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ESTIMATED HEAT CAPACITY, ENTHALPY, THERMAL CONDUCTIVITY, AND DIFFUSIVITY OF SOLID D-T

P. C. Souers

R. T. Tsugawa

May 4, 1976

MASTER

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Symbols

All terms refer to properties measured along the saturated solid-vapor boundary. The subscript "S" denotes saturation for total properties only.

A_L	Low-temperature heat capacity constant ($J/mole-K^4$)
B_L	Amplitude constant in empirical equations for enthalpy and heat capacity ($J/mole-K^{(1+n)}$)
C_L	Crystal lattice heat capacity ($J/mole-K$)
C_Q	Quadrupolar [m_J -sublevel] heat capacity ($J/mole-K$)
C_Q^m	Quenched, metastable quadrupolar heat capacity ($J/mole-K$)
C_R	Rotational [J -level] heat capacity ($J/mole-K$)
C_R^m	Quenched, metastable rotational heat capacity ($J/mole-K$)
C_S	Total saturated heat capacity ($J/mole-K$)
ΔC_S	Total heat capacity difference between metastable and equilibrium hydrogen ($J/mole-K$)
c	Mole fraction of $J = 1$ molecules in a mixture of $J = 0$ and $J = 1$ (dimensionless)
c_J	Mole fraction of molecules in the J^{th} rotational level with any number of total levels (dimensionless)
D_S	Total saturated thermal diffusivity (m^2/s)
d	Crystal or crystallite size (m)
E_R	Rotational internal [J -level] energy as obtained from statistical mechanics for a perfect gas ($J/mole$)
E_R^m	Quenched, metastable rotational internal energy ($J/mole$)
E_Q	Quadrupolar [m_J -sublevel] internal energy ($J/mole$)
ΔE_J	Rotational energy gap from the $J = 0$ level to the J^{th} level ($J/mole$)
g_C	Number of nuclear and molecular states in $J = 0$ rotational energy level (dimensionless)
g_1	Number of nuclear and molecular states in $J = 1$ rotational energy level (dimensionless)

g_2	Number of nuclear and molecular states in $J = 2$ rotational energy level (dimensionless)
H_L	Crystal lattice enthalpy (J/mole)
H_Q	Quadrupolar enthalpy (J/mole)
H_Q^m	Quenched, metastable quadrupolar enthalpy (J/mole)
H_S	Total saturated enthalpy (J/mole)
ΔH_S	Total enthalpy difference between metastable and equilibrium hydrogen (J/mole)
I	Nuclear spin quantum number (dimensionless)
J	Molecular rotational quantum number (dimensionless)
K_d	Thermal conductivity due to crystallite boundary scattering (W/m-K)
K_{rad}	Thermal conductivity of heavily irradiated solid hydrogen (W/m-K)
K_S	Total saturated thermal conductivity (W/m-K)
K_u	Thermal conductivity due to Umklapp processes (W/m-K)
k	Boltzmann constant (1.381×10^{-23} J/molecule-K)
m_J	Molecular rotational sublevel quantum number (dimensionless)
n	Temperature exponent in empirical equations for enthalpy and heat capacity (dimensionless)
Q_R	Molecular rotational partition function (dimensionless)
Q_Q	Quadrupolar partition function (dimensionless)
R	Gas constant (8.314 J/mole-K)
T	Temperature (K)
u	Speed of sound (m/s)
λ_u	Phonon mean free path determined by Umklapp processes (m)
ρ_S	Density of solid (mole/m ³)
θ_D	Debye temperature (K)
θ_D^0	Debye temperature at 0 K (K)
θ_R	Molecular rotational temperature (K)
θ_Q	Quadrupolar temperature (K)

ESTIMATED HEAT CAPACITY, ENTHALPY, THERMAL CONDUCTIVITY, AND DIFFUSIVITY OF SOLID D-T

Abstract

We continue our program to estimate the physical properties of the thermonuclear fusion fuel, D-T (actually the mixture deuterium-deuterium tritide-tritium). We review the literature on the heat capacity and thermal conductivity of solid hydrogen, hydrogen deuteride, and deuterium. Our discussion of heat capacity and its attendant enthalpy deals with the crystal lattice, rotational, and quadrupolar mechanisms. For thermal conductivity, we describe phonon scattering at crystallite boundaries and self-collisions (Umklapp processes) that reduce the phonon mean free path. We then discuss the effect of rotational energy in either reducing crystallite size or causing phonon scattering from quadrupolar sublevels. Thermal diffusivity is derived from the above properties plus density. Finally, we estimate all the properties for the solid D-T mixture. Thermal conductivity and diffusivity prove especially interesting because they may vary as much as five orders of magnitude as a function of temperature, rotational energy, and radiation damage.

Introduction

The physical properties of cryogenic heavy hydrogen will be of increasingly strong interest in research on hydrogen fusion by laser implosion,¹ electron beam implosion,² and magnetic confinement.³ To aid future cryogenic engineering, we have begun a program to experimentally measure the important properties of D-T [actually the mixture deuterium-deuterium tritide-tritium (D_2 -DT- T_2)].⁴ We are also reviewing a number of physical properties of hydrogen to extrapolate the values for D-T. This program includes collecting and correlating all the related literature data we can. To date, we have reviewed the phase diagram;⁵ liquid density, surface tension, and viscosity;⁶ solid density and refractive index in all phases;⁷ and infrared vibration-rotation spectra in the 2- to 5- μ m region.⁸ A recent publication summarizes these reviewed properties.⁹

For this report, we shall review the literature data for solid hydrogen (H_2), hydrogen deuteride (HD), and deuterium. We shall also estimate

the heat capacity, enthalpy, thermal conductivity, and thermal diffusivity of solid D_2 -DT- T_2 . For our calculations, we shall fix the D-T ratio at 1:1 to simulate actual fusion fuel. Our calculations shall involve five of the six solid hydrogens (hydrogen tritide shall be omitted).

Cryogenic hydrogen studies center about the triple points, where gas, liquid, and solid are in equilibrium. The pure component hydrogens have the following triple point temperatures and pressures:¹⁰

Isotope	Temperature (K)	Pressure (Pa)
H_2^*	13.80	7 042
HD	16.60	12 400
D_2^*	18.7	17 139
DT	19.7 ⁺	19 400 ⁺
T_2^*	20.6	21 600

All properties in this report are those along the solid-vapor equilibrium line; i.e., they are the "saturated" properties. We shall not, therefore, use "S" subscripts to denote saturation except for "total," summed properties.

The species DT is a pure isotopic form of hydrogen. However, it will chemically equilibrate by the reaction

at a rate that is unknown. The equilibria of this reaction have not been measured at low temperatures but calculations have been made.¹¹ These calculations show that "real" 1:1 D-T will be a solution of the components D_2 -DT- T_2 in the proportions: 0.46/0.08/0.46 at 4.2 K and 0.31/0.38/0.31 at the triple point of 19.7 K (estimated). We shall use these proportions in our D-T calculations.

*Actually, for equilibrium- H_2 and equilibrium- D_2 , with the terms to be defined shortly. Tritium is probably the equilibrium form.

⁺Estimated.

The heat capacity of the solid hydrogens is a sum of three mechanisms. In descending order of importance, they are: vibrations of the crystal lattice, rotation of the molecule, and deviations of molecular rotation caused by electric quadrupole forces. The crystal lattice heat capacity is zero at 0 K and increases steeply as the temperature cubed.

Total enthalpies are quite small. For fully equilibrated D-T, we calculate 0.14 J/mole at 4.2 K and 143 J/mole at the triple point. This may be compared with the estimated heat of fusion, which is about 200 J/mole. We do not expect the presence of radiation (from tritium) to increase the heat capacity significantly, although energy may instead be bound up in point defects.

Heat travels through a hydrogen crystal mainly by vibration of the lattice. These thermal waves are thought to be impeded at low temperatures by crystallite boundaries that cannot be seen in the optically transparent crystals. These invisible crystallites decrease in size with increasing rotational energy possessed by the molecules.

At higher temperatures, the heat transfer is "self-impeded" by the Umklapp processes. Therefore, thermal conductivity is low at high and low temperatures and peaks in-between. The highest peak corresponds to a thermal conductivity between that of room temperature iron and tungsten. The lowest measured conductivity (at 0.2 K) is like that of room-temperature air -- a good insulator. At the triple point, the thermal conductivity is like that of glass or water. Intense radiation may lower the thermal conductivity as much as five decades at low temperatures but should have little effect near the triple point. The time needed for radiation effects to take place is completely unknown.

Heat capacity and enthalpy may be estimated for D-T without too many qualms. However, the thermal conductivity, which ranges over four to five decades depending on the particular parameters, leaves many uncertainties. These uncertainties are passed on directly to the thermal diffusivity.

A knowledge of the thermal conductivity will be essential for any fusion application involving frozen DT. This property varies many decades between insulator and conductor. A knowledge of its eccentricities will be essential to engineering the removal of any large amount of radioactive decay heat. Several questions are of considerable scientific interest: Do crystallites really exist in solid hydrogen? What kind of radiatic damage takes place?

Are the rotational or quadrupolar energies available for heat conduction?

In summary, we present estimated values of heat capacity, enthalpy, thermal conductivity, and thermal diffusivity for solid D-T. These values, in the absence of actual data, will allow materials engineering of upcoming cryogenic laser targets. We feel that a measurement of the thermal conductivity of solid D-T is of high priority (because we expect it to vary as much as five decades as a function of temperature, rotational energy, and radiation damage).

Experimental Data for Crystal Lattice Heat Capacity

Considerable solid heat capacity data has been taken.¹²⁻³⁰ Most of it is saturated or at constant pressure, which we shall take to be the same. This is because H_2 vapor pressure at 25 K, our highest temperature of interest, is only 0.3 MPa (3 atm); and this is not enough to compress the crystal lattice. We shall not consider pressure studies that yield heat capacity at constant volume.

A quick listing of solid hydrogen heat capacity data includes: H_2 ¹²⁻²³; HD ^{13,24,25}; and D_2 ^{13,16,19,20,22,26-30}. Mixtures of H_2 and D_2 are also reported.¹⁹⁻²² Much of the data is reported in the recent National Bureau of Standards (NBS) cryogenic hydrogen survey.³¹ Figure 1 shows some heat capacity data for solid H_2 .³¹ The rotational effects* (to be described later) are quite obvious at low temperatures but die out as the temperature is raised. We shall first consider only data that contain no rotational effects. Such data are a function of the crystal lattice heat capacity, C_L .

The crystal lattice heat capacity arises from lattice vibrations, which form a continuous spectrum of energies up to some cutoff point. The cutoff energy is directly proportional to the Debye temperature, θ_D , of the lattice. The heat capacity associated with lattice vibrational energy levels rises steeply at low temperatures, then saturates and becomes constant at high temperatures - a characteristic of systems with an infinite number of energy levels. The saturation occurs at actual temperatures comparable to θ_D . The Debye function used in this theory does not admit of a simple analytical

*The numbers in Fig. 1 are the mole fractions of H_2 molecules in the first excited rotational state ($J = 1$). The remainder are in the ground state ($J = 0$). Data "without rotational effects" actually have a 0 to 2% $J = 1$ admixture.

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*The numbers in Fig. 1 are the mole fractions of H_2 molecules in the first excited rotational state ($J = 1$). The remainder are in the ground state ($J = 0$). Data "without rotational effects" actually have a 0 to 2% $J = 1$ admixture.

Fig. 1. Total saturated heat capacity, C_S , of solid H_2 . Hatched line represents hcp-fcc transformation; c represents mole fraction $J = 1$ state.

expression, but for temperatures less than $0.1 \theta_D$, the heat capacity reduces to the form

$$C_L = A_L T^3, \quad (1)$$

where C_L is the lattice heat capacity along the saturation line of solid-vapor equilibrium and A_L is the low-temperature heat-capacity constant.³²

From eq. (1), we expect A_L to be a constant. In practice, this is not quite true and many slightly different values of A_L have appeared in the literature. We, therefore, summarize all crystal lattice heat capacity data in Fig. 2, which shows A_L plotted as a function of temperature for H_2 ,¹³⁻¹⁷ HD,^{13,24,25} and D_2 .^{13,16,26,28} It can be seen that A_L is not truly constant but rises to a peak at about 12 K.* We note (with details to follow) that θ_D for solid hydrogen is 100 - 120 K, so that the $0.1\theta_D$ mark is exceeded near the triple points. For temperatures above $0.1\theta_D$, the Debye function grows less rapidly than T^3 . This produces the downward turn seen at high temperatures in Fig. 2. The upward behavior of A_L in Fig. 2 is caused by a decrease in θ_D with increasing temperature. This is shown in Fig. 3 for Debye

Fig. 2. Low-temperature heat capacity constant, A_L , of $J = 0$ solid hydrogen.

*There is considerable scatter in the high-temperature HD data, but the downward points of Ref. 24 are undoubtedly the best. The $J = 1$ molecules in low concentration cause a rise at 2 K.

Fig. 3. Debye temperatures of the solid hydrogens (from C_p data).

temperatures (from the literature) as derived from the heat capacity data.^{13,16,21-26, 28,30} From further theory, we expect A_L to be proportional to θ_D^{-3} . If θ_D decreases, A_L becomes larger. Hence, two effects combine to render A_L not really a constant.^{32,33}

We now return to summarize the A_L data of Fig. 2. We have chosen to break the curves into three temperature intervals, so that a function capable of easy integration may be used. The heat capacity is this function multiplied by T^3 , or just

$$C_L = B_L T^n. \quad (2)$$

The enthalpy associated with the lattice is

$$H_L = \frac{B_L T^{n+1}}{n+1} - (\text{constant}). \quad (3)$$

Table 1 contains the numerical constants for calculating the heat capacity and enthalpy for H_2 , HD, and D_2 from 0 K to the triple points. The constants B_L and n in the enthalpy equations have been adjusted for all lower-temperature intervals.

We have used Eqs. (2) and (3) with Table 1 and calculated values of C_L and H_L at various temperatures for the hydrogens. Table 2 shows these. Because the HD and D_2 data are almost the same, we use D_2 data to estimate DT and T_2 values. The triple point enthalpies increase from D_2 to T_2 even with the use of the same data, however, because triple point temperatures increase from D_2 to T_2 . We note also the extremely small H_L and C_L values at liquid helium temperature.

As approximate equations for the hydrogens in the range 0 K to the triple points, we compress Table 1 to the forms

$$C_L \approx \begin{cases} 1.7 \times 10^{-3} T^3, & H_2 \\ 2.0 \times 10^{-3} T^3, & \text{all others,} \end{cases} \quad (4)$$

J/mole - K,

$$H_L \approx \begin{cases} 4.2 \times 10^{-4} T^4, & H_2 \\ 5.0 \times 10^{-4} T^4, & \text{all others,} \end{cases} \quad (5)$$

J/mole .

Table 1. Heat capacity and enthalpy of the hydrogen crystal lattice. Using D_2 values for DT, we estimate at the triple point of 19.7 K, $C_L = 13.5$ J/mole-K, $H_L = 74$ J/mole. For T_2 , we estimate at the triple point of 20.6 K, $C_L = 15.1$ J/mole-K, $H_L = 87$ J/mole. All enthalpy equations have been adjusted for the lower temperature segments preceding them.

Isotope	Saturated crystal lattice heat capacity, C_L (J/mole-K)				
	H_2 (0-4.5 K) HD, D_2 (0-6 K)	H_2 (4.5-12 K) HD, D_2 (6-12 K)	12K to the triple point	Values at 4.2 K	Values at triple points
H_2	$1.27 \times 10^{-3} T^3$	$6 \times 10^{-4} T^{3.50}$	$6 \times 10^{-4} T^{3.50}$	0.09	5.9 at 13.80 K (0 J=1) 6.1 at 13.96 K (n-)
HD	$1.82 \times 10^{-3} T^3$	$1.1 \times 10^{-3} T^{3.29}$	$1.05 \times 10^{-2} T^{2.38}$	0.13	8.4 at 16.60 K
D_2	$1.82 \times 10^{-3} T^3$	$10^{-3} T^{3.34}$	$8.8 \times 10^{-3} T^{2.46}$	0.13	11.9 at 18.7 K (0 J=1; n)
	Saturated crystal lattice enthalpy, H_L (J/mole)				
	H_2	H_2	H_2		
H_2	$3.18 \times 10^{-4} T^4$	$1.33 \times 10^{-4} T^{4.5}$	$1.33 \times 10^{-4} T^{4.5}$	0.10	17.9 at 13.80 K (0 J=1) 18.9 at 13.96 K (n-)
HD	$4.55 \times 10^{-4} T^4$	$2.56 \times 10^{-4} T^{4.29}$	$3.11 \times 10^{-3} T^{3.38-2.9}$	0.14	39 at 16.60 K
D_2	$4.55 \times 10^{-4} T^4$	$2.30 \times 10^{-4} T^{4.34}$	$2.54 \times 10^{-3} T^{3.46-2.7}$	0.14	61 at 18.7 K (0 J=1; n-)

Table 2. Smoothed values of crystal lattice heat capacity and enthalpy.
From Eqs. (2) and (3) and Table 1.

Temperature (K)	Lattice heat capacity, C_L (J/mole-K)			Lattice enthalpy, H_L (J/mole)		
	H ₂	HD	D ₂	H ₂	HD	D ₂
2	0.01	0.01	0.01	0.005	0.007	0.007
4	0.08	0.12	0.12	0.08	0.12	0.12
6	0.32	0.39	0.39	0.42	0.59	0.59
8	0.87	1.0	1.0	1.5	1.9	1.9
10	1.9	2.1	2.2	4.2	5.0	5.0
12	3.6	3.9	4.0	9.6	10.9	11.1
13.80	5.9	5.4	5.6	17.9	19.3	19.6
13.96	6.1	5.6	5.8	18.9	20.1	20.5
14	-	5.6	5.8	-	20.4	20.8
16	-	7.7	8.1	-	33.6	34.5
16.60	-	8.4	8.8	-	38.5	39.6
18	-	-	10.8	-	-	53.3
18.7	-	-	11.9	-	-	61.3
19.7	-	-	(13.5) ^a	-	-	(73.9) ^a
20	-	-	(14.0) ^a	-	-	(77.9) ^a
20.6	-	-	(15.1) ^a	-	-	(86.9) ^a

^aExtrapolated for HT and T₂. For lower temperatures, use D₂ values as estimates (in parentheses).²

We may also simplify the Debye temperature data of Fig. 3, using mostly the data of Ref. 16. We employ the empirical formula

$$\theta_D = \theta_D^0 - 1.6T, \quad (6)$$

where θ_D^0 is the Debye temperature at 0 K and has values of 120, 110, and 110 K for H_2 , HD, and D_2 . The HD is extremely scattered, but we feel the 0 K value of 110 K to be the more accurate value at this time.²⁴ Both the H_2 and D_2 data yield 1.6 for the second constant in Eq. (6), and the same value is assumed for HD. We assume θ_D^0 estimates of 110 K for both DT and T_2 , along with the same temperature coefficient of 1.6. Eqs. (2) and (6) are the best fits to the data, and they will not perfectly relate to each other through the Debye function.

Finally, the heat capacities of H_2 - D_2 mixtures have been measured from 0.6 - 5 K²² and from 8 K to the triple point mixtures.^{19,20} Within error, the lattice heat capacities of the mixtures may be equated to the linear combinations of the pure component heat capacities.

Description of Rotational Energy Levels

The diatomic hydrogen molecules possess rotational energy levels, described by the quantum number J. The molecules are spread over many energy levels at room temperature but are almost completely in the J = 0 and 1 states below 25 K. When the temperature is rapidly lowered, species such as HD or DT deexcite rapidly because of their lack of molecular symmetry. They are always in the equilibrium (e) state. The equilibrium of states at room temperature is called normal (n).

Because of their molecular symmetry, H_2 , D_2 , and T_2 do not totally deexcite when the temperature is quickly lowered. All of the even-numbered rotational levels drop to the J = 0 ground state; all of the odd-numbered levels fall to the J = 1 first excited state. However, the J = 1 to J = 0 excitation takes weeks unless catalyzed. For example, T_2 will equilibrate in tens of minutes because of the catalyzing effects of its beta particle.^{5,34-36} Because the J = 1 to J = 0 deexcitation is almost completely forbidden for H_2 , D_2 , and T_2 , we have the possibility of holding large quantities of metastable rotational energy upon dropping the temperature. We are able,

for example, to have room temperature H_2 and D_2 stable for days at cryogenic temperatures.

Thus, H_2 , D_2 , and T_2 , each separate into "types" of hydrogen. The type with even-numbered J-levels we call "symmetric", although it is more commonly called "para" for H_2 and T_2 and "ortho" for D_2 . The type with odd-numbered J-levels we call "antisymmetric", although it is commonly called "ortho" for H_2 and T_2 and "para" for D_2 . Actual hydrogen is a mixture of symmetric and antisymmetric forms with the same definition of equilibrium and normal.

The possession of metastable rotational energy has little effect on most physical properties of the hydrogens. This is especially true in the gas and liquid phases. Rotational effects are of extreme importance, however, in the description of the thermal properties of the solid. We shall carefully delineate the two mechanisms caused by population of the molecular rotational energy levels.

The term "rotational," as applied to heat capacity, can be confusing, because there are two distinct mechanisms. The first is heat absorbed by transitions to higher rotational states of the diatomic molecule. These rotational states have a quantum number label, J, with zero being the ground state. There are an infinite number of rotational levels, although only the lowest two are of major importance below 25 K. The term "rotational," with the subscript "R," will be applied to properties associated with these J-levels.

A second set of rotationally related properties occurs only in the solid state. An internal force, due largely to electric quadrupolar interactions, creates a magnetic field that splits each rotational J-level into $2J + 1$ sublevels labeled with the quantum number, m_J . We shall call the thermal properties associated with these sublevels "quadrupolar," with the subscript "Q."

In this section, we shall calculate the rotational level populations; i.e., the number of molecules in the various J-levels. The splittings of the rotational levels are given by the rotational temperature, θ_R , which may be considered a constant for each species. It declines with molecular weight and has the following values: $H_2=87.5$ K, $HD=65.7$ K, $D_2=43.8$ K, $DT=36.7$ K (our estimate), and $T_2=29.2$ K.³⁷²

We have already mentioned the metastable aspects of the rotational energy for the species: H_2 , D_2 , and T_2 . We now add a second property peculiar to these three species, but not present in HD and DT. In the H_2 ,

D₂, and T₂ molecules, the rotational and nuclear magnetic fields lock together. This means that the distribution of rotational states partly depends on the number of nuclear magnetic states.

Let us consider HD and DT first, since their case is simpler. The rotational partition function, Q_R, is^{38,39}

$$Q_R \text{ (HD and DT)} = \sum_{J=0}^{\infty} (2J+1) \exp \left[- \frac{J(J+1)\theta_R}{T} \right]. \quad (7)$$

This basic function contains, for HD and DT, only rotational components - no nuclear effects enter. The energy jump to the Jth rotational level from the ground state is

$$\Delta E_J = J(J+1) R\theta_R. \quad (8)$$

The fractional population of the Jth level, c_J, is

$$c_J = \frac{(2J+1) \exp \left[- \frac{J(J+1)\theta_R}{T} \right]}{Q_R}. \quad (9)$$

For H₂, D₂, and T₂, the nuclear and rotational magnetic moments are locked together. The rotational partition function will actually be a product of rotational and nuclear terms. The nuclear spin quantum numbers, I, for H, D, and T in their ground states are 1/2, 1, and 1/2, respectively. For H₂ and T₂, the two 1/2 values combine to yield a total molecular nuclear spin of 0 or 1. Each of these states possesses (2I + 1) substates, or 1 and 3, respectively. The I = 0 nuclear state combines with the odd-numbered J-levels and the I = 1 nuclear states combine with the even-numbered J-levels. The partition function for H₂ and T₂ is

$$Q_R \text{ (H}_2 \text{ and T}_2\text{)} = \sum_{\substack{J=0 \\ \text{Even}}}^{\infty} (2J+1) \exp \left[- \frac{J(J+1)\theta_R}{T} \right] + 3 \cdot \sum_{\substack{J=1 \\ \text{Odd}}}^{\infty} (2J+1) \exp \left[- \frac{J(J+1)\theta_R}{T} \right]. \quad (10)$$

We see that the partition function splits into two parts, corresponding to the two "types" of hydrogen. The even-J term is the symmetric (para) and

the odd-J antisymmetric (ortho). We shall use the old symmetric-antisymmetric terminology from Dennison's 1927 heat capacity paper,⁴⁰ because the more widespread ortho-para terms are reversed in definition for D_2 , thus causing confusion.

At high temperatures (room temperature is close), the rotational populations of H_2 and T_2 spread over many levels. We find 25% in the symmetric state and 75% in the antisymmetric, corresponding to the 1 and 3 weightings of the terms in Eq. (10). The term "ortho" refers to that type in greater quantity at room temperature.

For D_2 , the nuclear spins of $I = 1$ combine to yield the molecular sums of 0, 1, and 2, with $(2I + 1)$ sublevels of 1, 3, and 5. The six 0 and 2 substates combine with the even-J rotational levels and the three spin 1 substates combine with the odd-J rotational levels. The partition function for D_2 is

$$Q_R(D_2) = 6 \cdot \sum_{\substack{J=0 \\ \text{Even}}}^{\infty} (2J+1) \exp \left[- \frac{J(J+1)\theta_R}{T} \right] + 3 \cdot \sum_{\substack{J=0 \\ \text{Odd}}}^{\infty} (2J+1) \exp \left[- \frac{J(J+1)\theta_R}{T} \right] . \quad (11)$$

At high temperatures, we have 6/9 or 66-2/3% symmetric D_2 and 33-1/3% antisymmetric D_2 , corresponding to the 6 and 3 weightings in Eq. (11). Since the symmetric form is in greater quantity at room temperature, the even-J D_2 is called "ortho" - exactly the opposite from H_2 and T_2 .

We now wish to calculate the equilibrium rotational populations for the saturated hydrogens from 0 to 25 K. In this temperature range, the first three terms ($J = 0, 1$, and 2) are sufficient to calculate all quantities. As we shall see, two terms are generally sufficient. The partition function representing the first three rotational levels is

$$Q_R = g_0 + 3g_1 \exp\left(-\frac{2\theta}{T}\right) + 5g_2 \exp\left(-\frac{6\theta}{T}\right) , \quad (12)$$

where g_0 , g_1 , and g_2 are the number of nuclear spin states associated with the $J = 0, 1$, and 2 rotational levels. These are calculated from Eqs. (7), (10), and (11). They are summarized in Table 3. Using Eq. (9), we calculate the three-level rotational level populations. Figure 4 shows the results.

Table 3. Rotational temperature and number of states associated with first three rotational energy levels.

Isotope	Rotational temperature, $\bar{\epsilon}_R^{37}$ (K)	Number of states			Coefficient for metastable energy, E_R^m $\left(\frac{6g_1}{g_0 + 3g_1} \right)$
		g_0	g_1	g_2	
H ₂	87.5	1	3	1	1.8
HD	65.7	1	1	1	1.5
D ₂	43.8	6	3	6	1.2
DT	(36.7) ^a	1	1	1	1.5
T ₂	29.2	1	3	1	1.8

^aEstimated value.

T₂ is the most easily excited, as we would expect, because it has the lowest rotational temperature.

The experimental data that led to the formation of the hydrogen rotational theory was taken in 1929.⁴⁰ In 1965, the equilibrium symmetric-antisymmetric ratios were measured for H₂ gas at 24 to 248 K, D₂ gas at 22 to 132 K, and T₂ gas at 21 to 77 K.³⁶ The measured and calculated symmetric hydrogen concentrations differed by only 1.6 and 0.6 mole% for H₂ and D₂, but by 6.0 mole% for T₂. It was thought that the tritium beta particle was the cause.

Fig. 4: Calculated rotational populations of the hydrogens from 0 to 25 K. The $J = 1$ line may be considered to represent antisymmetric hydrogen.

Rotational Heat Capacity

Rotational heat capacities and energies* may be calculated from the partition functions of the previous section. We may calculate results for a specific J-level, for the symmetric or antisymmetric sets of terms, or for all J-levels summed together.

The rotational energy, E_R , is the product of energy jumps to a particular level times the fractional population of that level, summed over all levels. This is

$$E_R = \sum_{J=0}^{\infty} \Delta E_J \cdot c_J = RT^2 \frac{1}{Q_R} \frac{dQ_R}{dT} \quad (13)$$

The corresponding heat capacity is

$$C_R = \frac{dE_R}{dT} \quad (14)$$

We shall use the three-term partition function of Eq. (12) for the temperatures 0 to 25 K.

Substituting Eq. (12) into Eq. (13), we obtain the three term, equilibrium internal energy

$$E_R = R\theta_R \left\{ \frac{6g_1 \exp\left(-\frac{2\theta_R}{T}\right) + 30g_2 \exp\left(-\frac{6\theta_R}{T}\right)}{g_0 + 3g_1 \exp\left(-\frac{2\theta_R}{T}\right) + 5g_2 \exp\left(-\frac{6\theta_R}{T}\right)} \right\} \quad (15)$$

The equilibrium heat capacity, C_R , is, from Eq. (14)

$$C_R = R \left(\frac{\theta_R}{T} \right)^2 \left\{ \frac{12g_0g_1 \exp\left(-\frac{2\theta_R}{T}\right) + 180g_0g_2 \exp\left(-\frac{6\theta_R}{T}\right) + 240g_1g_2 \exp\left(-\frac{8\theta_R}{T}\right)}{\left[g_0 + 3g_1 \exp\left(-\frac{2\theta_R}{T}\right) + 5g_2 \exp\left(-\frac{6\theta_R}{T}\right) \right]^2} \right\} \quad (16)$$

*We use the word "energy" for the result of an ideal system and "enthalpy" for a result that has been altered for the peculiarities of an actual system.

The results of these calculations are listed in Tables 4 and 5. Inclusion of the third ($J = 2$) term increases the 25 K value of E_R for DT by 1.4% and that for T_2 by only 1.3%. Thus, we may indeed consider all the hydrogens below 25 K to be essentially a mixture of the $J = 0$ and $J = 1$ states.

We see, further, that equilibrium rotational effects will not affect the heat capacity data of Fig. 2, which is attributed to the crystal lattice. The worst possible case would be 2% $J = 1$ (it is supposed to be "zero") D_2 at the highest temperature, 18.7 K. From Table 5, we see this leads to 0.05 (2.5×0.02) J/mole-K or only 0.4% change in the low-temperature heat capacity constant, A_L , at 18.7 K.

However, H_2 , D_2 , and T_2 may not be in equilibrium states. They may instead be trapped with the metastable symmetric-antisymmetric combination of a higher temperature. The energies involved may be quickly estimated from a consideration of the $J = 0$ and $J = 1$ energy levels [neglect the third term in Eq. (12)]. The energy of the ground state is zero. The total rotational energy is that of the $J = 1$ state multiplied by the fraction of molecules, c , in that state. Freezing in this energy at low temperature is equivalent to setting $T \rightarrow \infty$. All exponential terms equal one. Then the metastable rotational energy, E_R^m , of a fraction c of $J = 1$ molecules would be

$$E_R^m = cR\theta_R \left(\frac{6g_1}{g_0 + 3g_1} \right). \quad (17)$$

For H_2 through T_2 , the term $(6g_2/g + 3g_2)$ has the values 1.8, 1.5, 1.2, 1.5, and 1.8, summarized with other pertinent values in Table 3. We multiply these by the proper rotational constants to get total (i.e., $c = 1$) E_R^m energies of 1310, 819, 437, 458, and 437 J/mole. The HD and DT values are not needed because these species deexcite instantly with a change of temperature. We include the values only for comparison. The most likely values of c to be used are those representing the initial state at room temperature; i.e., normal hydrogen, with $c = 0.75$.

The corresponding two-level heat capacity, representing a fraction c of metastably cooled $J = 1$ species, is

$$C_R^m = cR \left(\frac{\theta_R}{T} \right)^2 \frac{12g_0g_1}{(g_0 + 3g_1)^2} \rightarrow 0, \quad (18)$$

Table 4. Equilibrium rotational energy and total metastable energy of the hydrogens. Calculated from a three-term partition function.

Temperature (K)	Equilibrium rotational energy, E_R (J/mole)				
	H_2	HD	D_2	DT	T_2
2	1×10^{-34}	1×10^{-25}	1×10^{-16}	2×10^{-13}	9×10^{-10}
4	1×10^{-15}	2×10^{-11}	3×10^{-7}	2×10^{-5}	2×10^{-3}
6	3×10^{-9}	1×10^{-6}	5×10^{-4}	9×10^{-3}	0.26
8	4×10^{-6}	2×10^{-4}	2×10^{-2}	0.19	2.9
10	3×10^{-4}	6×10^{-3}	0.17	1.2	12.4
12	6×10^{-3}	6×10^{-2}	0.74	4.0	31.5
13.80	4×10^{-2}	0.24	1.9	8.8	56.2
13.96	5×10^{-2}	0.27	2.1	9.4	58.5
16	0.23	0.89	4.5	18.1	92.2
16.60	0.35	1.2	5.5	21.2	102
18	0.78	2.2	8.3	29.5	126
18.7	1.1	2.9	10.0	34.1	138
19.7	1.8	4.2	12.6	41.2	154
20	2.1	4.6	13.4	43.4	159
20.6	2.7	5.6	15.3	48.1	169
21	3.1	6.2	16.5	50.2	175
22	4.6	8.3	19.9	59.3	190
23	6.5	10.7	23.5	67.6	204
24	8.9	13.6	27.5	76.2	216
25	11.8	16.8	31.6	84.8	229
Total metastable energy, E_R^m (J/mole)					
	1310	819	437	458	437

Table 5. Equilibrium rotational heat capacity of the hydrogens. Calculated from a three-term partition function.

Temperature (K)	Equilibrium rotational heat capacity, C_R (J/mole-K)				
	H_2	HD	D_2	DT	T_2
2	6×10^{-33}	3×10^{-24}	2×10^{-15}	4×10^{-12}	1×10^{-8}
4	1×10^{-14}	1×10^{-10}	2×10^{-6}	9×10^{-5}	7×10^{-3}
6	1×10^{-8}	4×10^{-6}	1×10^{-3}	2×10^{-2}	0.42
8	1×10^{-5}	5×10^{-4}	3×10^{-2}	0.22	2.7
10	6×10^{-4}	8×10^{-3}	0.15	0.87	7.0
12	7×10^{-3}	5×10^{-2}	0.45	2.0	11.9
13.80	4×10^{-2}	0.17	0.88	3.4	15.2
13.96	4×10^{-2}	0.18	0.92	3.5	15.5
16	0.16	0.46	1.5	5.0	17.1
16.60	0.22	0.57	1.7	5.5	17.2
18	0.42	0.89	2.2	6.4	17.0
18.7	0.57	1.1	2.5	6.8	16.6
19.7	0.82	1.4	2.8	7.3	16.1
20	0.91	1.5	2.9	7.5	15.9
20.6	1.1	1.7	3.1	7.7	15.4
21	1.2	1.9	3.2	7.9	15.2
22	1.6	2.2	3.5	8.2	14.4
23	2.1	2.6	3.8	8.4	13.5
24	2.7	3.1	4.1	8.7	12.7
25	3.3	3.5	4.3	8.8	12.0

because when $T \rightarrow \infty$, $C_R^m \rightarrow 0$. Thus, we have no rotational heat capacity due to metastable states at low temperature. This is because the states are frozen as though they were at an infinite temperature.

Description of Quadrupolar Sublevels in Solid Hydrogen

The second type of rotational phenomenon found in solid hydrogen is that associated with the splitting of the J -levels into m_J -sublevels. This interaction is not as well understood as the previously described rotational effect. Hence, we shall briefly trace the history of development in this area.

To summarize an immense amount of work, we find there is a force in solid hydrogen that aligns the rotational magnetic moments of the $J = 1$ molecules. The force is believed to be the rotational electric quadrupole moment of the $J = 1$ molecules themselves. The effect of the force is to create a set of rotational sublevels (of quantum numbers, m_J) with an energy-splitting on the order of several degrees K. When the mole fraction of $J = 1$ molecules surpasses ~ 0.60 , a crystallographic transformation occurs from high-temperature hexagonal-close-packed (hcp) to face-centered-cubic (fcc) structures. Figure 1 shows this transition with the heat capacities. Despite considerable efforts, the exact details of this low-temperature interaction are still unknown.

The discovery of heat capacity peaks in the 2 to 3 K region⁴¹ led Pauling in 1910 to first propose ordering of the $J = 1$ hydrogen molecules.⁴² By 1953, it was found that the nuclear magnetic resonance (NMR) spectra of solid hydrogen with high $J = 1$ concentrations split into two peaks at low temperatures.^{43,44} These peaks are caused by the interaction of the magnetic dipoles of the hydrogen nuclei in the H_2 molecule. At low temperatures, these dipoles "see" each other because molecular motion that normally blocks the view has been frozen. The more order in the sample, the wider is the splitting of the two NMR peaks. It was postulated (but is not believed today) that an internal crystal field separates the $J = 1$ H_2 molecules into two sub-types: those with $m_J = 0$ and those with $m_J = \pm 1$, with a splitting of 4 to 5 K. The former m_J value represents the ground state, the latter the excited state. The application of the dc magnetic field for NMR splits the $m_J = \pm 1$ sublevel so slightly that the conceptual model is unchanged.

In 1954, heat capacity studies of 0.66 and 0.74 $J = 1$ H_2 showed large spikes at 1.3 and 1.6 K (but not at 0.56 $J = 1$ down to 1.15 K).¹⁵ Such spikes, called lambda-points because of their shapes, are characteristic of order-disorder transitions. Such transitions, most common in ferro- or antiferromagnetism, are called "second-order" transitions. Such transitions do not have discontinuities in latent heat or specific volume at the transition

point, but do have discontinuities in the specific heat. The degree of order diminishes as the sample is heated to the transition point. At the transition point, the remaining order may be lost abruptly (first-kind) or gradually (second-kind). The heat capacity lambda-point usually shows a high temperature tail, representing a hysteresis of the transition.⁴⁵ It is also interesting to note that ordered solid H_2 has been described as an antiferromagnet (i.e., ordered spins but no net magnetic moment to the sample).⁴⁶ Because the H_2 spins involved are rotational, the result is an "ordered diamagnetism."

It is difficult to judge the onset of an order-disorder transition. The splitting of the $J = 1$ states into the two postulated substates represents a degree of rotational ordering. The filling of a finite number of these energy levels (i.e., destroying this order) also produces a heat capacity peak and tail. Let us consider a single ground state and a doubly degenerate excited state (i.e., two states at the same energy) separated by an energy gap represented by the quadrupolar temperature θ_Q . The partition function for these magnetic sublevels, Q_Q , is

$$Q_Q = 1 + 2 \exp \left(- \frac{\theta_Q}{T} \right) . \quad (19)$$

We may use the general formulas of the previous section to calculate the energy and heat capacity. Only the fraction of $J = 1$ molecules, c , gives rise to the partition function. The calculated equilibrium quadrupolar energy is

$$E_Q = 2cR\theta_Q \frac{\exp \left(- \frac{\theta_Q}{T} \right)}{1 + 2 \exp \left(- \frac{\theta_Q}{T} \right)} . \quad (20)$$

The calculated equilibrium quadrupolar heat capacity is

$$C_Q = 2cR \left(\frac{\theta_Q}{T} \right)^2 \frac{\exp \left(- \frac{\theta_Q}{T} \right)}{\left[1 + 2 \exp \left(- \frac{\theta_Q}{T} \right) \right]^2} . \quad (21)$$

The heat capacity, C_Q , rises quickly to a peak at a θ_Q/T value of 2.65, then decays in a long tail as T^{-2} . Such a peak is called a Schottky anomaly, which is characteristic of energy absorption by a finite number of energy levels.^{39,47,48} The two-level model, described by the Eqs. (19) to (21), is the simplest conceptual approach to rotational splittings in solid hydrogen.

The next theoretical development, in 1955, has had the largest impact on the theory of low-temperature heat capacity. Nakamura considered the interactions between pairs of H_2 molecules.⁴⁹ He concluded that the interaction between $J = 0$ and $J = 1$ molecules is not important in the hcp lattice (the fcc transformation had not yet been discovered). Of prime importance are the interactions of electric quadrupole moments of neighboring $J = 1$ hydrogen molecules. The three rotational substates ($m_J = -1, 0, \text{ and } +1$) of each molecule then combine to form the nine sublevels shown in Fig. 5.* The energy levels for three interacting $J = 1$ molecules have also been calculated.⁵⁰ Figure 5 shows the 27-sublevel scheme of one of the configurations of the three molecules. It can be imagined that the spectrum in a highly saturated concentrated sample of $J = 1$ H_2 may be complicated indeed.

In 1965, another major step occurred regarding the low temperature transition. Line changes in the infrared spectrum of normal H_2 at 1.5 K were interpreted as a crystallographic transition.⁵¹ Confirmation of the hcp-to-fcc transformation came from X-ray diffraction almost immediately.^{52,53} Although the transition is undoubtedly first order, the volume discontinuity is very small: only 0.15% upon cooling and 0.08% upon warming for a 0.73 mole fraction $J = 1$ sample. Virtually no volume change is seen at 0.63 $J = 1$. Extrapolation to pure $J = 1$ hydrogen yields less than 0.5% volume change. In contrast, $J = 1$ H_2 at 4.2 K expands 1.3 vol% just in converting to $J = 0$ H_2 .⁵⁴

Figure 6 shows the temperatures at which the first-order crystallographic transition takes place. The transition temperature, which increases with the mole fraction of $J = 1$ molecules, is higher for D_2 than for H_2 . The data is obtained from X-ray diffraction,⁵⁵ heat capacity lambda peaks,^{15,31} and the appearance of NMR peaks.⁵⁶ The hysteresis of the transition is evident from the transition temperature differences upon cooling or heating. Below 0.60 mole fraction of $J = 1$ H_2 , no heat capacity spike is seen down to 0.2 K.⁵⁷ The first-order transition apparently only extends from mole fractions of 0.6 to 1.0 $J = 1$ molecules. In the hcp mole-fraction region (0 to 0.6), there is a second-order transition to the ordered rotational state. The peak

*Energy level temperatures instead of quadrupolar coupling constants are used to give a better physical feel for the distance between levels. However, the splittings vary with sample temperature and must be considered approximate.

Fig. 6. Solid-solid transitions in solid H_2 and D_2 .

temperatures of the rotational heat capacities are plotted for three samples of 0.0022, 0.03, and 0.331 $J = 1$ mole fractions.^{20,21,28,29} We presume that the second-order transition crosses over into the region of the first-order change. The means of connecting the low- and high-mole fraction regions is not shown.

Data and Interpretation for Quadrupolar Heat Capacity

We obtained values of C_Q by subtracting the lattice heat capacity (found for $c = 0$) from the total heat capacity for a given fraction of $J = 1$ component, c . Rotational heat capacity, C_R , is not a factor, as already described, because H_2 and D_2 have rotational populations that are metastably frozen and HD values are small up to 14 K. The calculation of C_Q is subject to considerable error because of the subtraction of two large quantities. Figure 7 shows the most complete single $J = 1$ heat capacity curve yet measured: on 0.03 $J = 1$ D_2 .³⁰ There is a peak at 1.3 to 1.4 K followed by a long tail. The peak temperature corresponds to an energy gap of about 3.6 K, using the two-level model of Eq. (21). We drew a T^{-2} type curve through the tail points, but the spread of data was considerable.

Two other sources exist in which heat capacity peaks are measured for $J = 1$ concentrations less than the 0.60 needed to cause the hcp-to-fcc transition: 0.0022 $J = 1$ H_2 ^{21,22} and 0.33 D_2 .²⁹ All three peak temperatures are on the left side in Fig. 6. The remnants of this peak also appear in

Fig. 7. Quadrupolar heat capacity of 0.03 $J = 1$ D_2 .³³

the low temperature portion of Fig. 2, which we used to derive the "zero" $J = 1$ lattice heat capacity.

Figure 8 shows all remaining quadrupolar heat capacity data for H_2 and D_2 , both above and below the $0.60 J = 1$ mark that indicates the hcp-to-fcc transition. This data, which is above 2 K, represents only the tails. The H_2 data forms good plots^{15,17} that decline linearly with temperature - not as T^{-2} . The amplitude is directly proportional to c . The D_2 data is from many sources;^{16,26-29} and is quite scattered. It too is closest to being a function of c , but the temperature functionality cannot be obtained.

A complete temperature spectrum of the quadrupolar heat capacity has not been measured. Nevertheless, it is possible to roughly extrapolate known

Fig. 8. Quadrupolar heat capacity of solid H_2 and D_2 . The mole fraction $J = 1$ component, c , is listed.

curves either to 0 K or through the remainder of their tails. The curves can be integrated to obtain the quadrupolar enthalpy, H_Q . We have carried this out for all available H_2 , D_2 and H_2 - D_2 mixture data.^{15,21,22,29,30}

Figure 9 shows the results, which necessarily contain considerable uncertainty. All points but one fall near the line; only the very end of the line corresponds to the hcp-to-fcc transformation range. It appears that the second-order transition may indeed extend down to the lowest measured values of c . The enthalpy, H_J , is not directly proportional to c as expected from the two-level model and the H_2 data of Fig. 8, which spans a much smaller range of c . We fit all the data, covering c values of 0.0022 to 0.81, in Fig. 9 to the empirical equation

Fig. 9. Quadrupolar enthalpy of solid H_2 and D_2 .^{12,14-19,22-26}

$$H_Q \sim 25c^{1.5 \pm 0.1}. \quad (22)$$

All data, whether H_2 , D_2 , or H_2 - D_2 mixtures, fit Eq. (22).

It is also true that H_Q and C_Q for H_2 - D_2 mixtures are equivalent, within error, to linear combinations of the values of the pure components.^{19,20,22}

The actual theory of the quadrupolar heat capacity is much more complicated than the two-level model presented above. Roberts and Daunt²² use the nine-sublevel model of pairs of $J = 1$ molecules⁴⁹ and the 27-sublevel model of three $J = 1$ molecules.⁵⁰ They proceed via the partition function to the "pairs" and "triples" quadrupolar heat capacities. They overlay these combinations in various proportions and with different quadrupolar temperatures until a fit is achieved with the data (e.g., Fig. 7). The addition of a series of heat capacity terms, each decaying approximately as T^{-2} , yields an overall c_J tail that looks closer to being linear.

Roberts and Daunt also conclude, for their 0.0022 and 0.03 $J = 1$ samples, that "pair" interactions with splittings of about 0.9 K almost totally dominate the heat capacity. They assume that no crystal field exists in solid hydrogen strong enough to cause significant splitting of the levels of a single $J = 1$ molecule. The effect of a dominant "pair" mechanism at low $J = 1$ concentrations is to make the quadrupolar enthalpy, H_Q , proportional to c^2 ("triples" would be proportional to c^3). This may be compared with the 1.5 power of c found by us in Fig. 9. Finally, they conclude that the $J = 1$ moments are not "frozen-in" for solid H_2 but migrate by "rotation diffusion" to form more pairs than expected by chance.

In their next work, Roberts and Daunt extended their temperature range down to 0.3 K and found the low temperature heat capacity rise shown in Fig. 7.³⁰ They feel this rise is part of a lower temperature peak, although they were not able to cool the sample enough to locate the summit. They interpret this proposed peak as being caused by $J = 1$ pairs with molecules at next-nearest neighbor locations. The added distance between molecules reduces the quadrupolar coupling to about 0.2 K. With energy levels closer together, the peak occurs at a lower temperature. This mechanism produces an enthalpy proportional to c at low $J = 1$ concentrations. Also, the pairs model has been applied to 0.01 $J = 1$ H_2 and D_2 impurities in solid HD.²⁵ A nearest neighbor model is fitted by adjusting c to 0.76 and the quadrupolar coupling constant to 0.72 K. The above mentioned quadrupolar splittings

agree with values of 0.8 to 1.1 K obtained from an independent line of theoretical calculation.⁵⁸

A final complication concerns the energy level splitting of isolated $J = 1$ molecules in the $J = 0$ matrix. NMR measurements indicated that nonquadrupolar fields cause splittings of only 0.01 to 0.02 K.^{59,60} This led Roberts and Daunt to exclude single $J = 1$ molecules from their heat capacity analysis.²² A recent NMR study finds a crystal field splitting of 0.6 K, the same order of magnitude as the quadrupolar effect.⁶¹ It appears that the theory of the $J = 1$ heat capacity is not yet settled.

To summarize, we find no consistent description of the data possible and the theories complex and incomplete. We shall, therefore, summarize the findings with a simpler, empirical formula. We shall combine the two-level model of Eqs. (19) to (21) with the experimental enthalpy description of Eq. (22). In doing this, we will take the internal energy of a perfect gas of particles with individual quadrupolar interactions and convert it to a real enthalpy representing the solid. We propose the form

$$H_Q \sim 2c^{1.5} R\theta_Q \left[\frac{\exp\left(-\frac{\theta_Q}{T}\right)}{1 + 2 \exp\left(-\frac{\theta_Q}{T}\right)} \right], \quad (23)$$

where the only change to Eq. (20) is to substitute 1.5 instead of 1.0 as the power of c . The equation does not explicitly account for the possible low-temperature peak in Fig. 7. However, the amount of energy in such low-temperature peaks must be small. At high temperatures, the energy levels in Eq. (23) become filled, the enthalpy becomes constant, and the exponents equal one. We find that Eq. (23) for $T \rightarrow \infty$ produces enthalpies in agreement with Eq. (22) if we set $\theta_Q = 4.5$ K. This is like saying that the temperature peak of the quadrupolar heat capacity is always at 1.7 K. Figure 6 shows that this is approximately true for c values from 0 to 0.4, which covers the range expected in equilibrated hydrogen below 25 K. The enthalpy becomes

$$H_Q \sim 74.8c^{1.5} \left\{ \frac{\exp(-4.5/T)}{1 + 2 \exp(-4.5/T)} \right\}, \quad (24)$$

and the heat capacity is

$$C_Q \sim 337 \frac{c^{1.5}}{T^2} \frac{\exp(-4.5/T)}{[1 + 2 \exp(-4.5/T)]^2}. \quad (25)$$

Equations (24) and (25) fit both the experimental H_2 and D_2 data fairly well. We shall postulate their use to HD, DT, and T_2 as well. The equations give reasonable answers even for high c values in the hcp $\rightarrow$ fcc transformation region. However, it is not possible to relate our 1.7 K fixed-temperature peak to the higher temperatures of the crystallographic transformation. We have calculated Eqs. (24) and (25) from 1 to 20 K for unspecified values of c . The results are in Table 6 and may be applied, based on the similarity of H_2 and D_2 data, to all the isotopes.

Table 6. Quadrupolar enthalpy and heat capacity of solid hydrogen. Calculated from Eqs. (24) and (25); HD, DT, and T_2 data are complete estimates (in parentheses).

Temperature (K)	For $c = 1^a$		H_Q at equilibrium (J/mole)		
	H_Q (J/mole)	C_Q (J/mole-K)	D_2	(DT)	(T_2)
1	0.81	3.6	0	(0)	(0)
1.7	4.6	6.3	0	(0)	(0)
2	6.5	6.1	0	(0)	(0)
3	11.5	4.0	0	(0)	(0)
4	14.7	2.5	0	(0)	(0)
6	18.2	1.2	0	(0)	(0)
8	19.9	0.66	0	(0)	(0)
10	21.0	0.42	0	(0)	(0.1)
12	21.6	0.29	0	(0)	(0.4)
14	22.1	0.21	0	(0)	(1.1)
16	22.5	0.16	0	(0.2)	(2.2)
18	22.8	0.12	0.1	(0.4)	(3.5)
20	23.0	0.10	0.1	(0.7)	(5.0)
∞	24.9	0	—	—	—

^aFor other values of $J = 1$ component, multiply by $c^{1.5}$.

To better gauge the importance of these properties, let us calculate the actual equilibrium heats at the various temperatures. The heats per mole will then be multiplied by the equilibrium concentration of the $J = 1$ species, which, calculated for just two levels, is

$$c = \frac{3g_1 \exp\left(-\frac{29R}{T}\right)}{g_0 + 3g_1 \exp\left(-\frac{29R}{T}\right)}, \quad (26)$$

where g_0 and g_1 values are listed in Table 3. The quadrupolar equilibrium enthalpies and heat capacities up to 20 K are shown for D_2 , DT , and T_2 in Table 6. Only T_2 has an appreciable amount of $J = 1$ species to produce much enthalpy. But, at 20 K, where the $J = 1$ levels begin to fill, the m_J -sublevels are saturated and the heat capacity approaches zero. We see that the quadrupolar heat capacities are so small that they may be neglected for all equilibrium hydrogen.

If H_2 or D_2 is quenched and is in a metastable rotational state at some cryogenic temperature, there will be a metastable quadrupolar enthalpy, H_Q^m , and heat capacity, C_Q^m . These do not require new equations, as with the metastable rotational case. We may use Eqs. (24) and (25) with the proper metastable value of c . This value, in most experiments, will be the normal, room temperature figure. Because the metastable quadrupolar energy is frozen, we expect a zero heat capacity

$$C_Q^m = 0. \quad (27)$$

Basic Theory of Thermal Conductivity in Solids

Thermal conductivity does not separate into the lattice, rotational, and quadrupolar mechanisms found with heat capacity and enthalpy. This is because even for $J = 0$ hydrogen, there are two mechanisms in combination. If we add $J = 1$ hydrogen, we do not know whether there are still just two mechanisms or more. For the sake of simplicity, we shall assume two mechanisms, to be described as a function of c , the fraction of $J = 1$ hydrogen: the crystallite size mechanism at low temperatures and the Umklapp mechanism at higher temperatures.

Total thermal conductivity, K_S , is a sum of the crystallite conductivity, K_d , and the Umklapp conductivity, K_U , according to

$$\frac{1}{K_S} = \frac{1}{K_d} + \frac{1}{K_U} . \quad (28)$$

Heat is carried through a crystal, mostly by phonons. These are crystal lattice vibrations, which move like small bundles of energy. As heat is put into a sample and temperature increases, phonons are created that carry energy from the hot to the cold zone.

At low temperatures, not only are there very few phonons but they do not get in each other's way. Instead, they travel all the way across a crystallite (or single crystal) until they hit the edge and reflect. This collision with the wall sets up a bound to the thermal conductivity. We may consider the phonons to be like a gas, where the phonon "quasiparticles" have a mean free path determined by the crystallite size, d . From the kinetic theory of gases, we have the crystallite thermal conductivity, K_d , of

$$K_d = \frac{1}{3} C_L \rho_S u d , \quad (29)$$

where C_L is the crystal lattice heat capacity, ρ_S the solid density, and u the speed of sound in the solid.⁶²

The product $C_L \rho_S$ is the crystal lattice heat capacity per unit volume. Equation (29) assumes that rotational and quadrupolar energies are not available to the phonons.

The only highly temperature-dependent quantity in Eq. (29) is C_L , which increases as T^3 [Eq. (4)]. Hence, we expect a sharply rising thermal conductivity at low temperatures.

As the temperature continues to rise, ever more phonons are produced until they collide with one another more than with the walls of the crystallite. This becomes the dominant mechanism. The thermal conductivity decreases with temperature because of the ever higher production of phonons. At an intermediate temperature, where the two mechanisms are of equal strength, we find a thermal conductivity peak.

Umklapp (or U-) processes are phonon-phonon collisions that reduce the phonon mean free path with increasing temperature. A ready analogy is a pipe full of gas, closed at both ends.⁶² One end is hot, the other cold. By molecular collisions, energy passes from the hot to the cold end. Yet, there

is no mass transfer of gas molecules from one end to the other. Here the analogy ends because the gas will have a higher density at the cold end.

Phonons, however, are vibrational bundles of lattice energy that are created by heating the crystal. Their density and collision frequency will be higher at the hot end of a crystal. But, in analogy with the gas, although energy flows from the hot end of a crystal to the cold end, there is no mass transfer of phonons. Each collision of two phonons results in one moving forward and one bouncing backward — then there is no net movement of phonons. This collision is much like a chemical or cyclotron particle reaction in that a threshold energy of $k\theta_D/2$ per collision is required, where k is Boltzmann's constant. The number of phonons and the availability of the necessary threshold energy increase with temperature, so the rate of Umklapp collisions is a function of $\exp(-\theta_D/2T)$, where θ_D is the Debye temperature. The Umklapp phonon mean free path, λ_U , is the inverse of this; i.e., it decreases exponentially with temperature.⁶³ We use a higher temperature variant of Eq. (29) — again, the kinetic gas equation

$$K_U = \frac{1}{3} C_L \rho_S u \lambda_U, \quad (30)$$

so that we obtain the functionality

$$K_U \sim T^3 \exp\left(\frac{\theta_D}{2T}\right). \quad (31)$$

In practice, actual substances have a figure of 2 to 3 for the denominator of the exponent.

Experimental Thermal Conductivity of Solid Hydrogen

Solid hydrogen thermal conductivity data is nowhere as large as that for heat capacity. The literature consists of four papers with extensive data,⁶⁴⁻⁶⁷ four with fragmentary data,⁶⁸⁻⁷¹ and two purely theoretical works.^{72,73} Most of the data appear in the recent NBS survey⁷⁴ and are plotted in Fig. 10.

Looking at Fig. 10, we see that the thermal conductivity of "zero" $J = 0$ hydrogen forms a peak just below liquid helium temperature. The conductivity then drops two decades and starts to flatten out at the triple point. The effect of adding rotational energy is to flatten out the peak, with the peak temperature increasing with increasing $J = 1$ component. Most data are

for solid H_2 , but two runs have been made with solid HD containing $J = 1$ H_2 - and D_2 -doped impurities.

The right hand side of Fig. 10 also shows the thermal conductivities of various common materials.^{75,*} The highest thermal conductivity for solid H_2 , with "zero" $J = 1$ at 3.5 K, compares to a room-temperature metal with fair conductivity; e.g., tungsten. As the temperature rises to the triple point or as rotational energy is added, solid H_2 takes on the thermal conductivity expected of a dielectric.

We shall now briefly mention the fragmentary data on thermal conductivity. Figure 10 shows a single D_2 point with 0.33 $J = 1$. This trough minimum agrees with the H_2 data. Other data not shown in Fig. 10 include "zero" $J = 1$ H_2 at 15.1 to 17.1 K under pressures of 8.9 to 20.4 MPa (88 to 201 atm).⁶⁸ The values of 0.8 to 1.0 W/m-K fit right onto the 1 W/m-K line that the high-temperature data of Fig. 10 converge to.

Two other sources of D_2 data agree with each other but are a factor of three away from the data so far compiled. The D_2 measurements for 0.02 and 0.33 $J = 1$ from 16.3 to 17.7 K yield thermal conductivities of 2.6 to 3.2 W/m-K.⁷⁰ Finally, a single point of 2.6 W/m-K exists for D_2 at 16.75 K and 39 MPa (393 atm).⁷¹

We need other data for our analysis: C_L from Eq. (4), the Debye temperature, θ_D from Eq. (6), the speed of sound, u , and the solid density, ρ_S . We shall use the value 2000 m/s as an average longitudinal sound speed, u , for the solid hydrogens. (Sound velocity varies slightly with temperature and decreases slightly from H_2 to D_2 . It is also a function of the crystal orientation.)⁷⁶ For the solid densities, ρ_S , we shall ignore the slight decrease with temperature and use the triple point values. These are $H_2 = 43000 \text{ mole/m}^3$, $HD = 45800 \text{ mole/m}^3$, $D_2 = 48800 \text{ mole/m}^3$, $DT = 51000 \text{ mole/m}^3$ (estimated), and $T_2 = 53000 \text{ mole/m}^3$ (estimated).⁷

*The two sources of H_2 data differ by a factor of 4 to 5.^{64,65} The differences may be caused by uncertainties in the $J = 1$ concentration, c . This problem plagues all experiments, especially when c is low. The value of c is sometimes inferred from the means of production⁶⁴ or from NMR relaxation times, which often require supporting theory.⁶⁵

Analysis of Thermal Conductivity

Let us first fit equations to the H_2 "zero" $J = 1$ curves* of Fig. 10. The crystallite curve for H_2 is

$$K_d(c = 0) \approx 8T^3, \quad (32)$$

and the Umklapp curve is

$$K_U \approx 9 \times 10^{-6} T^3 \exp \left\{ \frac{120 - 1.6T}{2T} \right\}. \quad (33)$$

Combining Eqs. (29) and (32), we obtain a low-temperature mean free path in H_2 of 1.7×10^{-4} m. Combining Eqs. (30) and (33), we obtain high-temperature mean free paths in H_2 of 1.5×10^{-7} m at 8 K and 6×10^{-9} m at the triple point.

Now let us consider the solid H_2 with rotational energy. The number of phonon-phonon collisions is a function of temperature only. Therefore, the Umklapp formula - Eq. (33) - remains the same. We must modify the crystallite formula of Eq. (32) into an empirical form for H_2 :

$$K_d(c) \approx \frac{(1.9 \times 10^{-3}) T^3}{[c + (7 \times 10^{-4})]^{1.15}}. \quad (34)$$

We have used the data of Hill and Schneidmeyer,⁶⁴ which covers the larger range of c . Equation (34) contains the number 7×10^{-4} in the denominator to relate it to Eq. (32). This number is effectively the "zero" value of c in actual experimental runs. Combining Eqs. (29) and (34), we obtain the low-temperature phonon free path; i.e., the crystallite size, as a function of c . The crystallite size is

$$d \sim \frac{3.9 \times 10^{-8}}{[c + (7 \times 10^{-4})]^{1.15}}. \quad (35)$$

This decreases from 1.7×10^{-4} m for "zero" c to 5×10^{-8} m for normal (0.75c) H_2 .

Equations (32) to (35) carry the basic theoretical framework for the solid hydrogen thermal conductivity. They indicate that solid hydrogen consists of crystallites, whose size decreases as the fraction of $J = 1$ component increases. Wall scattering of phonons off crystallites is the dominant low-temperature mechanism. For high values of c , the crystallites

*Actually, c is 0.002 to 0.005.

are almost as small as the high-temperature Umklapp mean free path. Hence, the conductivity is almost constant, but with a small peak shifted to higher temperatures. At high temperatures, with low c , the Umklapp mechanism is dominant.

The early papers⁶⁴⁻⁶⁶ accepted this theoretical view but with a lingering reservation. Solid hydrogen easily forms beautiful, optically clear crystals with no visible grain boundaries. The first researchers, who grew 10^{-2} m-size sample crystals, could not entirely convince themselves of the existence of the crystallites.

In recent times, therefore, the ambiguity of the low-temperature conductivity has given rise to a host of proposed quadrupolar mechanisms. Possibly, phonons are scattered by the quadrupolar-induced sublevels; i.e., the lattice vibrational energy is used to excite a transition to an excited n_J state. These mechanisms have led to calculated conductivity functionalities of $c^{-2}T^{-2}$;⁷² $c^{-1}T^7$, $(cT)^{-1}$, $c^{-2}T^2$; $c^{-2}T$;⁶⁷ and $c^{-1}T$.⁷³ There is no evidence for any of these mechanisms. The actual data, as seen by Eq. (34), are closest to the $c^{-1}T^3$ dependence expected from a simple crystallite theory. Possibly, a combination of mechanisms yields the observed results. In any case, the crystallite approach is conceptually the easiest, although the crystallite boundaries have never been experimentally observed.

Quite possibly, crystallite and phonon-sublevel mechanisms are, in fact, the same. The reduction of the phonon mean free path by $J = 1$ molecules is equivalent to forming crystallites with invisible boundaries. However, the crystallite mechanism carries an easily understood T^3 dependence. Such a dependence has not been explicitly demonstrated for phonon-sublevel scattering.

Equations (32) to (34) are fair descriptions of the H_2 data, but extrapolation to the other hydrogens will be risky. First, these three equations tend to predict too high a conductivity for the H_2 peak conductivity. Changing their parameters worsens the fit considerably at other temperatures. Second, the HD conductivity peak is an order of magnitude lower than H_2 data of comparable $J = 1$ content. Quite possibly, crystallite size is a function of the history of manufacture of each given sample.

Estimated Effects of Radiation Damage

No heat capacity or thermal conductivity measurements have been made on irradiated solid hydrogen. We shall, therefore, consider some possible analogies. In fact, it is surprising how many systems show effects similar to those of the $J = 1$ hydrogen. For the heat capacity, this is a Schottky anomaly, which peaks and dies out below 10 K. A perfect example is seen for paramagnetic O_2 impurities in solid CO and N_2 . The heat capacity anomaly peaks at 1.8 K for a mole fraction of 0.002 to 0.005 O_2 .⁷⁷ The integrated energy is about 18 J/mole. The same two-level model used in Eqs. (19) to (21) is also employed in these oxygen experiments.

However, radiation can also produce defects with paramagnetic free electrons. Such free electrons have been measured by electron spin resonance (ESR) for solid hydrogen irradiated with Co^{60} γ -rays, 40-MeV electrons, and tritium beta particles.⁷⁸⁻⁸² Table 7 summarizes these experiments.

The species that gives rise to the ESR signal is thought to be atomic hydrogen, which saturates with radiation at about 2×10^{18} spins/mole. This is only 2×10^{-6} atomic fraction - a very small amount to give such a large signal. It is a thousand times lower than the O_2 amounts used in the previously described doping experiment. The total enthalpy is, therefore, about 0.018 J/mole. The attendant heat capacity must be zero for all practical purposes.

The He^3 produced by tritium decay will build up at a rate of 1 ppm per 5 min. Such helium atoms may be trapped in the solid at low temperature rather than diffuse out and bubble away. However, a neutral He^3 atom probably does not carry any force of strength comparable to the free electron. It probably will trap more heat as a defect than it will produce by splitting of the hydrogen sublevels.

We conclude, therefore, that there will probably be no large added heat capacity in solid hydrogen due to radiation. If anything, heating may anneal out defects with a production of stored energy from the sample. However, the results of damage studies in solid hydrogen could yield quite unexpected results.

Considerable evidence shows how defects affect thermal conductivity. The effect to look for will be a decreased conductivity, proportional to the concentration of the pertinent impurity, on the low temperature side of the

Table 7. Electron spin resonance measurements on irradiated solid hydrogen at 4.2 K.

Isotope	Type of irradiation	Irradiation rate (J/s-mole)	ESR signal saturation count (spins/mole)	Energy of signal saturation signal (J/mole)	Time to reach saturation	Ref. no.
H ₂	1 MeV γ	0.033	3.6×10^{18}	1200	10 h	78
D ₂	1 MeV γ	0.033	$>4.2 \times 10^{18}$	1200	>10 h	78
H ₂	40 MeV electrons	0.15-1.5	1.8×10^{18}	140	1.5-15 min	79
T ₂	Self-irradiation	1.9	—	$>3.5 \times 10^4$	>4.8 h	80
H ₂	1 MeV γ	0.033	6×10^{17}	<65	30 min	81
D ₂	1 MeV γ	0.033	$>5 \times 10^{19}$	$>3.7 \times 10^3$	30 h	81
D ₂	1 atom % T ₂	0.013	3×10^{17}	4×10^3	3.5 d	82

minimum. At temperatures above the minimum, all conductivity curves tend to the same value.

Extensive examples may be found in the alkali halides and metal oxides. When pure and annealed, such materials show thermal conductivity peaks from 5 to 30 K, with crystal size controlling the low-temperature portion and Umklapp processes operating at high temperatures. Decreased thermal conductivity appears in alkali halides doped with impurities at birth (e.g., Li^+ ,⁸³ Ni^{++} ,⁸⁴ CN^- ,⁸³ or OH^- ,^{83,85}), impurities from irradiation (e.g., U-centers⁸⁶ or colloidal silver⁸⁷), or even dislocations caused by mechanical stress.⁸⁸ Identical effects occur in alumina, doped with transition elements, irradiated, or both.⁸⁹⁻⁹¹

The low-temperature conductivity again shows a temperature dependence of about T^3 , despite a possible variety of mechanisms. Phonon scattering from magnetic sublevels is a prominent theory because so many papers have been done on crystals doped with paramagnetic ions. However, no one has obtained satisfactory theoretical conclusions for the low-temperature conductivity.

The thermal conductivity peak is lowered one order of magnitude with the inclusion of 2×10^{-5} to 0.002 mole fraction of impurity, depending on the type. The peak is simultaneously moved to a temperature higher by a factor of 5 to 10.

Especially interesting results occur for lithium fluoride (LiF) crystals irradiated with neutrons (probably just above room temperature) to 10^{18} nvt (integrated neutron dose). An unirradiated, annealed crystal has a maximum thermal conductivity at 17 K; at 10^{18} nvt, the maximum is 1 to 1/2 decades lower and shifts upward to 110 K. The conductivity appears to be saturating between 10^{17} and 10^{18} nvt. All conductivity curves intersect at 150 K, indicating that radiation effects do not matter at higher temperatures.⁹² It should be mentioned that 10^{18} nvt is a large enough dose to cause chemical breakdown of the LiF; 2% decomposition has been seen by NMR.⁹³ This extent of damage caused by neutrons is illustrated by a 20% volume growth in samples irradiated at 350 K.⁹⁴

We will expect a radiation-induced decrease in the thermal conductivity of solid hydrogen. The effect of free electron species, possible point defects, and trapped He^3 atoms will be to reduce the effective grain size of the hydrogen crystal, as far as phonon conduction is concerned, by physically breaking up the lattice. The ions and point defects in solid D-T may saturate in ppm quantities, but the He^3 will grow to much larger concentrations.

Freshly made solid D-T will probably have the thermal conductivity of unirradiated hydrogen. Over the space of a few days, accumulating damage may reduce the phonon mean free path to the constant value of about 10^{-8} m or less. Then we have a possible situation with a small mean free path but also a small heat capacity. This is the situation that will produce the lowest possible thermal conductivity. Defects scatter the phonons; yet the energy bound in the defects is probably not available to the phonons.

We use the form of Eq. (29) with the crystallite size limited to a small, constant value at all temperatures by the radiation damage. Let us use the d value of 10^{-8} m, close to the very lowest value obtained from the Umklapp calculation at the H_2 triple point. Then, we have the approximate estimate of

$$K_{\text{rad}} \sim 1.3 \times 10^{-8} T^3 \rho_S. \quad (36)$$

For H_2 , we obtain an equation much like Eq. (32) but yielding thermal conductivities 10 000 times lower. At 3.5 K, the conductivity has finally risen to that of room-temperature air — a good insulator. The conductivity continues to rise with temperature until it intersects the unirradiated Umklapp line near the triple point.

Estimates for D-T

It is easy to estimate values for D-T, if the likely assumption is made that the D_2 and T_2 are in equilibrium rotational states. Below 25 K, the rotational effects of equilibrium $J = 1$ molecules are not great. We need not sum properties for each component — D_2 , DT, T_2 — but we may condense all properties as though only DT were present. Figure 11 shows the crystal lattice heat capacity estimate for D-T, which is basically just an extension of the D_2 data of Table 1.

Figure 11 also shows the estimated thermal conductivity for solid D-T. The available data are simply not good enough to make straightforward estimates. We, therefore, present "high" and "low" estimates. The former curves are based on the H_2 data of Fig. 10; the latter curves are a decade lower and are representative of the HD data.

The extreme sensitivity of the thermal conductivity adds further uncertainty. "Just frozen" D-T drops two decades in conductivity upon warming from 4 K to the triple point. Low-temperature D-T may drop as much as four

Fig. 11. Estimated crystal lattice heat capacity and thermal conductivity of solid D-T (assumed equilibrium).

to five decades in conductivity as radiation damage destroys the crystal lattice. The rate of this important transformation is unknown.

We now move on one more step to estimate the thermal diffusivity of solid D-T. Thermal diffusivity, D_S , is

$$D_S = \frac{K_S}{C_L \rho_S}, \quad (37)$$

where, again, only the crystal lattice heat capacity is used as the energy term.⁹⁵ Figure 12 shows the estimates, which range over a remarkable five-and-a-half decades as functions of temperature and radiation.

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Fig. 12. Estimated thermal diffusivity of solid D-T (assumed equilibrium).

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Appendix: Calculation of Heat Capacities and Enthalpies at 4.2 and 19.7 K

We have mentioned that eD_2 -DT- eT_2 does not require component-by-component summation of thermal properties. We shall show the results of such a calculation here anyway. This will be contrasted with a calculation for nD_2 -DT- nT_2 , which we shall assume to be metastably trapped at low temperature. In this case of high rotational energy, each component must be calculated and the results summed. We recall that DT is always in the equilibrium form.

The compositions for 1:1 D-T (D_2 -DT- T_2) are: 0.46/0.08/0.46 at 4.2 K equilibrium; 0.31/0.38/0.31 at 19.7 K equilibrium; and 0.25/0.50/0.25 at normal temperature.¹⁰

Tables 8 and 9 present estimated and calculated heat capacities and enthalpies for D-T.

Table 8. Estimated enthalpy and heat capacity for solid D-T at 4.2 K

		Enthalpy (J/mole)					
		Pure component				Mixture	
Isotope	mole fraction of J = 1 (c)	H_L	E_R	F_Q	H_S	H_S	ΔH_S
$\begin{bmatrix} eD_2 \\ DT \\ eT_2 \end{bmatrix}$	1×10^{-9}	0.14	1×10^{-6}	7×10^{-13}	0.14	0.14	—
	8×10^{-8}	0.14	5×10^{-5}	3×10^{-10}	0.14		
	8×10^{-6}	0.14	4×10^{-3}	4×10^{-7}	0.14		
$\begin{bmatrix} nD_2 \\ DT \\ nT_2 \end{bmatrix}$	0.33	0.14	145.5	2.9	148.5	122	122
	8×10^{-8}	0.14	0	0	0.14		
	0.75	0.14	327.7	9.9	337.7		

Table 8. (continued)

Isotope	Heat capacity (J/mole-K)						
	Pure component					Mixture	
	c	C _L	C _R	C _Q	C _S	C _S	ΔC _S
[eD ₂]	1 × 10 ⁻⁹	0.13	5 × 10 ⁻⁶	1 × 10 ⁻¹³	0.13	0.13	—
[DT]	8 × 10 ⁻⁸	0.13	2 × 10 ⁻⁴	5 × 10 ⁻¹¹	0.13		
[eT ₂]	8 × 10 ⁻⁶	0.13	0.013	5 × 10 ⁻⁸	0.13		
[nD ₂]	0.33	0.13	0	0	0.13	0.13	0
[DT]	8 × 10 ⁻⁸	0.13	0	0	0.13		
[nT ₂]	0.75	0.13	0	0	0.13		

Table 9. Calculated enthalpy and heat capacity for solid D-T at 19.7 K (estimated triple point).

Isotope	Enthalpy (J/mole)						
	Pure component					Mixture	
	mole fraction of J = 1 (c)	H _L	E _R	H _Q	H _S	H _S	ΔH _S
[eD ₂]	0.017	73.9	12.6	0.05	86.6	143	—
[DT]	0.067	73.9	41.1	0.40	115.4		
[eT ₂]	0.32	73.9	154.0	4.1	232.0		
[nD ₂]	0.33	73.9	145.5	4.4	223.8	197	54
[DT]	0.067	73.9	0	0	73.9		
[nT ₂]	0.75	73.9	327.7	14.9	416.5		

Table 9. (continued)

Isotope	Heat capacity (J/mole-K)						Mixture	
	Pure component							
	c	C _L	C _R	C _Q	C _S	C _S	ΔC _S	
$\left[\begin{array}{c} \text{eD}_2 \\ \text{DT} \end{array} \right]$	0.017	13.5	2.8	2×10^{-4}	16.3	}	22.0	—
$\left[\begin{array}{c} \text{DT} \\ \text{eT}_2 \end{array} \right]$	0.067	13.5	7.3	2×10^{-3}	20.8			
	0.32	13.5	15.8	0.018	29.3			
$\left[\begin{array}{c} \text{nD}_2 \\ \text{DT} \end{array} \right]$	0.33	13.5	0	0	13.5	}	13.5	8.5
$\left[\begin{array}{c} \text{DT} \\ \text{nT}_2 \end{array} \right]$	0.067	13.5	0	0	13.5			
	0.75	13.5	0	0	13.5			