton nuclear spin is $\frac{1}{2}$ (in units of $\hbar$), and the total nuclear spin $I$ for the hydrogen molecule can be 1 or 0, the value 1 corresponding to the symmetric nuclear spin state and 0 to the antisymmetric state. The deuterium nuclear spin is 1, and the total nuclear spin $I$ for the molecule can be 2, 1, or 0; the values 2 and 0 correspond to the symmetric spin state and 1 to the antisymmetric state. The Pauli exclusion principle requires that the total wave function be antisymmetric for nuclei with an odd number of elementary particles and symmetric for nuclei with an even number of particles. Therefore, hydrogen will have a totally antisymmetric wave function and deuterium a totally symmetric wave function. Accordingly, the odd rotational states of hydrogen combine with $I=1$, and the even rotational states with $I=0$. For deuterium the odd rotational combine with $I=1$, and the even rotational states with $I=2$, or 0.

The multiplicity of any energy level is given by the product $(2J+1)(2I+1)$, where $J$ is the rotational quantum number, and $I$ represents the total nuclear spin associated with that particular rotational level. The total statistical weight for the $J=0$ state of hydrogen is one. For the $J=1$ state, the total statistical weight is nine. In deuterium the $J=0$ state has a total statistical weight of six, five for $I=2$ and one for $I=0$; the $J=1$ state has a total weight of nine. The states of higher spin statistical weight are called ortho, while the less populous states are
called para. The J=1 state for hydrogen is ortho, while for deuterium this state is para. Normal hydrogen and normal deuterium are defined as the limiting equilibrium mixtures of ortho and para states at very high temperatures. The ortho-para ratio for normal hydrogen is 3:1, and for normal deuterium the ratio is 2:1, and is effectively attained for both at room temperature.

A comparison of the third law entropy of gaseous normal hydrogen at its boiling point, as determined from calorimetric data above 120°K, with that calculated statistically from spectroscopic data was first made by Giauque. (3) The difference was found to be nearly equal to the 'frozen in' entropy of mixing of the ortho and para states (including the rotational degeneracy of the J=1 ortho state). (4) Following the discovery of deuterium, Clusius and Bartholome (5) measured the heat capacity of normal deuterium. They found a discrepancy between the calorimetric and spectroscopic entropies, which again was approximately equal to the 'frozen in' entropy of mixing of the ortho and para states (including the rotational degeneracy of the J=1 para state). The experiments of Johnston et al. with 20°K equilibrium hydrogen (6) and deuterium (7) (nearly pure para and ortho, respectively) provided additional verification of the origin of the discrepancy. Both cases showed good agreement with the statistical calculations when proper account was taken of the 'frozen in' entropies of mixing of the ortho and para states (for pure para hydrogen in the J=0 state there is only one nuclear spin state and no mixing entropy, but even for pure ortho deuterium in the J=0 state there remains the entropy of mixing of the six nuclear spin states).

The experiments of Mendelssohn, Ruhemann, and Simon (8) were the first to show that the entropy discrepancies mentioned above are not en-
tirely due to entropy which remains 'frozen in' at absolute zero. They showed that the heat capacities of several ortho-para mixtures of hydrogen were anomalous below 110°K, and that the anomalies persisted to temperatures as low as 2.50°K. The increase in the anomalous heat capacity with increasing ortho concentration to a 75% mixture showed that the anomaly was not connected with phase separation but attributable to molecules in the J=1 state. The authors ascribed the anomaly to a change in the distribution of the ortho molecules among the various substates of the split J=1 multiplet. The work of Gonzalez, White and Johnston (9) showed that a similar anomaly in the heat capacity of solid deuterium was not associated with the removal of the nuclear spin degeneracy, but with the lifting of the threefold rotational degeneracy of the J=1 state by the crystalline field.

The nuclear magnetic resonance for what is assumed to be normal solid hydrogen (10, 11) confirmed that the removal of the rotational degeneracy was indeed an explanation for the anomalous heat capacity. In addition a transition was observed to occur at about 1.50°K. Hill and Ricketson (12) confirmed the presence of this transition from temperature-time measurements at very low temperatures as the sample warmed due to the heat liberated by the ortho to para conversion of the hydrogen. By taking the derivative of this heating curve, they obtained an estimate of the heat capacity. The transition temperature of approximately normal hydrogen was 1.60°K which was consistent with the nuclear magnetic resonance results. At concentrations greater than 60%, (13) a sharp maximum in the heat capacity curve, classified as lambda-type by the authors, was found to have an approximately linear dependence on the ortho concentration in the temperature range 1.1 to 1.60°K. For lower ortho concentrations the
curve was found to have a flat maximum at about 10 K. With the assumption of a constant heating rate, the anomalous entropy of the solid was calculated to be a few tenths of an entropy unit less than \( R \ln 3 \) per mole of ortho hydrogen. This is the expected value for the entropy of removal of a threefold rotational degeneracy.

In solid hydrogen the rapid temperature rise caused by the ortho to para conversion prevents the precise measurement of heat capacities and a detailed examination of the transition. Since the rate of heating due to conversion is approximately twenty times slower in deuterium than in hydrogen, it is much more desirable to make heat capacity measurements of deuterium, provided it is possible to prepare samples of deuterium of high para content \((J=1)\). Cunningham, Chapin, and Johnston (14) demonstrated that the \( J=1 \) concentration could be increased above the value in the heretofore limiting normal mixtures. The purpose of this research was to prepare samples of deuterium of high para content and to examine in detail the thermodynamic properties of these samples in the condensed state.
Apparatus

I. Para Deuterium Separator

The separation apparatus is identical to that previously described (1h) except for a modification to reduce heat leak. This modification was the replacement with monel of the copper pumping tubes that also served as supports for the chambers. Briefly, the apparatus consisted of three adsorption units of the type shown in Figure 1. The inside chamber of each unit was filled with about 300 grams of r-alumina free of paramagnetic material.

II. Calorimeter and Cryostat

The essential details of the calorimeter and attendant equipment are shown in Figure 2. The calorimeter is a cylindrical can (A), 1.25 in. long and 0.75 in. in diameter, with a re-entrant well, 0.25 in. in diameter and 0.938 in. deep, both having a wall thickness of 0.031 in. Copper of the oxygen free, high conductivity type was used throughout except for the outer can and the tubing. After machining, the calorimeter was washed with acid to remove all traces of oxidation, and stored in a desiccator until gold-plated. A carefully machined gold-plated copper cone at the top of the calorimeter provides thermal contact with the shield (b) and heat station (E) through the gold-plated copper shaft (D) when it is desired to cool the calorimeter. The gas is condensed through an inconel tube (H), 0.035 in. o.d. and 0.022 in. i.d., which is soldered to the top of the calorimeter.

The re-entrant well contains a carbon resistance thermometer (F),
Figure 1
Adsorption column for para-ortho separations
Figure 2

The calorimeter with radiation shield and vacuum jacket
which is held securely in place by GE 7031 low temperature adhesive. Not only does the adhesive give mechanical support, but it provides thermal contact with the calorimeter and electrical insulation. The thermometer has a room temperature resistance of thirty-six ohms and the resistance increases to approximately 120 ohms at 1.2°K. The heater (G) is wound bifilarly with 100 ohms of B and S No. 34 silk insulated manganin wire, which is cemented in place with GE 7031 adhesive. The adhesive is allowed to air dry, which insures a better coating. Only two heater leads and two thermometer leads were provided at the calorimeter, because the current-potential junctions were made midway between the calorimeter and the radiation shield. This detail is not shown in Figure 2.

The radiation shield is a cylindrical gold-plated copper can (B), 2.75 in. long and 1.277 in. in diameter with a thickness of 0.062 in., with a thermometer well, 0.188 in. in diameter and 0.875 in. deep, which is soldered to the bottom of the shield. The top lid is silver soldered to the shaft (D). This unit is then soft soldered in three spots to the main shield. The capillary (H) passes through this lid, but is soldered to it by means of a flexible copper wire to provide thermal contact. The spot soldering and three holes near the outer edge of the bottom of the shield enable this can to be evacuated. The carbon resistance thermometer (F) for the bottom well has nearly the same characteristics as the thermometer for the calorimeter. The heater (G) is wound bifilarly with ten ohms of B and S No. 30 silk insulated manganin wire, which is cemented in place with GE 7031 as is the thermometer. This shield heater is in series with a ten ohm heater wound with B and S No. 34 silk insulated manganin wire on the capillary (H) from the top of the shield to a point above the heat station (E). The leads from the calorimeter emerge through
holes at the bottom of the shield where they are cemented for thermal contact with GE 7031. These leads merge with the leads from the shield thermometer to form a bundle, which is wound spirally around the shield and cemented in place with GE 7031.

The gold-plated copper heat station (E) is cylindrically curved in the upper portion, which is soldered to the monel pumping tube (J), and the lower portion is a solid cylinder. This 'dog-leg' construction utilizes the reflective gold-plated surface of the heat station as a radiation shield to reduce the heat leak down the pumping tube. The electrical leads (K) of No. 31 manganin pass through the heat station as does the capillary. The leads are thermally contacted to the station with GE 7031. The capillary is soldered to the station by means of a flexible copper wire that allows motion through the station without loss of thermal contact. The heat station serves as the means to transfer heat to the cooling bath. Everything contacted to the station will be brought to bath temperature. The conical well in the heat station serves as the receptacle for the conical tip of the shaft (D). These conical surfaces along with the two conical surfaces at the calorimeter were polished to a high luster with jeweler's rouge.

The calorimeter and radiation shield are surrounded by a cylindrical monel can (C), 5.5 in. long and 2 in. in diameter with a thickness of 0.031 in., which serves as the vacuum jacket. This can is soldered to a flange, which serves as a lid, of the monel pumping tube (J). The shield is supported from the can by three loops of nylon radio dial cord (I), 0.028 in. in diameter, which pass through eyelets at the bottom of the monel can and at the top of the shield. The main support for the calorimeter is the capillary tube soldered to it. Additional support
is provided by a nylon cord, identical with the above, which is knotted within the cone of the calorimeter. This nylon cord passes through the shaft (D) and the heat station (E). It is in thermal contact with the heat station by means of a flexible copper wire to which it is attached with GE 7031. The wire is soldered to the heat station. The nylon cord is tied to a metal stopcock (Hoke valve No. 318), which serves as a windlass, at the top of the pumping tube. This windlass is used to bring the cones in thermal contact with the cooling bath.

The monel pumping tube (j), 0.75 in. in diameter and 0.031 in. wall, also serves as a conduit for the electrical leads and capillary. The top of the tube is soldered to a flanged cylindrical monel head which is stationary and has connections leading to the Kinney vacuum pump and the manometer system. The capillary exits through a soldered joint. The leads emerge through a perforated lucite disk which is sealed vacuum tight with Apiezon W wax. (15) The pumping tube connects to its vacuum system by means of a Kovar-pyrex ball joint. A pyrex dewar vessel, on m. long and 5.5 cm. in diameter, slips inside the monel head where it is held in place by a rubber sleeve. This sleeve is given additional support with waterproof tape coated with an Araldite adhesive. The vacuum jacket of this dewar vessel is connected to the vacuum system through a stopcock. Another larger, permanently evacuated dewar vessel surrounds the cryostat. The inner dewar is used for liquid hydrogen or liquid helium. The outer dewar contains liquid nitrogen to reduce the evaporation of the inner dewar's liquid. Both dewars are silvered and have parallel slits to permit viewing.

The pressure of the liquid hydrogen or liquid helium is lowered by means of the Kinney pump. The pressure is monitored on either a mercury
or oil manometer depending on the pressure range. The pressure can be maintained by means of a mechanical manostat (16) which is located in an alternate pumping line. The mercury manometer is made of large bore glass tubing, 19 mm bore. The oil is DC 703 silicone oil. Both manometers are side lighted and read with a Wild cathetometer. A heater is located at the bottom of the helium dewar to return the pressure to atmospheric or to prevent stratification.

III. Gas Burette System

The gas burette consists of three glass spheres of accurately known volume, approximately 5 liters, 2.5 liters and 0.5 liters, immersed in a thermostatted bath and connected to a wide bore constant volume manometer. Another flask of ten liters is immersed in the bath to act as a mercury reservoir. Gas is drawn into the calibrated spheres by lowering the mercury level in the spheres, and condensed into the calorimeter by raising the mercury level. Capillary tubing connects the spheres with the mercury manometer. The manometer is enclosed in a case. The measuring system is connected to the calorimeter by fifty ft. of 1/8 in. copper tubing.

IV. Electrical Circuitry

The thermometer circuit is a simple DC circuit. It consists of seven Edison cells in series with the calorimeter thermometer, the shield thermometer, a 100 ohm standard resistor, and a ballast resistor. A double throw switch provides a choice between a 250,000 or 350,000 ohm ballast resistor. The heater circuit consists of fifteen Nicad cells, which can be used in multiples of five, in series with a ten ohm standard resistor, a multi-range milliammeter, a stepwise resistor (0-15,000 ohms), another step-wise resistor (0-90,000 ohms), and either the heater
or an exerciser circuit. The exerciser circuit consists of two resistances in series which can be adjusted to the resistance of the heater. This arrangement prevents surges of current when the heater is switched on from the exerciser circuit. The shield heater circuit uses an AC to DC converter in series with the heaters and a 150 ohm variable resistor. The heater current and voltage were measured with a type B Rubicon potentiometer. The thermometer current and voltage were measured with a 1000 microvolt range double White potentiometer. A box type Rubicon 3402H galvanometer was used with the Rubicon potentiometer. With the White potentiometer, an illuminated meter scale was read in the mirror of a Leeds and Northrup high sensitivity galvanometer, with a telescope over a light path of about eight meters.

V. Timing

Times were measured with a Standard Electric model S-6 precision timer. Times were estimated to 0.0002 minute and read directly to 0.001 minute. The timer uses a high speed 60 cycle synchronous motor with an electro-mechanical compensated clutch. The clutch is accurate to ±0.0002 minute per operation. The timer is powered by a type 2005A frequency standard from American Time Products. This frequency standard furnishes a precise frequency of 60 cycles at ten watts produced by an electrically maintained tuning fork with nearly zero temperature coefficient. The frequency is accurate to one part per million. The timer was activated by the same switch that activated the heater.
Experimental Procedure

I. Separation of Para Deuterium

The separation procedure was essentially the one described previously (14) with modifications prescribed by the differences between hydrogen and deuterium. Deuterium from the cylinder was used without further purification. Mass spectrographic analyses indicated an average impurity of 0.6% HD and 0.1% N₂ in the cylinder. As an added precaution against oxygen contamination of the alumina adsorbent, the gas was passed through a 'deoxo' purifier and liquid nitrogen cold trap and through a duplication of this combination. Before each run the alumina was baked at 120°C until the pressure dropped to less than a micron of Hg. After passing through the purification train, the normal deuterium was passed continuously and simultaneously into the center tube and out the annular space of all three adsorption units of the type shown in Figure 1. These units were immersed in a bath of liquid hydrogen with helium exchange gas in their outer chambers. Each unit was independently connected to a mercury bubbler set for a pressure of 35 mm. This pressure is greater than the monolayer pressure of 17 mm. for deuterium, (17) but it was impracticable to maintain that pressure because of excessive splashing in the bubblers. Since preliminary experiments indicated no dependence of separation on pressure in this low pressure range, this expediency was of little consequence.

After equilibrium was reached, the first and second units were
evacuated for thirty seconds. At the same time the helium exchange gas was pumped from the outer chamber of unit one. The first unit was then heated and the desorbed gas from this unit was passed through the second unit. After the bubbling stopped in the second bubbler, the above procedure was repeated for the second and third units. When bubbling stopped in the third bubbler, the third unit was evacuated for thirty seconds and then heated as the exchange gas was removed. The desorbed gas was collected in sequence in three 5 liter bulbs. Samples were taken at predetermined pressures. The last fraction of gas was pumped from the surface of the alumina by means of an evacuated 5 liter bulb. The ortho-para content was determined by the macro-thermal-conductivity method.²(18)

II. Calorimetric Samples

The gas used for the normal deuterium measurements came from the same cylinders used in the separation procedure. After passing through the previously described 'deoxo'-cold trap system, the gas was passed over platinized-asbestos at 800°C to insure the normal composition. For the first normal sample the HD and \( \text{N}_2 \) content were approximately the same as that of the cylinder. For the second sample there was 4.78% HD. This HD was attributed to a reaction between residual hydrogen on the platinized-asbestos and the deuterium from the gas passed for the first sample. The HD was entrained in the gas passed for the second sample. Since the separation procedure also separates the hydrogen isotopes, the HD in deuterium after a three stage separation was reduced to as low as 0.03%, which is in agreement with theory. (19) The \( \text{N}_2 \) was removed by solidification at the temperature of the liquid hydrogen bath. After measurements

²I am indebted to Mr. James Eberhart for these analyses and for the proof of the linearity of the calibration curve.
on the sample of highest para content were completed, it was mixed with either normal deuterium or nominal ortho deuterium to make a sample of lower para content. This procedure added an impurity of HD to these samples. These mixtures were made in the gas burette system described previously. The gas mixture was allowed to equilibrate for about twelve hours in the thermostatted bath.

To correct for this HD impurity, it was decided to determine the heat capacity of HD. A sample was prepared for me by Dr. Donald Freeman of the Linde Company. Mass spectrographic analysis indicated 1.00% H₂ and 0.26% D₂.

All samples were introduced into the calorimeter in the same manner. Gas was pumped into the gas burette by lowering the mercury level and pumped out by raising the mercury level in the calibrated spheres. The observed pressure was corrected for capillary depression, gravity, and the thermal expansion of the scale and of the mercury in the manometer. The Geodesy Department determined the gravity to be 980.095 cm/sec² at the laboratory. The temperatures of the gas were taken to be the temperature of the thermostatted bath, the temperature of the manometer case, and the ambient temperature of the calibrated capillary tubing that connects the gas burette with the manometer. The gas pumped from the gas burette was condensed in the calorimeter at the temperature of liquid hydrogen by means of hydrogen exchange gas in the vacuum space of the monel can. When the gas pressure returned to the vapor pressure at the boiling point of hydrogen, the stopcock was closed between the calorimeter and the gas burette. The pressure and temperatures of this residual gas were measured as above. The moles of gas were computed from the virial equation using the values of the second virial coefficients com-
The number of moles of gas in the calorimeter is the difference between the moles of gas initially in the gas burette and the residual gas.

The temperature of the calorimeter was lowered to 190K. The heater at the heat station and the heaters around the radiation shield and condensing capillary were turned on for about ten to fifteen minutes until there was an indication that the liquid in the capillary had entered the calorimeter. Cooling was then resumed until the triple point of the gas was reached. At this point the system was isolated by the removal of the hydrogen exchange gas. A rough determination of the triple triple point was made. Cooling was then continued mechanically through the heat station by means of the cooling shaft. This method made possible continuous cooling while the exchange gas was being pumped out of the vacuum space. The temperature was maintained at 150K until the pressure in the vacuum chamber was reduced to 10^-6 mm of Hg. After 90K was reached, the calorimeter was thermally isolated and the liquid hydrogen boiled out of the dewar by putting hydrogen exchange gas in the dewar vacuum jacket. The additional hydrogen gas evolved from the walls of the monel can was pumped off during the boiling stage. The dewar was again evacuated, and then filled with liquid helium. Since the heat station had to be cooled first, the calorimeter was not contacted immediately. When this procedure was followed, isolation was so good during the change of liquid hydrogen and helium that the temperature did not rise more than 10K.

The calorimeter was cooled quite rapidly to 40K by contacting. The mechanical cooling to this temperature was as effective as that found by the original users. (15) But in the region below this temperature, achieved by pumping on the liquid helium bath with the Kinney pump, the cooling rate...
was much slower because of the heat of conversion and the unusually high heat capacities of the deuterium samples. The empty calorimeter and the HD sample cooled rapidly to 1.20K. The sample was removed from the calorimeter by lowering the level of the helium bath below the heat station and turning on all the heaters. On some occasions the gas was returned to the gas burette without difficulty. On other occasions extensive pre-heating of the capillary was required to remove the solid plug lodged there. This plug invariably was formed in the samples with the largest non-hydrogenic impurities. Any non-hydrogenic impurity was subtracted from the quantity of gas in the calorimeter whether a plug was formed or not, since it most likely condensed on the capillary walls. The significance of the deuterium in the capillary, whether gas or solid, will be discussed in the section on errors. Several samples were taken before condensation and after removal for mass spectrographic analyses and determination of the ortho-para content.

III. Calorimetry

The measurement of heat capacity is relatively simple in principle. One measures an initial temperature, supplies a known amount of energy to the sample, measures a final temperature, and the ratio of energy to temperature difference is the heat capacity at the mean temperature. The energy to the calorimeter was determined by measuring the potential drop across the 100 ohm heater at the midpoint of the heating interval, measuring the current at 0.21 and 0.79 of the heating interval, since the average of these values will give $I_{ave}$ exactly when any quadratic equation represents the current, (21) and measuring the time on the electric timer. The product of voltage, average current, and time gives the energy in joules. Following the National Bureau of Standards recommendation, the calorie is taken to be 4.1833 int. joules.
Thermometry is the most significant part of any type of calorimetry. Two types of thermometers were used in this research. To determine temperatures precisely (as distinguished from accurately) and conveniently, a secondary thermometer of the carbon resistance type was used. This thermometer was calibrated against the 1958 He$^4$ vapor pressure scale (22) and the 20.40K equilibrium hydrogen vapor pressure scale proposed by Durieux. (23) These vapor pressure scales of temperatures are empirical scales that closely approximate the thermodynamic temperature scale. To obtain consistent results from vapor pressure measurements required close attention to detail. Space considerations dictated that the vapor pressure of the liquid in the dewar be measured, though a separate vapor pressure bulb would have been ideal. The pressure was measured with the manometric system described in the section on the cryostat. The same manometric corrections were applied as mentioned in the preceding section. For the low pressure measurements, sensitivity was gained by the use of the oil manometer which was calibrated against the mercury manometer for each series.

In this apparatus the measurement of the vapor pressure and the calibration of the carbon thermometer were interdependent. The level of the liquid in the dewar was lowered to a point 10 cm or less above the top of the monel can after the calorimeter was contacted to the heat station and exchange gas was added to the vacuum space in the monel can. The procedure was to start at atmospheric pressure and to work to lower pressures. The pressure was controlled, as mentioned, by a manostat. The approach to equilibrium was monitored by reading the voltage of the carbon thermometer. When the reading on the galvanometer scale was
oscillatory, equilibrium had been reached. The height of the liquid level above the thermometer was determined in order to correct for the hydrostatic pressure head. The level was not allowed to drop more than 2 cm below the top of the monel can. Since in some instances there was a slight drift, the resistances and pressures were read as a function of time.

Starting from the relationship between resistance and temperature for simple impurity semiconductors, Clement (24) developed a semiempirical equation relating the resistance $R$ and temperature $T$,

$$ \left[ \frac{\log R}{T} \right]^{\frac{1}{2}} = a + b \log R $$

where $(a)$ and $(b)$ are adjustable constants. He suggested that the slight failure in fitting the experimental data to the equation could be remedied by allowing $(a)$ to be actually variable, a smoothed curve of $(a)$ vs log $R$ being constructed from actual calibration data. Since this thermometer did not have the extreme sensitivity of Clement's thermometers, it was more expedient to plot $(\log R / T)^{\frac{1}{2}}$ vs. log $R$ on a large scale and smoothly join the helium region $1.2-1.2^0K$ and the hydrogen region $10-20^0K$. This was quite easy since the curve was nearly linear. Since warming to room temperature necessitated a recalibration of the thermometer, a family of parallel curves, slightly displaced, resulted. A coincidence indicating the reliability of the thermometer occurred when the first calibration curve coincided with the last calibration curve plotted three years later.

There were additional observations which merit reporting because they validated the experimental procedure in the thermometry or else confirmed the observations of other investigators. Since liquid helium below
its lambda point has a high thermal conductivity, hydrostatic head corrections were not made. If the corrections were not applied above the lambda point, a discontinuity in the calibration curve resulted. If the hydrostatic head correction exceeded $5 \text{m}^\circ K (\text{m}^\circ K = \text{milli-degree})$, the calibration point fell off the curve in a manner indicating an over correction. Similar results (23) were obtained by Durieux in comparing the vapor pressure thermometer with the bath vapor pressure in a glass dewar with the deviations being more pronounced just above the lambda point. After an exposure of the carbon resistance thermometer to the atmosphere, the calibration curve had a large displacement from the other curves. If the thermometer was kept in a helium atmosphere or under vacuum, the various calibration curves approached a limiting curve with the displacement between the curves gradually diminishing. The temperatures at various depths in the bath were measured as a function of time after the surface had been rapidly brought to atmospheric pressure from a pressure of 60 mm of Hg. Supercooling persisted for several hours with the time for equilibration longer in hydrogen than in helium.

To determine heat capacities with the same precision as the temperature measurements, it was necessary to determine the heat input precisely. The electrically measured quantities discussed at the beginning of this section were of sufficient precision. The next consideration was the heat leak. The use of a mechanical cooling device eliminated the heat leak problem from conduction by residual exchange gas or desorbed gas and the heat transfer problems associated with desorption from the calorimeter. The only other sources of heat leaks to the calorimeter are from radiation and by conduction along the supports and leads. These leaks can be eliminated only if the calorimeter can be completely surrounded by
a shield maintained at exactly the calorimeter temperature, at all times. This ideal state was approximated by insuring thermal contact of all leads and supports with the bath and allowing the bath temperature to follow the calorimeter temperature to minimize the temperature gradient. Above the helium boiling point this procedure could not be followed, but in this temperature range the heat leak was to the surroundings and a very small quantity.

The heat leak was not measured directly, but the heat capacity measurements were corrected for heat leak from measurements of the temperature during the fore and after periods of heat input. These temperature drifts were recorded by noting potentiometer readings and galvanometer deflections every half or quarter minute until the drift rate was constant. Excessively long after drift periods were avoided by limiting the temperature rise during the heat input to a tenth of the mean temperature. For the deuterium experiments the method of drifts also corrected for the para to ortho heat of conversion which was about fourteen times larger than the heat leak. Though the heat leak to the calorimeter became negligible at the boiling point of helium, the heat of conversion continued to supply heat to the calorimeter.

The procedure for measuring the heats of transition and fusion was in principle the same as for a heat capacity measurement. The actual heat leak, was determined from the drift curves, was then either subtracted or added, depending on its direction, to the measure heat input. During the heat of transition determinations, the thermometer voltage was read every quarter minute. A sudden increase in voltage marked the end of the transition. The heating was continued slightly beyond this point to insure that the transition was completed. The temperature where the voltage in-
creased sharply was the transition temperature after correcting for the lag in sample temperature due to superheating.

Since the heating interval started below and continued beyond the triple point in the heat of fusion measurements, the integrated heat capacities of the calorimeter, solid deuterium, and liquid deuterium over this temperature interval were subtracted from the total heat input. The triple point of a given sample was determined by extrapolating a plot of the fraction melted vs. the equilibrium temperature for the fraction to a reciprocal of zero value.

IV. Para to Ortho Conversion Rate

This experiment was conducted as a part of the heat capacity experiment. The conversion rate at a given temperature was calculated from the heating rate by using the known value of the energy between the \( J=1 \) and \( J=0 \) state and the total heat capacity at that temperature. The heating rate was corrected for the heat leak and experiments were restricted to below 50K where the heat leak was small compared to the heat of conversion.
Experimental Results

I. Separations

The results of a single stage separation of para from ortho deuterium are presented graphically in Figure 3. The solid curve represents a rate of stripping of the surface two times faster than the rate for the dashed curve. The maximum para concentration was 61.2% for the solid curve and 54.2% for the dashed curve. A maximum para concentration of 79% resulted from a two stage separation and 83% resulted from a three stage separation. The highest enrichment attained was 88% during an attempt at a six stage separation that failed.

II. Calorimetric Results

The heat capacity results are recorded in Tables I to XII as the saturation heat capacities per mole of deuterium. The saturation heat capacities per mole of HD are recorded in Table XIII. These tables also indicate the composition of the sample as to para-ortho content and hydrogenic impurities. In the calculation of the molar heat capacities the contributions of these impurities have been subtracted. The heat capacities are plotted in Figures 4 to 6.

The transition temperatures are listed in Table XIV and presented in Figure 7 together with the hydrogen results reported in the literature. (12, 13) The reduced mass is used as a parameter to compare the

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aFor a complete discussion of the theory of separation see reference 18.
two isotopes. Since is unity for deuterium, the deuterium transition temperatures then can be read directly. The para-ortho composition, as determined by analyses of samples taken at condensation and removal, was corrected to the time the transition temperature was determined by means of the theoretical rate equation for conversion in the solid. (25)

The heat of fusion results are listed in Table XV. The two triple points are 18.781°K for 75.1% para D₂ and 18.787°K for 85.0% para D₂. Additional triple points would have been desirable, but time was not available in view of the volume of other data also required.

The results of the study of the rate of para to ortho conversion in solid deuterium are summarized in Table XVI. The experimental values in this table represent an averaging of ten to twenty rate determination for each para-ortho composition in a temperature region where the temperature change of the sample in the calorimeter between energy inputs was almost entirely due to conversion. For this temperature region below 5°K, conditions were nearly adiabatic. There was no temperature dependence of these rates within the experimental error for this temperature range, excluding the transition region.
Figure 3

Para deuterium composition as a function of the fraction stripped in a single stage separation. The circles represent a fast rate and the squares a slow rate of stripping.
### Table I

Heat Capacity of 33.1% para D₂

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Table III

Heat Capacity of 36.5% para D₂

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**Second Series**

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Table IV (cont'd)
### Table V

Heat Capacity of 49.9% para D₂

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<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₐ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.497</td>
<td>0.0331</td>
<td>0.289</td>
</tr>
<tr>
<td>1.585</td>
<td>0.0464</td>
<td>0.289</td>
</tr>
<tr>
<td>1.707</td>
<td>0.0493</td>
<td>0.313</td>
</tr>
<tr>
<td>1.829</td>
<td>0.0523</td>
<td>0.325</td>
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<td>2.016</td>
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<tr>
<td>2.018</td>
<td>0.0473</td>
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<td>2.156</td>
<td>0.0478</td>
<td>0.316</td>
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<td>2.346</td>
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<td>2.510</td>
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<td>0.1101</td>
<td>0.359</td>
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<td>2.960</td>
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<td>3.301</td>
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<td>0.14397</td>
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<td>0.6888</td>
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<tr>
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<td>0.431</td>
</tr>
<tr>
<td>8.698</td>
<td>0.9062</td>
<td>0.498</td>
</tr>
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<td>9.590</td>
<td>0.9568</td>
<td>0.599</td>
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<td>10.607</td>
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<td>14.161</td>
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### Table VI

**Heat Capacity of 59.1% para D₂**

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<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₚ (cal/mole-°K)</th>
</tr>
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<tbody>
<tr>
<td>1.551</td>
<td>0.0171</td>
<td>0.365</td>
</tr>
<tr>
<td>1.603</td>
<td>0.0224</td>
<td>0.376</td>
</tr>
<tr>
<td>1.682</td>
<td>0.0307</td>
<td>0.356</td>
</tr>
<tr>
<td>1.753</td>
<td>0.0359</td>
<td>0.376</td>
</tr>
<tr>
<td>1.813</td>
<td>0.0496</td>
<td>0.381</td>
</tr>
<tr>
<td>1.944</td>
<td>0.0700</td>
<td>0.389</td>
</tr>
<tr>
<td>2.077</td>
<td>0.0868</td>
<td>0.392</td>
</tr>
<tr>
<td>2.203</td>
<td>0.0890</td>
<td>0.394</td>
</tr>
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<td>2.356</td>
<td>0.1192</td>
<td>0.402</td>
</tr>
<tr>
<td>2.589</td>
<td>0.2159</td>
<td>0.415</td>
</tr>
<tr>
<td>2.967</td>
<td>0.3804</td>
<td>0.415</td>
</tr>
<tr>
<td>3.418</td>
<td>0.3896</td>
<td>0.408</td>
</tr>
<tr>
<td>3.888</td>
<td>0.4169</td>
<td>0.407</td>
</tr>
<tr>
<td>4.477</td>
<td>0.4109</td>
<td>0.409</td>
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<tr>
<td>5.018</td>
<td>0.6148</td>
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<td>0.6253</td>
<td>0.412</td>
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<td>6.419</td>
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<td>0.418</td>
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<tr>
<td>7.068</td>
<td>0.6207</td>
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</tr>
<tr>
<td>7.705</td>
<td>0.7326</td>
<td>0.477</td>
</tr>
<tr>
<td>8.419</td>
<td>0.8659</td>
<td>0.534</td>
</tr>
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<td>0.9749</td>
<td>0.603</td>
</tr>
<tr>
<td>10.224</td>
<td>1.1922</td>
<td>0.734</td>
</tr>
<tr>
<td>11.274</td>
<td>1.1410</td>
<td>0.889</td>
</tr>
<tr>
<td>Temperature (°K)</td>
<td>ΔT (°K)</td>
<td>Cₚ (cal/mole°K)</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------</td>
<td>-----------------</td>
</tr>
<tr>
<td>12.455</td>
<td>1.4568</td>
<td>1.103</td>
</tr>
<tr>
<td>13.792</td>
<td>1.5060</td>
<td>1.389</td>
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</table>

Second Series

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₚ (cal/mole°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.521</td>
<td>0.0221</td>
<td>0.369</td>
</tr>
<tr>
<td>1.604</td>
<td>0.0262</td>
<td>0.370</td>
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<tr>
<td>1.717</td>
<td>0.0420</td>
<td>0.370</td>
</tr>
<tr>
<td>1.812</td>
<td>0.0439</td>
<td>0.382</td>
</tr>
<tr>
<td>2.000</td>
<td>0.0478</td>
<td>0.400</td>
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<td>2.124</td>
<td>0.0491</td>
<td>0.384</td>
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<td>2.251</td>
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<td>0.421</td>
</tr>
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<td>2.402</td>
<td>0.0691</td>
<td>0.393</td>
</tr>
<tr>
<td>2.584</td>
<td>0.0649</td>
<td>0.419</td>
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<td>2.739</td>
<td>0.0658</td>
<td>0.413</td>
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# Table VII

Heat Capacity of 69.3\% para D₂

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<th>ΔT (°K)</th>
<th>(C_s) (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.810</td>
<td>0.0275</td>
<td>0.572</td>
</tr>
<tr>
<td>1.884</td>
<td>0.0348</td>
<td>0.707</td>
</tr>
<tr>
<td>1.953</td>
<td>0.0210</td>
<td>1.211</td>
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<tr>
<td>1.992</td>
<td>0.0157</td>
<td>2.422</td>
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<tr>
<td>2.021</td>
<td>0.0178</td>
<td>3.436</td>
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<tr>
<td>2.095</td>
<td>0.0266</td>
<td>3.036</td>
</tr>
<tr>
<td>2.393</td>
<td>0.1015</td>
<td>0.490</td>
</tr>
<tr>
<td>2.610</td>
<td>0.1158</td>
<td>0.487</td>
</tr>
<tr>
<td>2.875</td>
<td>0.1578</td>
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<tr>
<td>3.156</td>
<td>0.2250</td>
<td>0.489</td>
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<td>3.562</td>
<td>0.3719</td>
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<td>0.4431</td>
<td>0.487</td>
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<tr>
<td>4.625</td>
<td>0.4375</td>
<td>0.490</td>
</tr>
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<td>5.240</td>
<td>0.6953</td>
<td>0.477</td>
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<td>6.088</td>
<td>0.8228</td>
<td>0.482</td>
</tr>
<tr>
<td>6.931</td>
<td>0.7637</td>
<td>0.507</td>
</tr>
<tr>
<td>7.703</td>
<td>0.6985</td>
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<tr>
<td>8.411</td>
<td>0.7156</td>
<td>0.604</td>
</tr>
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<td>9.169</td>
<td>0.8861</td>
<td>0.659</td>
</tr>
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<td>10.063</td>
<td>0.9599</td>
<td>0.771</td>
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<tr>
<td>10.948</td>
<td>0.9681</td>
<td>0.889</td>
</tr>
<tr>
<td>11.962</td>
<td>1.2228</td>
<td>1.049</td>
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</table>
Table VII (cont'd)

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>( C_s ) (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.136</td>
<td>1.3258</td>
<td>1.268</td>
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</tbody>
</table>

Second Series

| 1.766 | 0.0216 | 0.408 |
| 1.830 | 0.0264 | 0.554 |
| 1.908 | 0.0334 | 0.718 |
| 1.949 | 0.0415 | 1.462 |

Transition at 2.045°K

| 2.044 | 0.1568 | 0.479 |
| 2.088 | 0.1578 | 0.483 |
| 3.060 | 0.2212 | 0.479 |
Table VIII

Heat Capacity of 78.7% para D₂

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₗ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.827</td>
<td>1.3033</td>
<td>0.774</td>
</tr>
<tr>
<td>11.008</td>
<td>1.0627</td>
<td>0.940</td>
</tr>
<tr>
<td>12.048</td>
<td>1.0318</td>
<td>1.129</td>
</tr>
<tr>
<td>13.125</td>
<td>1.1710</td>
<td>1.326</td>
</tr>
<tr>
<td>14.438</td>
<td>1.5582</td>
<td>1.636</td>
</tr>
<tr>
<td>15.788</td>
<td>1.2525</td>
<td>1.956</td>
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<tr>
<td>17.183</td>
<td>1.7170</td>
<td>2.167</td>
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Triple point 18.791°K

<table>
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<th>ΔT (°K)</th>
<th>Cₗ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.915</td>
<td>1.1810</td>
<td>5.516</td>
</tr>
<tr>
<td>21.080</td>
<td>1.1166</td>
<td>5.806</td>
</tr>
<tr>
<td>22.031</td>
<td>0.7944</td>
<td>6.057</td>
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</table>
Table IX
Heat Capacity of 80.3% para D₂

<table>
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<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₗ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.667</td>
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<td>2.218</td>
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<td>0.524</td>
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<td>2.380</td>
<td>0.0904</td>
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<td>2.502</td>
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<td>2.633</td>
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</table>

Transition at 2.780°K

<table>
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<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₗ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.185</td>
<td>0.3487</td>
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<tr>
<td>3.611</td>
<td>0.4075</td>
<td>0.550</td>
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<tr>
<td>4.067</td>
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### Table X

Heat Capacity of 81.2% para D₂

<table>
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<th>ΔT (°K)</th>
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<tr>
<td>1.617</td>
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<td>1.982</td>
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<td>2.323</td>
<td>0.1068</td>
<td>0.587</td>
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<td>2.448</td>
<td>0.0819</td>
<td>0.771</td>
</tr>
<tr>
<td>2.536</td>
<td>0.0636</td>
<td>0.992</td>
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<td>2.613</td>
<td>0.0529</td>
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<td>2.725</td>
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<td>2.796</td>
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<td>2.813</td>
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<td>0.555</td>
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<td>0.3731</td>
<td>0.562</td>
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<td>0.564</td>
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<td>5.145</td>
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<tr>
<td>Temperature (°K)</td>
<td>ΔT (°K)</td>
<td>C₈ (cal/mole-°K)</td>
</tr>
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<td>7.958</td>
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<td>10.659</td>
<td>0.9710</td>
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<tr>
<td>11.564</td>
<td>1.2294</td>
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<tr>
<td>12.650</td>
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<td>13.769</td>
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<td>14.976</td>
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<td>1.1391</td>
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<td>2.468</td>
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Table XI
Heat Capacity of 83.0% para D₂

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₚ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.703</td>
<td>0.1281</td>
<td>0.123</td>
</tr>
<tr>
<td>1.911</td>
<td>0.0782</td>
<td>0.205</td>
</tr>
<tr>
<td>2.123</td>
<td>0.0558</td>
<td>0.312</td>
</tr>
<tr>
<td>2.267</td>
<td>0.0935</td>
<td>0.467</td>
</tr>
<tr>
<td>2.412</td>
<td>0.0776</td>
<td>0.611</td>
</tr>
<tr>
<td>2.513</td>
<td>0.0617</td>
<td>0.771</td>
</tr>
<tr>
<td>2.606</td>
<td>0.0491</td>
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<tr>
<td>2.698</td>
<td>0.0746</td>
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</tr>
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<tr>
<td>2.853</td>
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<td>4.786</td>
</tr>
<tr>
<td>2.899</td>
<td>0.0107</td>
<td>23.25</td>
</tr>
<tr>
<td>2.921</td>
<td>0.0097</td>
<td>29.56</td>
</tr>
<tr>
<td>2.945</td>
<td>0.0109</td>
<td>33.40</td>
</tr>
</tbody>
</table>

Second Series 82.3% para D₂

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₚ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.295</td>
<td>0.0865</td>
<td>0.510</td>
</tr>
<tr>
<td>2.414</td>
<td>0.0654</td>
<td>0.660</td>
</tr>
<tr>
<td>2.514</td>
<td>0.1171</td>
<td>0.860</td>
</tr>
<tr>
<td>2.661</td>
<td>0.0836</td>
<td>1.187</td>
</tr>
</tbody>
</table>

Transition at 2.910°K

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₚ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.119</td>
<td>0.1557</td>
<td>0.607</td>
</tr>
<tr>
<td>3.399</td>
<td>0.1604</td>
<td>0.586</td>
</tr>
<tr>
<td>3.687</td>
<td>0.1619</td>
<td>0.574</td>
</tr>
<tr>
<td>4.011</td>
<td>0.3219</td>
<td>0.574</td>
</tr>
<tr>
<td>Temperature (°K)</td>
<td>$\Delta T$ (°K)</td>
<td>$C_p$ (cal/mole-°K)</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>4.511</td>
<td>0.4996</td>
<td>0.571</td>
</tr>
<tr>
<td>5.071</td>
<td>0.5053</td>
<td>0.564</td>
</tr>
<tr>
<td>5.671</td>
<td>0.4857</td>
<td>0.581</td>
</tr>
<tr>
<td>6.302</td>
<td>0.5958</td>
<td>0.577</td>
</tr>
<tr>
<td>7.110</td>
<td>0.7619</td>
<td>0.592</td>
</tr>
<tr>
<td>7.977</td>
<td>0.8223</td>
<td>0.643</td>
</tr>
<tr>
<td>8.898</td>
<td>0.8793</td>
<td>0.717</td>
</tr>
<tr>
<td>9.851</td>
<td>0.9694</td>
<td>0.793</td>
</tr>
<tr>
<td>11.116</td>
<td>1.5734</td>
<td>0.969</td>
</tr>
<tr>
<td>12.493</td>
<td>1.2134</td>
<td>1.241</td>
</tr>
<tr>
<td>13.711</td>
<td>1.3243</td>
<td>1.482</td>
</tr>
<tr>
<td>15.161</td>
<td>1.6637</td>
<td>1.843</td>
</tr>
<tr>
<td>16.769</td>
<td>1.7087</td>
<td>2.326</td>
</tr>
</tbody>
</table>
Table XII

Heat Capacity of 87.2% para D₂

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₜ (cal/mole·°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.666</td>
<td>0.1020</td>
<td>0.0573</td>
</tr>
<tr>
<td>2.080</td>
<td>0.0873</td>
<td>0.187</td>
</tr>
<tr>
<td>2.535</td>
<td>0.0303</td>
<td>0.475</td>
</tr>
<tr>
<td>2.769</td>
<td>0.0343</td>
<td>0.739</td>
</tr>
<tr>
<td>3.044</td>
<td>0.1354</td>
<td>1.575</td>
</tr>
<tr>
<td>3.175</td>
<td>0.0301</td>
<td>6.687</td>
</tr>
<tr>
<td>3.213</td>
<td>0.0058</td>
<td>50.02</td>
</tr>
<tr>
<td>4.176</td>
<td>0.5350</td>
<td>0.582</td>
</tr>
<tr>
<td>4.785</td>
<td>0.5224</td>
<td>0.571</td>
</tr>
<tr>
<td>5.608</td>
<td>1.0485</td>
<td>0.575</td>
</tr>
<tr>
<td>6.513</td>
<td>0.9296</td>
<td>0.571</td>
</tr>
<tr>
<td>7.220</td>
<td>0.8261</td>
<td>0.592</td>
</tr>
<tr>
<td>7.834</td>
<td>0.7281</td>
<td>0.623</td>
</tr>
<tr>
<td>8.470</td>
<td>1.0013</td>
<td>0.680</td>
</tr>
<tr>
<td>9.258</td>
<td>1.0628</td>
<td>0.738</td>
</tr>
<tr>
<td>9.1147</td>
<td>1.2610</td>
<td>0.730</td>
</tr>
<tr>
<td>10.124</td>
<td>1.0552</td>
<td>0.812</td>
</tr>
<tr>
<td>10.771</td>
<td>1.0543</td>
<td>0.916</td>
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</tbody>
</table>

Second Series 86.4% para D₂

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔT (°K)</th>
<th>Cₜ (cal/mole·°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.678</td>
<td>0.0926</td>
<td>0.0712</td>
</tr>
<tr>
<td>1.982</td>
<td>0.0528</td>
<td>0.1142</td>
</tr>
<tr>
<td>2.321</td>
<td>0.0556</td>
<td>0.375</td>
</tr>
<tr>
<td>Temperature (°K)</td>
<td>ΔT (°K)</td>
<td>$C_s$ (cal/mole°K)</td>
</tr>
<tr>
<td>------------------</td>
<td>---------</td>
<td>------------------</td>
</tr>
<tr>
<td>2.529</td>
<td>0.0521</td>
<td>0.492</td>
</tr>
<tr>
<td>2.768</td>
<td>0.0740</td>
<td>0.924</td>
</tr>
<tr>
<td>2.930</td>
<td>0.0828</td>
<td>1.249</td>
</tr>
<tr>
<td>3.089</td>
<td>0.0533</td>
<td>2.610</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Transition at 3.169°K</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.867</td>
<td>0.3302</td>
<td>0.562</td>
</tr>
<tr>
<td>4.400</td>
<td>0.3928</td>
<td>0.572</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Third Series 86.3% para D₂</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.764</td>
<td>0.0922</td>
<td>0.963</td>
</tr>
<tr>
<td>2.923</td>
<td>0.0853</td>
<td>1.284</td>
</tr>
<tr>
<td>3.070</td>
<td>0.0853</td>
<td>2.642</td>
</tr>
<tr>
<td>3.138</td>
<td>0.0169</td>
<td>17.38</td>
</tr>
<tr>
<td>3.154</td>
<td>0.0089</td>
<td>44.27</td>
</tr>
<tr>
<td>3.164</td>
<td>0.0066</td>
<td>83.65</td>
</tr>
<tr>
<td>3.455</td>
<td>0.3331</td>
<td>0.588</td>
</tr>
</tbody>
</table>
Figure 1.

Saturation heat capacities of solid deuterium (33.1 - 87.2% para).
Composition (% para D₂)

- 33.1
- 36.5
- 42.0
- 49.9
- 59.4
- 69.3
- 81.2
- 80.3
- 83.0
- 82.3
- 87.2
- 86.4
- 86.3
Saturation heat capacities of solid deuterium (33.1 - 87.2% para) and liquid deuterium (78.7% para). The dashed line in the liquid region represents the results of Clusius and Bartholome for normal deuterium. The lowest lying solid line for both regions represents the data of Hill and Lounasmaa at the low temperatures and the data of Kerr et al. at the higher temperatures for ortho deuterium.
Composition (% para $D_2$)

- 33.1
- 36.5
- 42.0
- 49.9
- 59.4
- 69.3
- 81.2
- 80.3
- 78.7
- 83.0
- 82.3
- 87.2
- 86.4
- 86.3

$C_s$ (cal./mol.-°K)

Temperature (°K)

Triple Point Region
Table XIII
Heat Capacity of HD

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>AT (°K)</th>
<th>Cₜ (cal/mole-°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.521</td>
<td>0.0380</td>
<td>0.0184</td>
</tr>
<tr>
<td>2.897</td>
<td>0.0732</td>
<td>0.0183</td>
</tr>
<tr>
<td>3.317</td>
<td>0.1144</td>
<td>0.0269</td>
</tr>
<tr>
<td>2.601</td>
<td>0.0918</td>
<td>0.0128</td>
</tr>
<tr>
<td>3.186</td>
<td>0.3192</td>
<td>0.0252</td>
</tr>
<tr>
<td>3.585</td>
<td>0.8249</td>
<td>0.0240</td>
</tr>
<tr>
<td>3.812</td>
<td>0.6505</td>
<td>0.0335</td>
</tr>
<tr>
<td>4.050</td>
<td>0.6325</td>
<td>0.0483</td>
</tr>
<tr>
<td>5.009</td>
<td>0.6525</td>
<td>0.0543</td>
</tr>
<tr>
<td>5.562</td>
<td>0.3815</td>
<td>0.0762</td>
</tr>
<tr>
<td>6.038</td>
<td>0.5347</td>
<td>0.0937</td>
</tr>
<tr>
<td>6.469</td>
<td>0.6463</td>
<td>0.117</td>
</tr>
<tr>
<td>7.014</td>
<td>1.1292</td>
<td>0.156</td>
</tr>
<tr>
<td>7.714</td>
<td>0.9080</td>
<td>0.216</td>
</tr>
<tr>
<td>8.274</td>
<td>1.0461</td>
<td>0.282</td>
</tr>
<tr>
<td>8.904</td>
<td>1.0014</td>
<td>0.367</td>
</tr>
<tr>
<td>9.857</td>
<td>1.0367</td>
<td>0.510</td>
</tr>
<tr>
<td>10.815</td>
<td>1.1748</td>
<td>0.672</td>
</tr>
<tr>
<td>11.888</td>
<td>1.2102</td>
<td>0.889</td>
</tr>
<tr>
<td>12.935</td>
<td>1.2611</td>
<td>1.093</td>
</tr>
<tr>
<td>14.132</td>
<td>1.4337</td>
<td>1.369</td>
</tr>
<tr>
<td>15.381</td>
<td>1.4682</td>
<td>1.679</td>
</tr>
</tbody>
</table>
Figure 6
Saturation heat capacity of hydrogen deuteride with the heat capacities of para hydrogen and ortho deuterium and the earlier results of Scott and Brickwedde, as reported by Wooley, Scott, and Brickwedde, for HD.
<table>
<thead>
<tr>
<th>Composition (% para)</th>
<th>Transition Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.2 ± 0.8</td>
<td>3.220 ± 0.002</td>
</tr>
<tr>
<td>86.4</td>
<td>3.169 ± 0.006</td>
</tr>
<tr>
<td>86.2</td>
<td>3.164 ± 0.002</td>
</tr>
<tr>
<td>85.5</td>
<td>2.982 ± 0.001</td>
</tr>
<tr>
<td>85.0</td>
<td>3.084 ± 0.002</td>
</tr>
<tr>
<td>83.0</td>
<td>2.950 ± 0.005</td>
</tr>
<tr>
<td>82.3</td>
<td>2.910 ± 0.010</td>
</tr>
<tr>
<td>81.2</td>
<td>2.840 ± 0.010</td>
</tr>
<tr>
<td>80.3</td>
<td>2.780 ± 0.010</td>
</tr>
<tr>
<td>75.1</td>
<td>2.513 ± 0.003</td>
</tr>
<tr>
<td>69.3</td>
<td>2.045 ± 0.020</td>
</tr>
<tr>
<td>64.6</td>
<td>1.818 ± 0.002</td>
</tr>
</tbody>
</table>
Figure 7

Transition temperatures for deuterium and hydrogen as a function of composition. The dashed line represents the NMR measurements for hydrogen.
<table>
<thead>
<tr>
<th>Composition (% para)</th>
<th>Sample size (mole)</th>
<th>$H_f$ (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.7</td>
<td>0.08171</td>
<td>47.10</td>
</tr>
<tr>
<td>78.7</td>
<td>0.11089</td>
<td>47.14</td>
</tr>
<tr>
<td>78.5</td>
<td>0.11089</td>
<td>47.25</td>
</tr>
<tr>
<td>78.4</td>
<td>0.11089</td>
<td>47.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>47.19 ± 0.07</td>
</tr>
</tbody>
</table>
Table XVI
Rates of Para to Ortho Conversion in Solid D₂

<table>
<thead>
<tr>
<th>Composition (% para)</th>
<th>Expt'l Rate (hr⁻¹)</th>
<th>Theoretical Rate (hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.1</td>
<td>2.2 x 10⁻⁴</td>
<td>5.3 x 10⁻⁴</td>
</tr>
<tr>
<td>36.5</td>
<td>2.2</td>
<td>5.8</td>
</tr>
<tr>
<td>42.0</td>
<td>9.2</td>
<td>6.6</td>
</tr>
<tr>
<td>49.9</td>
<td>10.5</td>
<td>7.6</td>
</tr>
<tr>
<td>59.4</td>
<td>4.6</td>
<td>8.8</td>
</tr>
<tr>
<td>69.3</td>
<td>14.8</td>
<td>9.9</td>
</tr>
<tr>
<td>80.3</td>
<td>7.1</td>
<td>11.0</td>
</tr>
<tr>
<td>81.2</td>
<td>5.2</td>
<td>11.1</td>
</tr>
<tr>
<td>83.0</td>
<td>8.5</td>
<td>11.3</td>
</tr>
</tbody>
</table>
Treatment of Data

The uncertainty in the determination of the para composition does not affect the thermodynamic measurements; however, the relationships between the para content and the thermodynamic quantities, in particular the transition temperature and triple point, are important. The para content could be determined to a precision of 0.8%. Spurious values outside this precision limit were often obtained because of the time dependence of the thermal conductivity measurements due to small changes in the surface of the hot wire. This precision was achieved by taking several measurements for a given calorimetric sample. An indication of the reliability of this procedure was the remarkable fit at the higher para concentrations (where the transition is sharpest) of the experimental points to the straight line shown in Figure 7.

In order to estimate the probable error in a deuterium heat capacity determination at a given temperature, errors in the following quantities are considered: (a) the energy supplied to the sample; (b) the temperature rise in the sample; and (c) the mean value of the temperature. The energy which is supplied to the sample is determined from the measurements of time of heating, current, and potential drop. All these quantities have a total uncertainty of less than 0.1% and therefore do not contribute significantly to the total error. Most of the total energy input is used to heat the deuterium sample, while the remainder is supplied to the empty calorimeter, the HD impurity, and, at the highest temperatures,
vaporization into the dead space of the calorimeter. For convenience the effect of these quantities (which are subtracted from the total heat capacity) on the calculated heat capacity of deuterium are considered in three temperature ranges: the helium range, the hydrogen range, and the intermediate range between these two calibration regions. The heat capacity of the calorimeter introduced an error of 0.1% in the helium and hydrogen ranges and 0.3% in the intermediate range. With the exception of one normal sample, the heat capacity of HD had a negligible effect. The vaporization caused an error of 0.2% at the highest temperatures. The total uncertainty, expressed as a standard deviation, on the energy supplied to the sample was 0.2% at low temperatures and 0.4% at the highest temperatures.

Errors introduced by the uncertainty in the temperature rise were the largest sources of error in the experiment due to the uncertainty in determining the heat leak. The change in temperature for the worst case was known to 0.5% in the helium range and 0.3% elsewhere. The small temperature changes and the large drift rates caused the larger uncertainty of 0.6% for the helium range and 0.7% elsewhere resulting from the limitations in reading the smoothed calibration curves. The total uncertainty in the temperature rise corresponded to a standard deviation of 0.8%.

In addition there was a systematic error of 0.3% in constructing the smoothed calibration curve. Other systematic errors in the heat capacity determination were the error in determining the number of moles and the uncertainty in the temperature scale itself. The former was trivial except for small samples and the latter was at most 0.2%.

The statistical errors total approximately 0.9% for the entire temperature range as estimated from the individually determined quantities.
The standard deviation, as determined from actual scatter, was 1.3% for the helium range, 0.9% for the intermediate range, and 1.0% for the hydrogen range. The systematic errors, which total 0.5%, were apparently not too significant since they were not detected by the use of different sample sizes and thermometer calibrations for the samples with the same heat capacity in the 78-87% para content range.

The preceding discussion of errors is not applicable in the region of rapid heat capacity rise below the transition temperatures. The errors were much larger in this region because of the uncertainties in the very small temperature increments and the mean temperature for each increment. It was necessary to compute the heat leak because the heat capacity at the final temperature following an energy input was 10-20% greater than at the initial temperature of the input, and therefore drift curves were meaningless. The error was estimated to be 3-5% depending on the slope of the heat capacity curve. This error could not be compared readily with actual scatter because of the steepness of the curves below the transition temperatures.

The errors in the heat capacity of HD were treated separately because of its small heat capacity and the large amounts of impurity, H\(_2\) and D\(_2\) present. For the purposes of estimating the errors in the temperature rise and the mean temperature for an HD heat capacity determination, the errors in these two quantities were assumed to be the same as previously given for deuterium. The calorimeter heat capacity introduced an error of 0.3% for the entire temperature range. The contribution of the impurities to the error was 0.6% for the helium range and 0.1% elsewhere. This larger uncertainty at the lower temperatures resulted from the lack of knowledge of the ortho-para content of the im-
purities. The correction was applied by assuming complete conversion to the low temperature equilibrium forms. The sample vaporization added 0.7% in the high temperature range. The statistical errors total approximately 1.1% over the entire temperature range. The actual standard deviation was 8.1% for the helium range, and 1.3% for the intermediate range. There were not enough points at the highest temperatures to have a meaningful scatter. The deviation from the estimated error below 50K can be attributed to the small heat capacity rather than to the small sample size, since a deuterium sample of smaller size but larger heat capacity did not show this deviation. The calorimeter walls in the HD experiment superheated and this made the heat leak correction more uncertain.

The uncertainty in determining the transition temperature is listed in Table XIV with the transition temperatures. The deviation of 0.003°K in the He¹ vapor pressure scale of temperatures was not included in the uncertainty since it is systematic. The triple point temperatures had an uncertainty of 0.003°K with the vapor pressure scale having a systematic deviation of 0.01°K at most.

In order to estimate probable error in the heat of fusion measurements, errors in the following quantities are considered: (a) energy supplied to the sample, (b) heat leak, and (c) the heat capacities to be subtracted. As mentioned previously the energy is known to 0.1%. The heat leak was estimated to be uncertain by 0.1%. The uncertainties in the heat capacities caused a total error of 0.2%. The errors in thermometry are included in the heat capacity error. The average error from four determinations of the heat of fusion is given in Table XV as 0.07 cal/mole or 0.2%, which is less than the 0.4% for the cumulative statistical error.
It is difficult to determine the uncertainty in the kinetic measurements. These measurements depended strongly on the heat leak. The heat leak error is about 50%. The thermal history can influence the kinetic measurement. In the case of the 59.4% para sample an error of 50% was indicated as being caused by temperature recycling. Unless there is an actual change on recycling, it is difficult to say whether the results are uncertain to that order of magnitude.
Discussion

I. Comparison of Third Law and Statistical Entropies

It has been the practice in calculating the entropy associated with the heat capacity anomaly of solid hydrogen (12) or deuterium (9) to subtract as the lattice contribution the heat capacity of either para hydrogen or ortho deuterium. This practice assumes that the lattice properties of these two solids are identical to the lattice properties of the solids with the anomaly. As will be shown later there is no justification for this procedure and in fact it is probably erroneous. Anomalous entropies determined by this procedure were from 0.1 to 0.2 entropy units less than predicted by assuming the anomaly to be the removal of the threefold rotational degeneracy of the J=1 species present in the mixture (i.e., Rln3). This entropy deficiency has led to various speculations on the nature of the splitting of the J=1 multiplet by the crystalline field. To determine unambiguously the anomalous entropies, a comparison of the third law entropies of the gas were made with the calculated statistical entropies.

(a) Hydrogen deuteride

In the case of HD there is no unusual behavior in the solid. The nuclear spin degeneracy is undoubtedly 'frozen-in' at the lowest temperature of measurement and therefore a reliable extrapolation of the heat capacity of the solid to absolute zero is possible. Since a comparison of the third law and statistical entropies of HD had never been made, it
was decided to see what agreement could be achieved. The entropy summation in Table XVII from the experimental data for HD is typical of the procedure for obtaining calorimetric entropies. The data for fusion, vaporization, and the liquid heat capacity were taken from Woolley, Scott, and Brickwedde. (26) Corrections for the nuclear spin degeneracy of \( R \ln 6 \) and to the ideal gas state enable the calorimetric entropy to be compared with the spectroscopic value. The correction to the ideal gas state was made by use of the virial relationship

\[
S_{\text{ideal}} - S_{\text{real}} = (dB/dT) P
\]

with the temperature coefficient of \( B \) calculated from the equation proposed by Beenakker et al. (27) The corrected value of 19.99 ± 0.09 e.u. from the table compares very well with the spectroscopic value of 20.05 e.u.

(b) Deuterium

It is evident from the experimental data that it is only possible to make an entropy comparison for the para-ortho compositions where reliable extrapolations of the heat capacities to absolute zero can be made. For compositions in the range 33.1-69.3% para, the heat capacities are still quite large at the lowest experimental temperature (approximately 1.5°C), so that additional information is required. Fortunately in the case of 33.1% para deuterium, there is available heat capacity data down to 0.3°C, (9) the temperature at which the anomaly in the solid practically vanishes. For para compositions greater than 80%, the heat capacities at 1.5°C are small and their curvatures are uniform, so that it is possible to make a reliable extrapolation. Therefore, two entropy comparisons are made, one for 33.1% para content, which shows only a broad anomaly, and the other for 82.3% para content, which is typical of the sharp anomalies.
**Table XVII**

**Entropy of HD**

<table>
<thead>
<tr>
<th>State</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (0-2.5°K) graphical extrapolation</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Solid (2.5-16.60°K) numerical</td>
<td>0.758 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Fusion (16.60°K) 38.1/16.60</td>
<td>2.295 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Liquid (16.60-22.13°K) numerical</td>
<td>1.499 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Vaporization (22.13°K) 257/22.13</td>
<td>11.613 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Total calorimetric entropy</td>
<td>16.175 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>Correction to the ideal gas state</td>
<td>0.252 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Spin degeneracy of R ln 6</td>
<td>3.560</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.987 ± 0.09</td>
<td></td>
</tr>
</tbody>
</table>
The entropies were obtained by numerically integrating the quotient of the heat capacity by the temperature with respect to the temperature. The heat capacities were read from a smoothed curve through the experimental points for a given para content at temperature intervals of 0.1°K. In the transition region the intervals were 0.01 or 0.02°K. Since the intervals were small, the trapezoidal rule was deemed adequate. The triple points used in determining the entropies of fusion were read from a straight line through the two experimental points determined in this research and the triple point for ortho deuterium, as determined by Kerr et al., (7) corrected to the temperature scale proposed by Durieux. (23) Since this research showed that the heat of fusion and the heat capacity of the liquid were independent of para content within the experimental limits, the heat of vaporization also was taken to be independent of para content. The entropies of the liquid and of vaporization, as determined by Kerr et al., (7) were added to the entropies for the various para compositions of this research to obtain the total calorimetric entropies.

In order to compare the calorimetric entropy with the entropy calculated from spectroscopic data, the 'frozen-in' entropy of mixing and the correction to the ideal gas state were added to the calorimetric entropy. The 'frozen-in' entropy was calculated from the equation

\[ S = -R X_p \ln \left(\frac{X_p}{3}\right) - X_o \ln \left(\frac{X_o}{6}\right) \]

where \(X_p\) and \(X_o\) are the mole fractions of para and ortho deuterium, respectively, and \(R\) is the gas constant taken to be 1.9872 cal/mole-°K. This equation takes into account the para nuclear spin statistical weight of 3 and the ortho spin statistical weight of 6. The rotational weight of the para state is not considered in this equation, since it is assumed
that the degeneracy is removed in the solid at absolute zero (to which the heat capacities were extrapolated). The temperature coefficient of B for deuterium came from Beenakker et al. (27)

It is evident from Tables XVII and XIX that there is excellent agreement between the third law entropy and the statistical entropy. Therefore, there can be little doubt as to the origin of the anomaly in solid deuterium, and for that matter in solid hydrogen. The anomaly arises from the removal of the threefold rotational degeneracy of the J=1 level. The mechanism of removal will be discussed later.

In Table XX are given the entropy increments of solid deuterium from 1.5°K to the triple point for various para compositions. A detailed comparison with statistical entropy in most of these cases will have to wait for heat capacity measurements below 1.5°K. For 80.3% para content there is sufficient information to make an entropy comparison and the agreement is comparable to that for the case of 82.3% para content in Table XIX. In some cases an approximate estimate of the entropy below 1.5°K can be made. In these cases a comparison of the statistical and experimental entropies gives adequate agreement if proper account of the uncertainties of the summation and the estimate are taken.

II. Thermodynamic Properties of Liquid Deuterium

The experimental data for the heat of fusion and heat capacity of the liquid show that, unlike the solid, the behavior of deuterium above the triple point is independent of para content. There is essentially free rotation in the liquid, because the effect of molecular interactions in perturbing the rotational states is undoubtedly reduced by the randomness in the liquid, and in any case is small relative to KT at these temperatures.
Table XVIII
Entropy of 33.1% para D₂

<table>
<thead>
<tr>
<th>State</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (0-0.3°K) graphical extrapolation</td>
<td>0.165 ± 0.01</td>
</tr>
<tr>
<td>Solid (0.3-18.693°K) numerical</td>
<td>1.473 ± 0.01</td>
</tr>
<tr>
<td>Fusion (18.693°K) 47.19/18.693</td>
<td>2.524 ± 0.01</td>
</tr>
<tr>
<td>Liquid (18.693-23.59°K) numerical</td>
<td>1.318 ± 0.01</td>
</tr>
<tr>
<td>Vaporization (23.59°K) 293.9/23.59</td>
<td>12.459 ± 0.02</td>
</tr>
<tr>
<td>Total calorimetric entropy</td>
<td>17.939 ± 0.06</td>
</tr>
<tr>
<td>Correction to the ideal gas state</td>
<td>0.264 ± 0.01</td>
</tr>
<tr>
<td>Frozen-in entropy of mixing</td>
<td>4.326</td>
</tr>
<tr>
<td>Spectroscopic entropy</td>
<td>22.53 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>22.59 ± 0.01</td>
</tr>
<tr>
<td>Process</td>
<td>Value</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Solid (0-1.5°C) graphical extrapolation</td>
<td>0.052 ± 0.02</td>
</tr>
<tr>
<td>Solid (1.5-18.799°C) numerical</td>
<td>2.671 ± 0.02</td>
</tr>
<tr>
<td>Fusion (18.799°C) 47.19/18.799</td>
<td>2.510 ± 0.01</td>
</tr>
<tr>
<td>Liquid (18.799-23.59°C) numerical</td>
<td>1.289 ± 0.01</td>
</tr>
<tr>
<td>Vaporization (23.59°C) 293.9/23.59</td>
<td>12.459 ± 0.02</td>
</tr>
<tr>
<td>Total calorimetric entropy</td>
<td>18.982 ± 0.08</td>
</tr>
<tr>
<td>Correction to ideal gas state</td>
<td>0.264 ± 0.01</td>
</tr>
<tr>
<td>Frozen-in entropy of mixing</td>
<td>3.356</td>
</tr>
<tr>
<td>Spectroscopic entropy</td>
<td>22.60 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>22.69 ± 0.01</td>
</tr>
</tbody>
</table>

Table XIX
Entropy of 82.3% para D₂
Table XX

Entropy Increments of Solid D₂ for Various Para Compositions

<table>
<thead>
<tr>
<th>(X_p)</th>
<th>Temperature range (°K)</th>
<th>Entropy of solid (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.331</td>
<td>0.3-18.693</td>
<td>1.473</td>
</tr>
<tr>
<td>0.365</td>
<td>1.5-18.700</td>
<td>1.462</td>
</tr>
<tr>
<td>0.420</td>
<td>1.5-18.712</td>
<td>1.525</td>
</tr>
<tr>
<td>0.499</td>
<td>1.5-18.729</td>
<td>1.619</td>
</tr>
<tr>
<td>0.594</td>
<td>1.5-18.750</td>
<td>1.773</td>
</tr>
<tr>
<td>0.693</td>
<td>1.7-18.771</td>
<td>2.044</td>
</tr>
<tr>
<td>0.803</td>
<td>1.5-18.794</td>
<td>2.632</td>
</tr>
<tr>
<td>0.823</td>
<td>1.5-18.799</td>
<td>2.671</td>
</tr>
<tr>
<td>0.864</td>
<td>1.5-18.808</td>
<td>2.663</td>
</tr>
</tbody>
</table>
The heat capacity of 78.7% para deuterium in the liquid state confirms the measurements of Kerr et al. (7) rather than those of Clusius and Bartholome. (5) In Figure 5 the normal deuterium data of Clusius and Bartholome, represented by a dashed line, lies considerably lower than the ortho deuterium data of Kerr et al., represented by a solid line. The deviation of the 78.7% para data of this research from the ortho data can be attributed to the extrapolation of the thermometer calibration curve beyond the last calibration point at 20°K. Assuming this to be the source of the error, the heat capacity of liquid deuterium does not vary significantly with para content.

The heat of fusion compares well with the values of $47.07 \pm 0.1$ cal/mole for ortho deuterium (7) and $47.0 \pm 0.4$ cal/mole for normal deuterium. (5) The heat of fusion also shows no significant variation with para content. The entropies of fusion and vaporization will vary slightly with para content due to the boiling point and triple point variations with para content, but not sufficiently to affect the total entropy within the experimental limits.

III. Solid Deuterium

In the solid state there is a marked dependence of the heat capacity on para content. It can be seen easily from Figure 5 that for temperatures above 15°K the heat capacities are divided into two classes of curves. For para content of 78.7% or greater, the heat capacities are identical down to the transition region. There is a variation for these higher para composition in the heat capacity below the transition region, which will be discussed later. For para content of 50% or less, the heat capacities show a marked dependence on the para content up to about 15°K where all the heat capacity curves for concentrations less than 50% merge.
with the curve for ortho deuterium. Unfortunately the measurements on
the 60% and 70% samples did not extend to higher temperatures. Though
the direction of the 60% para curve above 150K is definitely uncertain,
it is the opinion of this investigator that the 70% curve will merge
with the heat capacity curve for the higher para compositions.

There are at least two possible explanations for the different heat
capacity curves above 150K, if the two distinct curves can be considered
to be due only to lattice vibrations. This difference could be caused
by a change in the lattice dimensions or by two different crystal struc-
tures, one characteristic of para deuterium and the other of ortho deu-
terium. Since the anomalous heat capacity does not extend above 150K,
the para and ortho designations are used for the two curves rather than
a range of mixture designations. Keesom et al. (28) using x-ray dif-
fraction determined the crystal structure of solid para hydrogen to be
hexagonal close-packed between 1.65-4.20K. These workers definitely
specified that their measurements were on para hydrogen. Recently Ko-
gan et al. (29) also using x-ray diffraction determined the structure of
solid hydrogen of unspecified composition, but presumably normal hydro-
gen, to be either hexagonal close-packed or body-centered-tetragonal at
4.20K. They also determined deuterium, tritium, and HD (30) to be body-
centered tetragonal. To resolve the hydrogen structure, they made neu-
tron diffraction measurements (31) at 120K on solid hydrogen and deu-
terium, both of presumably normal composition. According to these re-
sults solid hydrogen and deuterium are body-centered tetragonal, but not
isomorphous.

Van Kranendonk and Gush (32) have concluded from the infrared spec-
tra of solid para hydrogen that the body-centered tetragonal structure
is incompatible with the infrared measurements while the hexagonal close-
packed structure agrees with their calculations. The data of Kogan et al. were taken under uncertain experimental conditions and on a sample of uncertain ortho content. If their sample was normal hydrogen the ortho-para conversion could have changed the composition in the course of a 5-10 hour experiment to a composition between 65-70% ortho hydrogen. Assuming solid hydrogen also to have two distinct heat capacity curves at the highest temperatures as in the deuterium case, the hydrogen could have been in an intermediate region where two different crystal structures or solids with different lattice volumes coexisted. These conditions might well account for the extra lines that cloud the interpretation in the structure determination by Kogan et al. (31)

From the existing structural data it is impossible to conclude at this time whether the heat capacity differences above 150K for deuterium are due to different structures or different lattice dimensions. Since the rate of conversion in deuterium is ten times slower than in hydrogen and deuterium is more suitable for neutron diffraction experiments than hydrogen, an investigation of the deuterium structure at high para content should be undertaken. From the normal hydrogen heat capacity data (12) there seems to be an indication of a significant heat capacity difference between normal and para hydrogen. This difference is not as large as for deuterium, but the larger zero point energy and the lower triple point temperature for hydrogen might account for this smaller value.

As mentioned previously the lower heat capacity curve above 150K in Figure 5 represents ortho deuterium and the upper curve represents para deuterium. Therefore, the Debye \( \Theta \) for ortho is evidently greater than the Debye \( \Theta \) for para. If the Gruneisen constants for both forms are nearly
the same, then the molar volume of ortho deuterium must be greater than the molar volume of para deuterium. Data for the volumes of solid para and ortho deuterium are lacking, but the liquid volumes indicate that ortho deuterium has a larger volume than normal deuterium. (33) The liquid volumes for hydrogen (33) indicate similarly that para hydrogen has a larger volume than normal hydrogen, although the difference between para and normal hydrogen is six times the difference between ortho and normal deuterium. Thus it is reasonable to conclude that solid para deuterium will have a smaller volume than normal deuterium. These volume changes further reinforce the argument based on the heat capacity data that the character of the solid above the transition changes with increasing J=1 content. It is remarkable that the solids of high J=1 content, with essentially free rotation, are closer-packed than those of high J=0 content, with no rotational motion at all.

The anomalous heat capacities of solid deuterium are of two types, as seen in Figure 4, one characterized by a sharp transition and the other by a broad transition. The difference between the heat capacity for a given composition and the heat capacity of ortho deuterium is called the excess heat capacity for that composition. For the temperature range below 60K the excess heat capacities are linear with para content at a given temperature. The relationship is very good for compositions of 60% para or less, and surprisingly does not deviate too much for compositions with sharp anomalies, if they are neglected in calculating the excess heat capacity.

A comparison of the heat capacity results with the results of nuclear magnetic resonance (NMR) provides a wealth of additional information.

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*As explained in the entropy discussion, this is not strictly correct, but is good to a first approximation.*
The broadening of the NMR line for deuterium at 140K reported by Rollin and Watson (34) compares favorably with the temperature at which the anomalous heat capacity begins. Above this temperature, rapid motion of the molecules from one lattice site to another effectively reduces the magnetic interactions to zero due to an averaging out. The slowing down of this diffusion process allows the interactions between neighboring molecules to become effective. Unfortunately, this measurement is the only significant NMR result for deuterium. The remainder of the discussion refers to the NMR data for hydrogen. Reif and Purcell (11) and Sugawara et al. (35) have explained the removal of the rotational degeneracy of the ortho hydrogen molecule by the assumption of an asymmetric crystalline potential. In this potential field the J=1 state of an ortho molecule splits into three sublevels. When one of the nearest neighbor ortho molecules to a central ortho molecule makes a transition from one sublevel to another, the magnitude of the potential field and its orientation change. These changes result in different sublevel energies and direction for the rotational axis of the central molecule, which in turn affects the potential of surrounding molecules. These phenomena set in cooperatively throughout the crystal. As the temperature is reduced, the higher sublevels will depopulate. This depopulation makes the crystalline potential still more anisotropic and fixes its orientation, and finally the entire rotational degeneracy is removed. A single broad resonance line results from these intermolecular interactions of the ortho molecule.

At a temperature slightly lower than the thermodynamic transition temperature, there is a splitting of the resonance line due to the magnetic interaction between two protons in the same molecules. This intramolecular interaction is comparable to the effect in CaSO₄·2H₂O. In
this case the H$_2$O's, which cause the resonance splitting, are known to be fixed. In the Reif and Purcell and Sugawara experiments, both the single intermolecular and two intramolecular resonance bands are observed at the same time. This overlap can be explained by a random distribution of ortho molecules in the lattice. Each ortho molecule does not necessarily have the same number of other ortho molecules as its nearest neighbors. In addition there may be a variation in the distribution of ortho nearest neighbors around molecules with the same number of nearest neighbors. Thus at temperatures where a large number of molecules may have undergone the cooperative orientation, there are still small regions where the ordering process is just beginning.

If the para hydrogen molecule is regarded as spherically symmetric, it does not cause anisotropy in the crystalline field. Therefore, a particular ortho molecule surrounded by nearly all para molecules will see essentially an isotropic field. This condition might well account for the absence of a sharp transition in deuterium of low para content, since a para molecule will be almost completely surrounded by spherically symmetric ortho deuterium molecules. For hydrogen of low ortho content, the intramolecular splitting does not occur. Reif and Purcell did not detect any splitting at 1.160K for solid normal deuterium.

The results of Sugawara et al. and Smith and Housley (36) for the variation of transition temperature with ortho hydrogen content are represented by the dashed line in Figure 7. This NMR transition temperature does not necessarily correspond to the thermodynamic transition temperature. The NMR transition temperature is taken as the temperature at which the resonance line starts to split. This splitting may start to occur when the rotational effect takes place, but not necessarily so. In cool-
ing the calorimetric samples in this research, considerable supercooling was observed. Smith and Housley stated that their experimental temperatures were held constant after cooling the sample for as much as several minutes to produce thermal equilibrium. The observations of this investigator indicate that this time is too short for thermal equilibrium to be established in the samples. The equilibrium established was between the thermometer and the bath, and not the thermometer and the sample. The deviation of the NMR and calorimetric results is of the type to be expected if Newtopian cooling took place in the NMR experiments. The higher NMR transition temperatures on warming, when isolation is present, confirm this view. Reif and Purcell (11) in measurements of the transition temperature reported a hysteresis on cooling a second time from 1.35°K to 1.16°K. This effect was caused by ortho-para conversion of the hydrogen and not hysteresis. The decrease in ortho content caused a transition temperature shift downward at the rate of 0.04 to 0.06°K per hour. A three to five hour re-cycling would be sufficient to move the transition to 1.16°K from 1.35°K. Reif and Purcell's own statement of an increase in central line intensity on standing indicates the validity of this reasoning.

Theoretical treatments by several investigators (37-42) indicate that quadrupolar interactions are the dominant interactions producing the splitting of the rotational sublevels. This interaction exists only for ortho-ortho pairs in hydrogen and para-para pairs in deuterium, provided the distribution of the molecular axis is spherically symmetric for para hydrogen and ortho deuterium. For a model involving only nearest neighbors, irrespective of whether they are para or ortho, the quadrupolar terms vanish identically after summation, if unlike pairs are in-
volved. Thus, the J=1 level of a para deuterium molecule surrounded by ortho molecules is not split by quadrupolar interactions. Nakamura (37) suggested that the heat capacity for low ortho hydrogen concentration, where the quadrupolar interactions are small, would be dependent on the ortho concentration and that the origin of the splittings is the vibration of the ortho molecules in the lattice. This type of splitting would give rise to a Schottky type anomaly. Gonzalez (43) has shown that a Schottky treatment does not fit the data at low J=1 concentration in deuterium.

Friedman et al. (44) have shown that the critical constants, boiling points, triple point constants, and vapor pressures of six isotopic hydrogen molecules have an empirical relationship based on the square root of the molecular weights. A similar relationship is applicable for the transition temperatures of hydrogen and deuterium at a particular J=1 concentration. This is approximately the type of relationship to be expected if the cooperative effect is initiated by quadrupolar interactions. Since the quadrupole moment is determined by the electronic structure, it should be identical for hydrogen and deuterium. Therefore, the ratio of the quadrupolar interactions of deuterium to that of hydrogen, assuming only nearest neighbor interactions are important, should be equal to \( \frac{r^5_D}{r^5_H} \), where \( r \) is the average distance of separation of the quadrupoles in the lattice. From the available x-ray data, (29) this ratio is estimated to be approximately 1.3. In comparing the Raman spectra of solid para hydrogen and ortho deuterium, Bhatnagar et al., (45) assuming only quadrupolar interactions at nearest neighbor distances, found the \( r^5 \) ratio to be 1.3. The difference between 1.3 and 1.3 (i.e., the square root of 2) can be attributed to the lack of good structural data on which the \( r^5 \) calculations
were based, the assumption of nearest neighbor interactions only, and the method of averaging for a lattice of particular symmetry, as well as the small contribution of other forces (e.g., exchange and dispersion forces) to the interaction. The number of nearest neighbors in hydrogen and deuterium will be the same if the crystal structure is the same. The most recent x-ray data (29) yield a body-centered tetragonal structure for both deuterium and hydrogen. However, as previously discussed, it is doubtful that the structure of solid hydrogen or deuterium can be characterized by experiments that do not consider the ortho-para composition. An unambiguous determination of the crystal structure of both isotopes is imperative before the formidable task of developing a theory capable of a quantitative explanation of the cooperative behavior is attempted. Existing theories (37-42) formulated in the absence of such knowledge can at best provide a qualitative explanation.

The high pressure studies of McCormick (46) on normal hydrogen permit another approach to the nature of the interactions giving rise to the transition. Assuming identical structures, if hydrogen were compressed to the deuterium volume for a particular J=1 concentration, the transition should occur at the same temperature in hydrogen as in deuterium. The NMR experiments unfortunately were not too definitive due to the higher rate of ortho-para conversion in hydrogen under pressure. Therefore, the exact ortho-para composition is unknown in these experiments. Also the only temperature McCormick reported was 3.1°K for a pressure of 2300 atmospheres (which might be 25% higher). At this pressure the molar volume is ± 2% cm³/mole. The molar volumes of hydrogen and deuterium at solid-vapor equilibrium at 4.2°K are 22.65 cm³/mole and 19.56 cm³/mole, respectively. McCormick indicated a linear relationship with pressure
for the transition temperature as determined from NMR splitting. From this information it is possible to estimate the transition temperature of hydrogen which has a molar volume of 19.56 cm$^3$/mole, the molar volume of deuterium at 4.2°K. This temperature is found to be 2.1°K and is in agreement with the deuterium results, if the composition is 70% ortho, or in other words if the ortho content only changed 5% in the course of the experiment.

Because of the large uncertainties in the experiments and estimates, the preceding agreement may be fortuitous. Nevertheless, this result together with the $1.14$ ratio of the deuterium to hydrogen transition temperatures does suggest that the cooperative transition in both solids arises from identical interactions, probably principally quadrupolar, where the magnitude of the interactions depends only on the relative separation (and orientation) of the molecules in the crystal.

IV. Heat Capacity of Solid HD

The only previous thermal data for solid HD were the values reported in Woolley, Scott, and Brickwedde. (26) As seen in Figure 6, the slope of this data is not similar to the slopes for $H_2$, $D_2$, and the HD of this research. The hydrogen data were taken from the para hydrogen data of Hill and Lounasmaa (47) for the lower temperatures and from Johnston et al. (6) for the higher temperatures. The ortho deuterium data of Hill and Lounasmaa (47) for the lower temperatures and the data of Kerr et al. (7) for the higher temperatures were smoothed in the overlap region by means of the data of this research. No particular stress is placed on the HD results below 5°K for the reasons discussed in the section on errors. The data are reported for the lack of any other data.
Freeman (U8) has suggested the possibility of orientational entropy at low temperatures due to the unequal size of the hydrogen and deuterium nuclei in HD. The data indicate a larger heat capacity for HD than for hydrogen and deuterium below 50K. However, as mentioned previously, the data is not too reliable. Measurements of the heat capacity of a large sample would be desirable.

Between 5-100K the relationship of the three isotopes, all in the J=0 state, is in agreement with theoretical predictions from zero point energy consideration with the HD being closer to the D2 than to the H2 as predicted by Hobbs. (U9) This effect is more pronounced between 6.5-7.50K than elsewhere. Making a correction to C, the calculated Debye θ's are 99, 103, and 108 for D2, HD, and H2, respectively, for this temperature range. Using the relation \( E_0 = \frac{9}{8} R \theta \) where \( E_0 \) is the zero point energy, the values of \( E_0 \) for D2, HD, and H2 are 221, 230, and 241 cal/mole, respectively.

V. Para-ortho Conversion in Solid Deuterium

Motizuki (25) has treated theoretically the para-ortho conversion in solid deuterium assuming it arises from magnetic dipole-dipole interactions of molecular pairs and the coupling of the nuclear quadrupole of one molecule with the total quadrupole moment of the other. She considered the energy of conversion to be taken up by the lattice vibrations. On the basis of the Debye approximation for lattice vibrations, she considered the one phonon emission process to be the most important. Unlike hydrogen, deuterium has two nuclear states for the molecule that can interact nuclear-magnetically. The I=1 state for the para molecule can interact with other para molecules or it can interact with the I=2 state
of the ortho molecule. Both interactions cause the para-ortho conversion. The para concentration \(c\) then changes with time according to the equation

\[
\frac{dc}{dt} = -kc^2 - k'c(1-c) = -k'c - (k' - k)c^2
\]

with \(k = 1.27 \times 10^{-3}\) per hour and \(k' = 1.78 \times 10^{-3}\) per hour, as calculated by Motizuki.

The experimental and theoretical \((dc/dt)'s\) are compared in Table XVI. Following the usual practice of expressing the rate in per cent, the value is approximately 0.1% per hour. The two values for 59.4% para represent two coolings of the same sample, the second cooling being the faster rate. This faster rate probably reflects a closer packing of the solid on recooling, though it should be mentioned that the sample was not melted before recooling. Motizuki based her calculations on a hexagonal close-packed structure, though some recent experiments by Kogan et al. (31) indicate a body-centered tetragonal structure for deuterium. The latter structure would reduce the calculated conversion rate by one-sixth based on the number of nearest neighbors. Since the interaction of the magnetic dipole with the rotational magnetic moment is small compared to other interactions, no apparent change should be observed above and below the transition, as was the case. No measurements were made in the transition region because the higher heat capacity reduced thermal diffusivity.
References

   (b) Hund, ibid., 42, 93 (1927).


Autobiography

I, George Ernest Grenier, was born in Hartford, Connecticut on October 17, 1930. I received my Bachelor of Science degree from MIT, working in its low temperature laboratory under C. C. Stephenson. While at MIT I was elected a member of Sigma Xi. I worked in the low temperature laboratory of E. F. Westrum, Jr. at the University of Michigan from which I received the Master of Science degree. While at Michigan, I held a University Scholarship. In October, 1955, I received a research assistantship at Ohio State University to work on the heats of solution of sodium borates. In April, 1956, I was appointed a Research Fellow to work on an AEC problem in the Cryogenic Laboratory of the Department of Chemistry.