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**CRYOGENIC HYDROGEN DATA
PERTINENT TO MAGNETIC FUSION ENERGY**

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ABSTRACT

To aid future hydrogen fusion researchers, I have correlated the measured physical and chemical properties of the hydrogens below 30 K. I have further estimated these properties for deuterium–deuterium tritide–tritium (D_2 –DT– T_2) fusion fuel. My resulting synthesis offers a timely view and review of cryogenic hydrogen properties, plus some hydrogen data to room temperature. My general thrust is for workers new to the field, although my discussion of the scientific background of the material would suit specialists.

I. INTRODUCTION

1. The Need for a New Reference Work

The last half century has seen continuing reviews of the hydrogen isotope family. At the very dawn of heavy hydrogen exploration, A. Farkas published a complete book—now out of print—at Cambridge.¹ The book dealt with the preparation, properties, and common reactions of the newly discovered isotopes hydrogen deuteride (HD) and deuterium (D_2). He also reported data on the strange metastable rotational energy levels of H_2 and D_2 whose ortho–para terminology has confused so many non-hydrogen workers since.

All H_2 , HD, and D_2 work* was beautifully summarized in 1948 by Harold Woolley's review, which is still indispensable today.²

This review represented the start of three decades of continuous cryogenic hydrogen measurement and review by the National Bureau of Standards (NBS), first in Washington, D. C. and then at Boulder, Colorado. In the thirteen years between Farkas and Woolley, the addition of thermodynamic and pressure–volume–temperature (P–V–T) data gave the new review a modern look that has not changed subsequently. The tritium isotopes had been discovered about ten years before but its known properties in 1948 covered less than a page.

Since 1950, there has been an explosion of H_2 and D_2 research, with long-term programs on P–V–T and transport properties at Ohio State University, Los Alamos Scientific Laboratory, and NBS, Boulder. More elegant hydrogen measurements have been proceeding in universities, e.g., collision-induced infrared spectroscopy at Toronto. This area, of academic interest for

thirty years, joins the mainstream of hydrogen data in this report.

The most popular academic area in the last ten years has been the "ordered" state of solid H_2 and D_2 below 4 K. Here, the rotational magnetic moments align themselves into ordered patterns not possessing an overall sample magnetic moment (i.e., they are antiferromagnets). Excitation waves of various types may propagate down the chains of molecules. This field, now pushing downward into the milli-Kelvin range, has not as yet united with the main body of hydrogen data.

NBS, Boulder has had a special interest through the years in liquid and fluid H_2 . This was studied first for use as rocket fuel and then for the projected hydrogen economy. NBS developed a computerized cryogenic newsletter³ and wrote many cryogenic hydrogen reviews. The two most recent and comprehensive are McCarty's 1975 H_2 book⁴ and a 1973 survey of all isotopes.⁵ The former contains a detailed equation-of-state code for liquid and fluid hydrogen. A somewhat dated D_2 review can be useful, especially for its liquid-fluid code.⁶ Every cryogenic hydrogen researcher should possess these NBS documents.

A Ukrainian group at Kharkov has also specialized in fluid H_2 measurements for some years. In 1969, they published an H_2 survey,⁷ quite possibly for their own rocket fuel program. This Soviet survey contains a few tables of data not found in the NBS reviews, but its acquisition is optional.

In summary, H_2 and D_2 , the easy-to-get isotopes, have been studied in detail. The irritation of preparing and purifying HD has deterred almost an entire generation of researchers since Woolley.² Los Alamos carried out a splurge of measurements on the tritium isotope T_2 in 1951–1952. Since then, there has been an astonishingly small amount of T_2 work, even allowing for the

*See Appendix A for my discussion and listing of the symbols in this report. See Appendix B for useful relations between dimensional units.

radioactivity of the isotope. Some work has been done on the passive H_2 - D_2 mixture, but the D_2 - DT - T_2 mixture (abbreviated D - T) has been virtually shunned. Mixtures often yield messy experiments, but the radioactivity of the tritium adds a dynamic and frustrating new feature.

At the present moment, one would expect tritium to be acquiring a certain respectability. It is an ingredient in D - T , the fuel of easiest ignition in controlled hydrogen fusion.⁸ It burns by the reaction

where n is a neutron. Other reactions follow, each more difficult to trigger. They are:

and

where p is a proton.

Present magnetic fusion machines have neither committed themselves to tritium nor to low temperatures; but, development in fuel pellets, cryopumps, and tritium distillation has prompted this new hydrogen review. Researchers in the above areas desire D - T data, but there is almost none to report. Moreover, the only new measurements are being made by the tritium distillation group at Los Alamos⁹ and by ourselves.^{10,11} Any surge of researchers into the D - T properties field is unlikely, partly because of the considerable cost of preventing radioactive accidents and partly because of the present lack of fashion in measurements not directly linked to construction of a large and expensive machine. It indeed seems desirable to measure those D - T properties most likely to be affected by tritium radioactivity, so they will be available when needed.^{12,13} This will occur in only a few cases, and in this review, I seek to estimate D - T and T_2 properties by extrapolation of H_2 , HD , and D_2 data. This has required an isotopic consistency of approach not attempted since the Woolley 1948 review. This review will not attempt to report each experiment in isolation but will seek a synthesis—mostly empirical—for uniting the hydrogen isotopes.

2. Ortho-Para Terminology

The terminology of the metastable rotational states (ortho and para) will occur over and over before you reach the detailed section on this subject. I shall, therefore, briefly define these states.

Ortho-para terminology has not been applied to the heteronuclear hydrogens: DT , hydrogen tritide (HT), and HD . They are expected to lose their rotational energy quickly upon cooling and, in general, to behave themselves. At cryogenic temperatures, one expects virtually all molecules to be in the ground rotational state, with the quantum number, $J=0$.

The homonuclear hydrogens— T_2 , D_2 , and H_2 —are different. Upon cooling to near 0 K, there will be only partial rotational de-excitation. All even-numbered J states will de-excite to $J=0$; all odd-numbered rotational states will de-excite to $J=1$, the first excited state. Because of quantum mechanical symmetry rules, the $J=1$ level cannot easily drop to $J=0$.¹⁴ There is, therefore, a metastable trapping of energy in the $J=1$ level. It may take hours, days, or weeks to de-excite this system, depending on what catalysts are available.

Every time T_2 , D_2 , or H_2 is mentioned, one should include a statement as to their rotational populations. If equilibrated by waiting a long time at a given temperature, the sample is called "equilibrium," e.g., eT_2 . If the sample has the room temperature distribution of even and odd- J states, it is called "normal," e.g., nT_2 . A sample can be normal at any temperature, however, with different populations in the various levels. But the fraction in all even- J states and in all odd- J states remains the same at every temperature. The fractions in even- J states are, for nT_2 , nD_2 , and nH_2 : 0.25, 0.67, and 0.25. A later section will show the partition functions needed to calculate these.

Special names are given to the even- and odd- J series of states: "ortho" (o) and "para" (p). The even- J series are pT_2 , oD_2 , and pH_2 ; the odd- J series are oT_2 , pD_2 , and oH_2 . Notice that the definitions for D_2 are unlike those for H_2 and T_2 . This is because para was originally defined as the form in lower amount at room temperature and the isotopes are different in this respect. Fifty years ago, better names were proposed: symmetric (even- J) and anti-symmetric (odd- J), in reference to the quantum mechanical wave functions. These names, unfortunately, have not endured.

At temperatures under 30 K, almost all molecules are in either the $J=0$ or $J=1$ states, and one may label the appropriate fractions of each. Equilibrium hydrogen will be a combination of the two. For H_2 , however, the fraction of $J=1$ is low at cryogenic temperatures. Usually, eH_2 and $J=0$ (p) H_2 are used interchangeably. This cannot be done in general with D_2 or T_2 . At higher temperatures, one must carefully catalog the ortho-para

fractions and the many different rotational levels over which the molecules are spread.

The effect of the ortho-para ratio on the physical properties is usually only a few percent, and it diminishes as the molecular weight increases. However, the amount of energy trapped in the metastable rotational states can be large, amounting to hundreds of J/mole. All careful hydrogen work requires specification of the ortho-para ratio.

3. The Triple Point Region

The region covered by this review is largely from 0 to 30 K and 0 to several hundred MPa (several kbars).^{*} The selection of the upper temperature limit is arbitrary but designed to exclude the critical point. Some data for the gas phase to room temperature is also included, since everyone must traverse this road to the cryogenic region.

Figure 1 shows a schematic phase diagram for one of the pure hydrogens. The allowed physical states are all on the white surfaces; the shaded surfaces are forbidden areas. The largest region is that of the fluid phase, which extends to the nearly flat plains of the high vacuum on the right and up a high cliff to the super-dense fluid on the left. The fluid phase has special little regions. The peninsula between the two non-physical regions is the liquid—a unique and tiny geographical feature of the P-V-T surface. The liquid is in equilibrium with the isothermal vapor on the other side of the shaded zone. Beyond the vapor region, where the pressure is low, the fluid is now renamed a gas. The shaded tongue running upward on the right is the melting curve, and it separates the fluid and solid phases, where they leap upward in an unending cliff. The melting line region narrows somewhat as it climbs, but whether it is a peninsula or a bridge to infinite pressure is unknown. The precise distinction between fluid and solid is still there for H₂ at 1.9 GPa (19 kbar).^{15,†}

Two special places exist on the P-V-T surface. The critical point is the very crest of the non-physical liquid-vapor region. Here, the two phases unite into one, and the heat of vaporization is zero. This has always been the special reference point in statistical mechanics. In practice, the critical point is a nightmarish region to be avoided in almost all applied systems. Physical proper-

ties change with increasing acceleration as one moves toward the critical point, as though a repulsive force radiates outward over the P-V-T surface. The heat capacity rises in a gigantic spike like an astronomical white hole in the thermal phase space.¹⁶ There is no reason presently why any fusion machine would deliberately operate at the critical point, and I have concentrated on the more likely regions.

The second important feature of the P-V-T surface is the triple line, which isothermally connects the two non-physical regions. Only here are solid, liquid, and gas in equilibrium with each other. (When only P and T are considered, we have the triple point—a more common expression.) In the practical range of low temperatures and pressures, the triple line is the constant focus of attention. There is a volume discontinuity there, but no such singularity as occurs at the critical point. A real sample will indeed linger at the triple line, because it takes time to remove the heat of fusion. Only in the most careful experiments, however, is the triple line really close to being isothermal and isobaric the way it is supposed to be.¹⁷ Usually, it smears over some range of P and T depending on the exact conditions of passage. Nevertheless, one can look into the cryostat and observe the three phases (Fig. 2), and the triple line remains an outstanding feature.

Solid and liquid hydrogen are colorless, and they possess refractive indices so low that careful back lighting is often needed to find the surfaces. The lighting used for visual observation usually imparts too much energy, causing sublimation, and one closes all windows as much as possible and operates remotely by instruments.

4. Empirical Estimation of Properties

There are two kinds of effects to consider when estimating the properties of DT from H₂ and D₂. The first is the correction for the larger mass. Although some may argue about the exact details of such an extrapolation, the final result is likely to be close to the real thing. Examples of properties that probably fall in this category are liquid surface tension and viscosity, and heat of vaporization. This section deals with variables used in making these estimates.

The second effect is caused by tritium radiation, which breaks up surrounding molecules into atoms and ions. Such effects may be considerable with only ppm of tritium, e.g., the electrical conductivity or the ortho-to-para conversion rate. It is impossible to accurately estimate this kind of effect. Although one may guess, only experiment can tell. Other properties that probably fall in this category are solid thermal conductivity, heat capacity, and shear stress.^{12,13}

^{*}Metric SI units appear throughout this review, with older units included in parentheses. I can sympathize with those researchers who feel put upon by the pascal. However, I almost lost my mind by correlating units for this review and have now embraced the new system.

[†]A melting pressure of 5.7 GPa (57 kbars) at 298 K has just been measured. See H. K. Mao and P. M. Bell, *Science* **203**, 1004 (1979).

FIG. 1. Pressure-temperature-volume surface for a pure-component hydrogen.

FIG. 2. The three phases of normal deuterium (nD_2) together. I used a fast freeze to obtain the small crystals visible at the bottom. The light space above is the liquid. The large curve is the liquid meniscus, which is lower in the middle of the cell than at the edges. Vapor space is above. The oblique dark line is a metal pin used in a preliminary electrical experiment. Temp = 18.7 K; pressure = 17 150 Pa (128.6 Torr).

Let me return to estimating DT properties by mass. There is no single parameter that works for all properties, and six possibilities are shown in Table 1. The most obvious is the molecular weight.¹⁸ This can be useful in considering Debye temperatures or kinetic gas theory, but it contains a flaw. The species HT and D_2 have the same molecular weights, but HT is known to be more volatile.¹⁹ This may be fixed by going to the reduced molecular weight in center-of-mass coordinates, μ , where

$$\mu_{DT} = \frac{M_D M_T}{M_D + M_T}, \quad (5)$$

and where M_D and M_T are the atomic weights of D and T—in this case.²⁰ The variable μ has a peculiar sequence across the isotopes. As seen in Table 1, HT has now been dropped halfway between H_2 and D_2 . In this sequence, HD and HT are almost comparable. I seek another step by continuing to the harmonic oscillator model. Here, the frequency of vibration is proportional to the square root of the quotient of a force constant divided by the reduced molecular weight.²⁰ I assume the force constants for generalized vibration to be the same for all the hydrogens, and the third column of Table 1 lists the values of $(\mu)^{-1/2}$. This set is useful for actual vibrational processes, and the sequence across the isotopes is more illustrative of the comparative properties. There is one more stage in the harmonic oscillator model. This is the dimensionless quantum parameter, Λ_{eff}^* , from the quantum theory of corresponding states. Section 20 treats this parameter in detail. Basically, the theory says that light elements cannot be described just by P, V, and T. This is because light molecules exhibit quantum effects, which are summarized by a new, all-

Table 1. Basic hydrogen isotope parameters useful for empirical extrapolation. HT and DT are estimated, as is the nT_2 critical point temperature.

Isotope	Mole wt (10^{-3} kg/mole)	Reduced mole wt, μ (10^{-3} kg/mole)	$(\mu)^{-1/2}$ (mole/kg) ^{1/2}	Quantum parameter Λ_{eff}^*	Critical point temp (K)	Triple point temp (K)
eH_2	2.0157	0.50391	44.547	1.731	32.976	13.81
nH_2					33.19	13.956
HD	3.0219	0.67171	38.584	1.471	35.91	16.60
HT	4.0239	0.75540	36.384	1.354	37.13	17.70
eD_2	4.0282	1.0071	31.512	1.224	38.26	18.69
nD_2					38.34	18.73
DT	5.0302	1.2076	28.776	1.111	39.42	19.79
nT_2	6.0321	1.5080	25.751	1.000	40.44	20.62

purpose parameter. This parameter contains the inverse square root of the molecular weight as though it were some sort of vibrational frequency.²¹ A correction term is applied to DT, HT, and HD to adjust for the fact that HT and D₂ vapor pressures are markedly different.¹⁹ The resulting quantum parameter, Λ_{eff}^* , is zero for classical molecules with no quantum effects, and it is a large 3.08 for the most quantum mechanical molecule, helium-3 (He³). Column 4 in Table 1 shows that the hydrogens are intermediate. H₂ is the most quantum mechanical of the hydrogens and T₂ is the least.

The parameter Λ_{eff}^* has the advantage of being theoretically important and applicable to every isotope, whether hydrogen or not. It has several drawbacks. It is not easy to visualize, and it is often described as the size ratio of the wave function to the classical, hard-sphere molecule. It is not easily related theoretically to physical properties either, and its use is often empirical. Only a little work has been done in relating the quantum parameters in mixtures.²² It is based on a Lennard-Jones potential energy well,²¹ and H₂ and D₂ have been found to deviate somewhat.²³ This means nobody knows to within a few percent what the Λ_{eff}^* values really are.

In Table 1, I finally come to the last two parameters, the critical point temperature²⁴ and the triple point temperature, Θ_1 .^{2,25-27} The two sets of temperatures are not mutually consistent, because they come from different sources. This is especially true for the HT, DT,

and T₂ estimates, which are my own for the triple points (and will be described in section 7) and from an older source for the critical points.²⁸ I have gone to considerable effort to make the triple point temperatures as self-consistent a set as possible; the critical temperatures are values selected best by NBS for each isotope.²⁴

Both sets of temperatures form a smooth converging sequence. The temperatures both contain the small differences between the equilibrium and normal forms—a feature not found in the other parameters. Also, one may linearly combine temperatures, as will be seen in the hydrogen mixture section. The temperatures have the disadvantages of being strictly empirical and applicable only across the hydrogens. Also, because of quantum effects, the critical and triple point sequences are different, and one has to decide on one or the other.

The only data that isothermally stretch across H₂, HD, D₂, and T₂ are, as you shall see, those for saturated vapor pressures and liquid densities. For these, Λ_{eff}^* fits better as a parameter than does the triple point temperature, Θ_1 . Not surprisingly, Θ_1 often works better in fitting at the triple point, which is an important step in tying together liquid and solid vapor pressures. For this reason, Θ_1 will appear throughout with Λ_{eff}^* , and in special cases, with the molecular weights. Although this report seeks to unite the hydrogens in a consistent manner, it has not yet been possible to link them by a single parameter.

II. SATURATED, PURE-COMPONENT VAPOR PRESSURES

5. Experimental Liquid-Vapor Equations

Saturated* vapor pressure is possibly the most basic of all bulk properties. The liquid-vapor curve is certainly the most measured single property, and it is used in the calibration of hydrogen sample temperatures over and over. Figure 3 shows the triple point region of the phase diagram. The solid and liquid are separated by the almost-vertical melting curve. The rising lines are the saturated liquid-vapor and solid-vapor curves. At the triple point, the solid, liquid and vapor are in equilibrium with each other. H_2 is more volatile than D_2 or T_2 ; i.e., H_2 rises to a higher pressure at a given temperature.

The liquid-vapor pressures resist efforts to weld them into an isotopically consistent set of values. This is because of (a) the large quantity of experimental data, much of it reported beyond its true accuracy; (b) the use of complicated, empirical equations without a record of the raw data for future reference; and (c) the lack of experimental comparison between isotopes. I shall report the data that appear the best and then attempt to smooth them across the isotopes.

All of the really good data has been taken on H_2 . An international committee has taken three fixed points of eH_2 as primary definitions of the low temperature scale. These points are the triple point of 13.81 K; the 33.3306-kPa (25/76 atm) point — 17.042 K; and the normal boiling point (0.101325 MPa or 1 atm) — 20.28 K. The following equation combines these points for vapor pressure, P^s , in Pa:

$$\ln P^s(eH_2) = 15.46688 - \frac{101.3378}{T} + 5.432005 \times 10^{-2} T - 1.105632 \times 10^{-4} T^2 \quad (6)$$

We may subtract $\ln 133.322$ from the first constant in Eq. (6), obtaining 10.57411, if we wish the pressure in Torr. Equation (6) defines the temperature in the International Practical Temperature Scale of 1968 in the range 13.81 to 23 K. The stated accuracy is a few mK.²⁵ The form of Eq. (6) is a familiar one in describing the saturated liquid and gas. It has been used as long ago as 1948.²

*Saturated means the liquid or solid in equilibrium with the vapor. It is another archaic term that sows confusion. It dates from the days when chemists saturated liquids with gases by bubbling them through.

The statement of the 1968 temperature scale is terse.²⁵ There are no raw data, references, or discussion of how previous work was synthesized. A detailed study was carried out the year before on eH_2 .¹⁷ The eH_2 triple point is reported as 13.802 ± 0.008 K and 7030.2 Pa (52.731 Torr) ± 1.3 Pa. The pressure (rounded off to 7030 Pa) was kept in 1968 but the temperature shifted upward. The triple point data are taken from time curves, and there is some slope even for the purest substances. Hence, extremely accurate definition of a triple point is not easy. Better accuracy is usually obtained on the liquid-gas curve itself. One may extrapolate downward to the triple point pressure to obtain the more elusive triple point temperature.

Equation (6) may be used up to 30 K with a probable 0.25% accuracy.^{2,29,30} However, eH_2 has been measured for the special region 20 to 32 K.³⁰ The equation is, in Pa,

$$\ln P^s(eH_2) = 7.67696 - \frac{71.102}{T} + 2.44498 \ln T \quad (7)$$

Of interest is that this form fits the data better than did the form of Eq. (6), which was also tried. However, Eq. (7)

FIG. 3. Pressure-temperature in the vicinity of the triple point, showing the differences between normal hydrogen (nH_2), deuterium (nD_2), and tritium (T_2). The vertical lines are the melting curves. This section deals with the gently rising curves for solid-vapor and liquid-vapor equilibrium.

does not extrapolate well to lower temperatures. It is for the 20- to 32-K range only.

Normal hydrogen has been accepted as a secondary standard of the 1968 temperature scale.²⁵ The triple point and normal boiling point temperatures are given as 13.956 and 20.397 K. The vapor pressure equation from 13.956 to 30 K is

$$\ln P^s(nH_2) = 15.52059 - \frac{102.7498}{T} + 5.338981 \times 10^{-2}T - 1.105632 \times 10^{-4}T^2 \quad (8)$$

For the pressure in Torr, the first constant is 10.62789.

The best HD liquid-gas data are from a 1951 set of eH_2 , HD, and eD_2 measurements. The data have been smoothed and are presented in tabular form.³¹ They are fitted to previously measured triple point values of 16.60 K and 12370 Pa (92.8 Torr).²

There are not as much good data on D_2 , as might be expected. There are tabular data for eH_2 ,³¹ and for nD_2 ,

$$\ln P^s(nD_2) = 18.3408 - \frac{161.282}{T} + 1.057 \times 10^{-3}(T - 23)^2 \quad (9)$$

which may be used from the triple point to 28 K. The triple point is 18.73 K and 17150 Pa (128.6 Torr).²⁶

The T_2 data are represented from the triple point to 29 K by the equation

$$\ln P^s(nT_2) = 18.7852 - \frac{181.732}{T} + 4.605 \times 10^{-4}(T - 25)^2 \quad (10)$$

The triple point values are 20.62 K and 21600 Pa (162.0 Torr).²⁶ An updated version of equal value is^{26,27}

$$\ln P^s(nT_2) = 19.11365 - \frac{182.0038}{T} - 2.560401 \times 10^{-2}T + 5.133943 \times 10^{-4}T^2 \quad (11)$$

Equation (11) uses the same triple point pressure but raises the corresponding temperature to 20.627 K as a result of temperature-scale changes over the years. My feeling is that the isotopes other than H_2 are no better

than ± 0.01 K in accuracy. New experiments are probably more valuable than adjustment of old data for temperature-scale redefinitions.

6. Experimental Solid-Vapor Equations

The saturated solid-vapor pressure data is not even close to the quality of the liquid values. It has not been considered for use as a temperature scale. I shall present several old equations, which cover limited ranges just below the triple points. These equations are probably no better than the smoothed versions of the next section. I shall use the letter Q^s to denote the pure-component solid-vapor pressure and to distinguish it from the liquid-vapor pressure, P^s . For eH_2 , from 10.5 K to the triple point,²

$$\ln Q^s(eH_2) = 15.5408 - \frac{108.261}{T} + 0.08370T \quad (12)$$

and for nH_2 ²

$$\ln Q^s(nH_2) = 15.4038 - \frac{108.696}{T} + 0.09070T \quad (13)$$

For nD_2 , from 14 K to the triple point,²⁶

$$\ln Q^s(nD_2) = 19.1918 - \frac{177.476}{T} + 6.63 \times 10^{-3}(T - 16.5)^2 \quad (14)$$

And for T_2 , from 14 K to the triple point,²⁶

$$\ln Q^s(nT_2) = 19.8073 - \frac{202.632}{T} \quad (15)$$

These equations are probably good to the nearest 0.01 to 0.02 K near the triple point.

Some outstanding low temperature measurements have been taken in recent years for astrophysical interests.^{32,33} These equations may be used in their narrow, low temperature regions. For thick layers of solid

(probably normal) H_2 condensed on copper between 2.5 to 4.5 K the vapor pressure is

$$Q^s(H_2) = 1.135 \times 10^6 \exp \left[-\frac{813.8}{RT} \right], \quad (16)$$

where the 818 J/mole is a measure of the heat of sublimation, given this form of equation. The equation for (probably normal) solid D_2 on copper in the range 3.8 to 5.3 K is

$$Q^s(D_2) = 8.146 \times 10^6 \exp \left[-\frac{1224}{RT} \right]. \quad (17)$$

The largest error, according to the researchers, is in the energy term of the exponent, which is accurate to ± 20 J/mole. Although this is less than 2-1/2%, its effect in an exponential equation at low temperature is large. It amounts to an uncertainty in pressure of -45% and +60 to 80%. This, in turn, may seem large but it is the best by far ever done on low temperature hydrogen. At vapor pressures of 10^{-7} Pa (10^{-9} Torr), accuracy even to an order of magnitude is difficult.* Below 3 K for H_2 and 4.5 K for D_2 , the presence of almost any heat source, including hotter condensing hydrogen molecules, will cause a vapor pressure above those predicted by Eqs. (16) and (17).

A recent study by H. Halama and T. S. Chou has yielded the first measurement on low temperature solid T_2 . At 4.2 K, the vapor pressure is below the 5×10^{-9} -Pa (4×10^{-11} -Torr) sensitivity limit of the quadrupole mass spectrometer.³⁴ It appears, at least, that the radiation does not produce any sizeable anomalous vapor pressure. In a thick layer of solid T_2 , however, there may be thermal gradients caused by the radioactive heat of decay. The edge farther from the copper backing may become hot, with a corresponding increase in vapor pressure.

7. The DT Triple Point and the Rule of the Geometric Mean

Molecular DT and HT have never been isolated in bulk and their triple point constants measured. One must estimate them to complete the isotopic sequence.

*Nevertheless, Eq. (16) at 4 K is only 35% off from the theoretical value of J. C. Mullins, W. T. Ziegler, and B. S. Kirk, *Adv. Cryogenic Engineering* 8, 116 (1963).

I first turn to the rule of the geometric mean as a means of relating vapor pressures.³⁵ This empirical rule considers a trio of isotopes like H_2 , HD, and D_2 (isotope numbers 1, 2, and 4), which are related by their chemical equilibrium. At a given temperature, the rule states that

$$P_2^s = \chi_{124} [P_1^s \cdot P_4^s]^{1/2}, \quad (18)$$

where χ_{124} is 1 if the rule holds perfectly. Equation (18) resembles the chemical equilibrium relation at high temperature. However, Eq. (18) consists of pure-component vapor pressures considered individually. The only trio of isotopes ever measured together in one experiment is eH_2 -HD- eD_2 .³¹ For the liquid-vapor equilibrium, χ_{124} is 0.965 at 18 K and 0.98 at 30 K; for the solid and vapor, it is 0.90 to 0.915 at 10 to 13 K. We find χ_{124} to be lower for the solid than for the liquid. If high-temperature assumptions are indeed built into Eq. (18), one might expect normal vapor pressures to be more useful. I combine the various references of parts 1 and 2 for nH_2 -HD- nD_2 to obtain a liquid χ_{124} of 0.994 to 0.998 from 14 to 30 K and a solid χ_{124} of 0.991 at 14 K. There is indeed better agreement mostly because the nH_2 vapor pressure is lower than that of eH_2 . I shall use Eq. (18) with χ_{124} equal to 1 to obtain DT and HT vapor pressures, with normal hydrogens on the right side, even though their use is empirical.

An earlier triple point estimate exists, and it also uses the rule of the geometric mean.²⁸ The steps were (a) estimate all critical temperatures and pressures, (b) work one's way empirically to the triple point temperatures, (c) estimate isothermal vapor pressures by the rule of the geometric mean, and (d) empirically estimate the triple point pressure from the triple point temperature. This procedure gave these results: DT — 19.71 K and 19 425 Pa (145.7 Torr) and HT — 17.62 K and 14 600 Pa (109.5 Torr). The second step above was not so good, however. Its prediction for the HD triple point temperature was low by 0.08 K.

I shall make my own stab at the triple point constants. First, I shall borrow an observation from hydrogen solutions, i.e., that the first freezing point, Θ , is close to

$$\Theta(\text{first freeze}) \approx \sum_i x_i \Theta_i, \quad (19)$$

where x_i is the liquid mole fraction of isotope i and Θ_i is its pure-component triple point temperature. I, thus, consider HD to be an "atomic solution" of equal parts of eH_2 and eD_2 , and write

$$\Theta_2 = \frac{\Theta_1 + \Theta_4}{2} + 0.07172(\Theta_4 - \Theta_1). \quad (20)$$

The first term on the right corresponds to Eq. (19), and it yields 16.25 K. The second term represents the deviation from the ideal solution, which is 0.35 K. It is also true that non-idealities of solutions become larger as the pure-component triple points become farther removed from one another. The more different the isotopic pair, the larger the non-ideality. I, thus, make my correction term a function of the triple point temperature differences. I now use Eq. (20) to calculate Θ_i for DT and HT, and obtain 19.79 K and 17.70 K. These are probably better than the lower values estimated previously,²⁸ if only because of the 0.08 K lost in the HD fit.

For the triple point pressures, I return to the rule of the geometric mean, which holds only at a given temperature. I use the references of part 1 to find that $\chi_{124} = 0.996$ for the HD triple point pressure as derived from the 16.60 K values of nH_2 and nD_2 . I set χ_{124} equal to 1 and obtain for the other hydrogens: DT — 20 060 Pa (150.5 Torr) and HT — 14 510 Pa (108.8 Torr). However, in the next section, I develop some simplified equations for vapor pressure. Using the same triple point temperatures, these upcoming equations yield pressures of 20 080 Pa (150.63 Torr) for DT and 14 580 Pa (109.35 Torr) for HT. It is these values that I include in Table 2.

8. Making Handy Vapor Pressure Equations

For closely calibrating temperatures, one should use Eqs. (6) through (9) for eH_2 , nH_2 , or nD_2 . For laboratory calculations of tritium mixtures, it is convenient to prepare a set of simple equations. I shall use the form of Eq. (7), which is

$$\ln P^s(\text{or } Q^s) = A - \frac{B}{T} + C \ln T \quad (21)$$

There will be a different set of constants, A, B, and C for P^s and for Q^s . I now use the Clausius–Clapeyron equation for a liquid in equilibrium with its vapor:

$$\frac{d \ln P^s}{dT} = \frac{1}{z \left(1 - \frac{\rho}{\rho_L}\right)} \cdot \frac{H_v}{RT^2} \quad (22)$$

where z is the gas compressibility, ρ the gas density, ρ_L the liquid density, H_v the heat of vaporization, and R the gas constant.³⁶ For a solid, I use its density, ρ_s , and the heat of sublimation, H_s . I use Eqs. (21) and (22) to derive

$$H_v = \left[z \left(1 - \frac{\rho}{\rho_L}\right) \right] R(B + CT) \quad (23)$$

This adds a certain amount of theoretical substance to the vapor pressure equations.

The choice of Eq. (21) stems from my earlier attempt to fit a four-constant vapor pressure equation across the isotopes, which resulted in considerable scattering of the constants. Also, the analysis of the quantity

$$H_v \left[z \left(1 - \frac{\rho}{\rho_L}\right) \right]^{-1}$$

for both liquid and solid showed it to be almost linear with temperature.³⁷ I, thus, select the simple three-constant form of Eq. (21).

Table 2. Various saturated liquid and solid properties used in the construction of the three-constant vapor pressure equations. DT and HT are estimates.

Isotope	Triple point		Normal boiling point (K)	Calculated				
	Temp (K)	Pressure, Pa (Torr)		$z \left(1 - \frac{\rho}{\rho_L} \right)$	Triple point			0 K
					H _v (J/mole)	H _s (J/mole)	H _f (J/mole)	H _s (J/mole)
eH ₂	13.81	7030 (52.73)	—	0.9826	—	—	—	—
nH ₂	13.956	7200 (54.00)	20.41		908	1025	117	728
HD	16.60	12370 (92.8)	22.14		1102	1261	159	946
HT	17.70	14580 (109.35)	22.91	0.9759	1199	1377	178	1056
eD ₂	18.69	17130 (128.5)	—	0.9744	—	—	—	—
nD ₂	18.73	17150 (128.6)	23.67		1266	1463	197	1137
DT	19.79	20080 (150.63)	24.37		1360	1577	217	1246
nT ₂	20.62	21600 (162.0)	25.04	0.9718	1447	1680	233	1347

I shall proceed with the liquid-vapor pressures as follows: (a) use the best references to calculate nH_2 , HD, nD_2 , and T_2 vapor pressures at the triple point, 30 K (29 K for T_2), and half-way between, (b) fit Eq. (21) to these three points, (c) calculate A from Eq. (21) at the triple point, (d) calculate H_v from Eq. (23), (e) estimate the DT and HT vapor pressures using the rule of the geometric mean at the same three temperatures, and (f) repeat the previous steps for these isotopes.

Now, I consider the details. The three-constant fit is worst between the pairs of points used in the fitting. For nH_2 , which covers the largest temperature range, the fit deviates a maximum of 0.8% at 17 K. For HD, nD_2 , and T_2 , the maximum deviations are 0.3, 0.4, and 0.1%. The resulting constants are in Table 3. Note that the sequences of B and C are now in the proper order, except for the pair HT and nD_2 . The normal boiling points (1 atm) calculated from Table 3 are in Table 2. Those of HD, nD_2 , and T_2 are the same for both the four- and three-constant vapor pressure equations. That of nH_2 is increased from the accepted value of 20.397 K²⁵ to 20.41 K. Table 2 also lists the triple point heats of vaporization, H_v , as calculated from Eq. (23). To obtain these, I borrow, from data to be presented later, the expression derived for H_2 , HD, and D_2 :

$$z \left(1 - \frac{\rho}{\rho_L} \right) \simeq (1.058) \Theta_i^{-0.028} \quad (24)$$

Equation (24) holds only at the appropriate triple points.

I proceed to the solid vapor pressures as follows: (a) use a power fit of nH_2 , HD, and nD_2 heats of fusion at the triple point with Θ_i to generate the isotopic set, (b)

calculate all triple point heats of sublimation, H_s , (c) use low temperature nH_2 and nD_2 data to derive the B and C constants for this pair, (d) derive C for the other isotopes using a power fit with Θ_i , (e) calculate B from Eq. (23), and (f) calculate A from Eq. (21).

The estimating is much more liberal with the solid because the available HD and T_2 data are scattered and descend in temperature only to 10 K. The 4-K vapor pressures are so many decades down that one cannot estimate well from 10 K. One must, thus, fit with the data that does go to 4 K, which is available for only two isotopes. Also required is a reasonable set of heats of fusion. One starts, thus, with three calorimetrically measured heats of fusion, H_f : $nH_2 = 117.2$,³⁸ HD = 159.4,² and $nD_2 = 196.6$ J/mole.³⁹ At the triple point, I obtain the heat of sublimation, H_s , by

$$H_s = H_f + H_v \quad (25)$$

I divide H_s by $z(1 - \rho/\rho_L)$ from Eq. (24), even though this does not strictly apply to the solid. I pair these points with the two low temperature data: $nH_2 = 818$ J/mole at 4 K³² and $nD_2 = 1224.5$ J/mole at 4.5 K.³³ This is enough to obtain B and C for nH_2 and nD_2 . The first constraint is in the isotopic set of H_s . I next employ a power fit for C with Θ_i as the second constraint. I then calculate B for each isotope from the triple point relation:

$$B = \frac{H_v}{Rz \left(1 - \frac{\rho}{\rho_L} \right)} - C \Theta_i \quad (26)$$

Table 3. Three-constant saturated vapor pressure equations — a partially smoothed isotopic view of the hydrogen isotopes. DT and HT are estimates.

		$\ln P^s \text{ (or } Q^s) = A - \frac{B}{T} + C \ln T$		
		A, Pa (Torr)	B (K)	C
Liquid-vapor	nH_2	9.64596 (4.75319)	83.5177	1.98042
	HD	11.5827 (6.68995)	109.419	1.57756
	HT	12.7295 (7.83671)	123.995	1.34440
	nD_2	12.6317 (7.73898)	130.249	1.38962
	DT	14.2203 (9.32752)	147.349	1.04950
	nT_2	15.8148 (10.9220)	164.486	0.707997
Solid-vapor	nH_2	7.98227 (3.08950)	87.5045	2.71994
	HD	9.28372 (4.39095)	113.784	2.48948
	HT	9.84277 (4.95000)	127.063	2.40929
	nD_2	10.1915 (5.29874)	136.742	2.34074
	DT	10.6890 (5.79620)	149.916	2.27590
	nT_2	11.0907 (6.19797)	161.969	2.22868

This tiresome procedure yields the set of Table 3 constants that are now in the proper isotopic sequence. My equations possess geometric mean χ_{ijk} values a little below 1. These decline with temperature and show the desired isothermal decrease from DT to HD to HT. The

calculated solid heats are in Table 3. Note that RB is the heat of sublimation at 0 K, because the gas over the solid is now so diffuse as to be perfect.

An expanded list of solid and liquid vapor pressures is in Appendix C for nH_2 , nD_2 , DT, and nT_2 .

III. THERMODYNAMICS OF THE SATURATED PURE-COMPONENT HYDROGENS

9. The Virial Coefficients and Gas Densities

I take 30 K as my high temperature limit and consider as the highest pressure the 0.8-MPa (8-atm), 30-K value for H₂. The corresponding gas compressibility, z , is 0.6. This may be compared to 1 for a perfect gas and to about 0.3 for the critical point fluid. At my disposal are two virial coefficients. I expand z by the equation

$$z = \frac{PV}{RT} = 1 + B\rho + C\rho^2 = 1 + \frac{B^*P}{RT} + \frac{C^*P^2}{RT}, \quad (27)$$

where ρ is the density and P the pressure. B is the second virial coefficient in terms of density; B^* is in terms of pressure. C and C^* are the corresponding forms for the third virial coefficient. B and B^* have the same units (m³/mole), but C (m⁶/mole²) and C^* (m⁶/mole²-J) do not. One may relate B and C to pressure by the formula

$$z \simeq 1 + \frac{BP}{RT} + (C - B^2) \left(\frac{P}{RT} \right)^2 \quad (28)$$

This assumes an infinite series of virial coefficients,⁴⁰ which is not true in my case. The error in using Eq. (28) instead of Eq. (27) is 11% for nH₂ at 30 K but only 1.6% for nD₂. Usually, one has the pressure but not the density. If Eq. (28) won't do, then one must solve Eq. (27) for ρ . The inverse of V is ρ , and the equation to be solved is

$$C\rho^3 + B\rho^2 + \rho - \frac{P}{RT} = 0. \quad (29)$$

The second virial coefficient has been measured in the range 14 to 30 K for H₂, HD, and D₂.^{2,41-45} Extensive data exist for eH₂ and nH₂, but the range of values between them spreads over $\pm 2.5\%$. However, the relative difference is known to be only 1% (eH₂ is less negative.⁴⁶ It is clearly difficult to select the best second virial coefficients for H₂, and it is worse for HD and D₂. I represent the second virial coefficient by the empirical equation

$$B = B_0 T^b. \quad (30)$$

Table 4 lists constants B_0 and b . I estimate those for T₂, DT, and HT from a power fit of the constant with Λ_{eff}^* (Θ_1 does not work very well). Note that B is negative, and it causes z to decrease below 1. As temperature increases, B becomes less negative. As one proceeds from H₂ to T₂, B becomes more negative.

There are only two H₂ sources for the third virial coefficient,^{2,43} and they, unfortunately, show opposite temperature dependences. I shall skirt the issue by observing that one only needs C near 30 K, where the pressures are highest. I have no isotopic data at low temperatures (although there are some from 105 K up⁴⁷), and I use a single value for all the hydrogens:

$$C = 1.8 \times 10^{-9} \frac{\text{m}^6}{\text{mole}^2}. \quad (31)$$

At lower temperatures, C will not be right, but its effect will be negligible. Note that C is positive.

A more detailed set of gas densities and compressibilities for nH₂, nD₂, DT, and nT₂ is available in Appendix C.

Table 4. Second and third density-dependent virial coefficients of the hydrogen from 14 to 30 K. HT, DT, and T₂ are estimates. C is really for H₂, but is to be used for all.

Isotope ^a	$B = B_0 T^b$ (m ³ /mole)	
	B_0 (m ³ /mole-K ^m)	b
eH ₂	-0.0112	-1.44
nH ₂	-0.0113	
HD	-0.0159	-1.52
HT	-0.0196	-1.58
D ₂	-0.0250	-1.64
DT	-0.0310	-1.70
T ₂	-0.0395	-1.77

^aFor all isotopes, $C = 1.8 \times 10^{-9} \text{ m}^6/\text{mole}^2$.

10. Liquid Densities

Quite a bit of work has been done on the saturated liquid densities. Those of $J=0$ H_2 and nH_2 have been measured by absolute methods to better than $\pm 0.05\%$.^{2,48-50} Less data is available for the other isotopes. It consists of HD — 16.60 to 20 K;² D_2 — 18.73 to 24.2 K;^{2,38,51} and T_2 — 20.62 to 29 K.⁵² The three isotopes, nH_2 , HD, and nD_2 , were measured together.^{53,54*} but the method was relative, and the data had to be fit to the previous absolute H_2 values. The stated accuracy was 0.1 to 0.2%, although it appears that deviations of perhaps 1% were present at 30 K. We have not, therefore, used this latter source.

For quarter-percent work, one may use a simple quadratic formula from the triple point to 24 to 28 K, depending on the isotope. The equation for the liquid density, ρ_L , is

$$\rho_L = A - BT^2, \quad (32)$$

where the constants are in Table 5. The constants for DT and HT are obtained by interpolation as a function of Λ_{eff}^* above the upper temperature given in Table 5, and ρ_L grows more rapidly than expected in Eq. (32). The actual liquid densities to 30 K for nH_2 , nD_2 , DT, and nT_2 are in Appendix C.

Another relation must be satisfied in my extrapolations: a geometric mean-type relation for liquid density at a given temperature. It has been proposed that, for nH_2 –HD– nD_2 ,^{53,54}

*The English translations [Russ J Phys Chem 42, 126(1968); 43, 434(1969)] contain an error. The experiments, done with normal H_2 and D_2 , are reported as the para form I, thus, reference the original Russian sources.

Table 5. Simple equations for liquid hydrogen densities, from the triple point to the upper temperature listed. HT and DT are estimates.

Isotope	$\rho_L = A - BT^2$		Upper temp (K)	Calc at triple point	
	A (mole/m ³)	B (mole/m ³ –T ²)		ρ_L (mole/m ³)	V (m ³ /mole)
eH_2	40860	14.03	24	38180	26.19
nH_2	41060	14.19	24	38300	26.11
HD	44690	13.93	25	40850	24.48
HT	46150	13.56	26	41900	23.87
D_2	47780	13.15	28	43170	23.16
DT	49480	13.30	28	44270	22.59
T_2	51050	13.45	28	45330	22.06

$$\rho_{L2} = \chi_{124} [\rho_{L1} \cdot \rho_{L4}]^{1/2}, \quad (33)$$

where χ_{124} is close to 1. Comparison of the same isotopes from the same equipment yielded an χ_{124} of 0.9996 from 19 to 22 K and 1.0000 from 23 to 30 K.^{53,54} If I use preferred values for this sequence,^{2,48-50} I obtain χ_{124} values of 1.010 to 1.011 at 19 and 20 K. Equation (32) with Table 5 values gives densities quite in agreement with the latter χ_{124} values.

11. Solid Densities

Two brand-new equation-of-state studies have forced a hasty reconsideration of the solid densities.^{55,56} Would that someone would simply measure the saturated densities.

Table 6 contains a detailed list of recent solid molar volumes.^{2,55-63} The "low temperature" volumes cover the range 1.5 to 7 K; they may be considered to have no significant temperature dependence in this region. Moreover, I shall use these values as well for extrapolation to 0 K. Older bulk density work⁶⁴ and the first x-ray measurements,^{65,66} including the only T_2 point,⁶⁷ have been dropped from the list. These give rise to a long-accepted 4-K volume of 22.65 $\mu(\text{m}^3)/\text{mole}$ for $J=0$ H_2 .⁴ Swenson has recently shown experimentally that this volume must be greater than 22.79 $\mu(\text{m}^3)/\text{mole}$.⁵⁵ The newly derived values are obtained by calculation and adjustment of other data. The two final H_2 volumes are in excellent agreement,^{55,56} and I have selected 23.14 $\mu(\text{m}^3)/\text{mole}$ for $J=0$ H_2 for no better reason than that the author went on to do D_2 as well. Note that the low temperature solid arranges itself in two crystal structures: hexagonal close-packed (hcp) and face-centered cubic (fcc). There is only a 0.1 to 0.2% density change upon transformation between these structures.⁶⁸ One may, thus, consider them to be directly comparable as far as density is concerned.

Note from Table 6 that one cannot ignore the mole fraction of $J=1$ states, $c(1)$. The only good comparison data exist for 0.02 and 0.29 $c(1)$ hcp D_2 at 1.5 to 4 K. These have the molar volumes⁶¹

$$V(D_2, \mu(\text{m}^3)/\text{mole}) = 19.998 - 0.203c(1) \pm 0.013. \quad (34)$$

I extrapolated these a little farther to 0 and 0.33 $c(1)$ for Table 6. As part of the experimental procedure, the D_2 was injected into liquid helium. This leaves open the possibility that helium trapped in the frozen D_2 might

Table 6. Recent molar volumes of the solid hydrogens. The abbreviations are: hcp—hexagonal close-packed crystal structure; fcc—face-centered cubic; and c(1)—the mole fraction of the J=1 rotational state. I believe the solid HD volumes from 2.8 to 7 K to be in error. The abbreviation “diff” indicates diffraction.

Isotope	Temp (K)	Mole vol [$\mu(\text{m}^3)/\text{mole}$]	Claimed accuracy [$\mu(\text{m}^3)/\text{mole}$]	Ref.	Method used	Remarks
nH ₂	2.8-4.5	22.91	± 0.11	58	Electron diff	fcc
nH ₂	4.5-7.0	22.91	± 0.13	58	Electron diff	hcp
nH ₂	4.2	22.90	± 0.1	62	X-ray diff	
J=0 H ₂	4.2	23.20	± 0.05	55	Calc	hcp
J=0 H ₂	4.2	23.14 ^a	± 0.08	56	Calc	hcp
nH ₂	13.96	23.25	—	2	Calc	
J=0 H ₂	13.81	23.31 ^a	—	57	Calc	
nH ₂	13.96	23.23-6	—	57	Calc	
HD	2.8-4.5	20.96	± 0.11	58	Electron diff	fcc
HD	4.5-7.0	20.59	± 0.21	58	Electron diff	hcp
HD	16.60	21.84 ^a	—	2	Calc	
nD ₂	2.8-4.5	19.88	± 0.08	58	Electron diff	fcc
nD ₂	4.5-7.0	19.90	± 0.11	58	Electron diff	hcp
D ₂	1.9	19.67	± 0.10	59	Neutron diff	fcc, c(1)=0.80
D ₂	2.0	19.73	± 0.12	59	Neutron diff	hcp, c(1)=0.63
D ₂	4.2	19.85	± 0.12	59	Neutron diff	hcp, c(1)=0.80
J=0 D ₂	1.5-4.0	20.00	± 0.013	60, 61	Neutron diff	hcp
nD ₂	1.5-4.0	19.93	± 0.013	60, 61	Neutron diff	hcp
D ₂	4	19.87	± 0.09	63	?	
J=0 D ₂	4.2	19.95 ^a	± 0.05	56	Calc	
nD ₂	18.73	20.48 ^a	—	2	Calc	

^aMy “official” values.

have expanded the lattice. You shall see in a later section that the helium solubility in liquid D₂ is small at low pressures. One would expect it to be smaller yet in the solid, although the quenching in this experiment appears to have been very rapid.^{60,61} In any case, adding rotational energy decreases the molar volume.

Table 6 also includes solid volumes at the triple point. These are generally “calculations” in that a liquid volume is combined with the Clausius–Clapeyron equation to work one’s way across the melting point. The thirty-year-old points for HD and D₂ seem good.² Note, however, that the sequence of accepted (asterisk-marked) points shows the low temperature HD data to be seriously out of order,⁵⁸ and I shall not accept these points.

I need one other thing: a set of data along the saturation curve as a function of temperature. The closest available data are eight thermal expansivities taken at 0.39 MPa (3.9 atm) on J=0 H₂ from 10 to 13.5 K.⁶⁹ These points show a temperature dependence to the fourth power. I integrate to obtain

$$\ell_n \frac{\rho_s(0)}{\rho_s(T)} = \ell_n \frac{V(T)}{V(0)} = AT^5, \quad (35)$$

where the densities, ρ_s , and volumes, V , are listed at 0 K and temperature T . The coefficient A has the value $2 \times 10^{-8} \text{ K}^{-5}$.⁶⁹ If I take my “official” H₂ values at 4 K (which is the same as 0 K to me) and at the triple point, I obtain the more desirable A value of $1.48 \times 10^{-8} \text{ K}^{-5}$. Equation (35) appears to work, and I shall apply it to obtain estimated densities from 0 K to the triple points.

My “good” data now consist of two points for J=0 H₂ and D₂; this allows me to calculate the A constants, listed in Table 7. I also have single values at the triple point for nH₂ and HD. Everything else will have to be estimated. I fit two basic quantities to the quantum parameter, Λ_{eff}^* : the % density change upon freezing and the constant A . The first allows me to estimate across the triple point; the second allows me to extrapolate to 0 K. The resulting estimates are also in Table 7.

Table 7. Densities of the solid hydrogens. Note how far the 0 K HD value is from the measured values of Table 6.

Isotope	% Density change upon freezing	Density (mole/m ³)		Volume [μm^3]/mole		
		$\rho_n \frac{\rho_s(0)}{\rho_s(T)} = AT^5$		$\rho_n \frac{V(T)}{V(0)} = AT^5$		
		0 to 4.2 K	Triple point	A, $\times 10^{-8}$ (K ⁻⁵)	0 to 4.2 K	Triple point
J=0 H ₂	12.4	43220	42900	1.48	23.14	23.31
nH ₂	12.3	43370 ^a	43030	1.48 ^a	23.06 ^a	23.24
HD	12.1	46550 ^a	45790	1.31 ^a	21.48 ^a	21.84
HT	12.9 ^a	48320 ^a	47300 ^a	1.23 ^a	20.69 ^a	21.14 ^a
nD ₂	13.1	50130	48830 ^a	1.14	19.95	20.48
DT	13.3 ^a	51800	50160 ^a	1.06 ^a	19.30 ^a	19.94 ^a
nT ₂	13.5 ^a	53360	51450 ^a	0.98 ^a	18.74 ^a	19.44 ^a

^aMy estimate.

Saturated hydrogen crystallizes in the structure from the triple point to just below 4 K. Then the structure changes to fcc in a first order transition (i.e., with a volume change).^{66,68} The fcc phase possesses an ordering of the J = 1 spins by means of an electric quadrupole interaction.^{70,71} The accompanying excitational waves and molecular clusters are a physicist's delight, and they have been the subject of intense study in university laboratories for the past decade. The crystallographic

transition temperature, called the lambda point, increases with molecular weight and the percent of J = 1 molecules. So nH₂ transforms at about 1.6 K, nD₂ at about 2.2 K,⁶⁶ and one might expect nT₂ at 2.8 K. For 100% J = 1 T₂, the lambda temperature would be expected at about 4.8 K, but there is no reason for most people to enrich the T₂ in this way. As you shall see in a later chapter, the tritium beta particle will convert (at 4.2 K anyway) the J = 1 to J = 0 T₂ with a half-time of about an hour. It is unlikely that a high J = 1 concentration can be maintained for long. Below about 50% J = 1, the fcc structure no longer appears, as there are not enough J = 1 molecules to produce the necessary alignment. For less than 50% J = 1 molecules, the solid remains in the hcp form. A low temperature "spin glass" phase has been postulated for the hcp structure,⁷² but the existence of an hcp-to-hcp transition has yet to be demonstrated.⁷³

All ordinary applications of heavy hydrogen to 4.2 K will almost certainly involve just the hcp phase. This is not an easy structure to visualize; it is shown in Fig. 4. Each ball in Fig. 4 represents a diatomic hydrogen molecule; the white or black is used just to distinguish between planes of molecules. Figures 4a and 4b show the unit cell, the basic building block. It is a prism of height c and a base made of an equilateral triangle of side a. There are two kinds of prisms — one with a molecule and one without, and they are situated next to each other

FIG. 4. Hexagonal close-packed crystal structure, which is the usual lattice for solid hydrogen. Each ball represents a diatomic molecule; white and black are used only to distinguish between planes. This figure shows (a) the triangular-prism unit cell with a molecule inside; (b) the unit cell with no molecule inside; and (c) the assembly of unit cells, showing the white and black interpenetrating hexagonal sublattices.

in the crystal. Figure 4a shows the cell with the molecule in the middle. If molecule 1 is at the X,Y,Z location of (0,0,0), molecule 2 is at (2a/3, a/3, c/2). In this cell of volume (3^{1/2}a²c)/4, there are 1-1/2 molecules (each corner molecule counts 1/6). In Fig. 4b is the next-door cell with the same volume but only 1/2 molecule inside. Each unit cell, then, contains an average of 1 molecule. There is an Avogadro's Number, N₀, of unit cells per mole, and the solid density, ρ_s, is

$$\rho_s = \frac{4}{\sqrt{3} N_0 a^2 c} = \frac{3.834 \times 10^{-24}}{a^2 c} \quad (36)$$

If the molecules were perfectly round balls, the ratio c/a would be 1.633.⁷⁴ Neutron diffraction in solid D₂ yields a ratio of 1.6317,⁶¹ which shows that the ball molecule model is good. One may substitute the perfect c/a value to obtain

$$a \approx \frac{1.329 \times 10^{-8}}{\rho_s^{1/3}} \quad (37)$$

and

$$c \approx \frac{2.171 \times 10^{-8}}{\rho_s^{1/3}} \quad (38)$$

Note that a is the nearest neighbor (center-to-center) distance in the horizontal plane of molecules. The average nearest neighbor distance is that from molecule 1 to 2 or about 1.80a. There are two interstitial locations. The tight one is inside the tetrahedral cage formed by four molecules in Fig. 4a. The distance from the center of this cage to the center of the nearest neighbor is 0.76a. The other interstitial location is the spacious prism with no center molecule of Fig. 4b. The cage center-to-nearest neighbor distance is 1.80a.

I now put Figs. 4a and 4b together with four more unit cells to obtain the white-molecule hexagonal prism of Fig. 4c. Inside this prism are three black molecules floating half-way up. This can be expanded into a black hexagonal prism slightly displaced from the white one. The two hexagonal sublattices interpenetrate each other.

12. Translational Energy of the Gas

The energy of the gas is the sum of the vibrational, rotational, and translational modes of motion. Below 30 K, the molecular vibrational energy is

so small that one may ignore it. For DT, HT, and HD the rotational energy, E_R, must be added. To a first approximation, the same energy will be added to the solid or liquid, and the heats of sublimation and vaporization will not be affected. E_R is calculated in Section 33. For T₂, D₂, and H₂ in many experiments, one may ignore E_R. Although it may in fact be very large, E_R is locked away in its own insulated compartment, only to issue forth with appropriate catalytic stimulation.

Most of the easily accessible energy of hydrogen gas is translational. The internal energy of the gas, E(gas), is⁷⁵

$$\begin{aligned} E(\text{gas}) &= \frac{3}{2} RT + \left(B^* - T \frac{dB^*}{dT} \right) P \\ &\quad + \left(C^* - T \frac{dC^*}{dT} \right) \frac{P^2}{2} + E_R \\ &\approx \frac{3}{2} RT + (1-m)BP + \frac{(C-B^2)P^2}{2RT} + E_R, \end{aligned} \quad (39)$$

where the second and third virial coefficients from Section 9 are used to describe the non-ideal gas contribution. The term (3RT)/2 is the ideal gas contribution. The corresponding enthalpy, H(gas), is Eq. (39) plus RT.

The heat capacity at constant volume is the first derivative of E(gas) with respect to temperature. We have⁷⁵

$$\begin{aligned} C_V(\text{gas}) &= \frac{3}{2} R - T \left[\left(\frac{d^2 B^*}{dT^2} \right) P \right. \\ &\quad \left. + \left(\frac{d^2 C^*}{dT^2} \right) \frac{P^2}{2} \right] + C_R \approx \frac{3}{2} R \\ &\quad - \frac{m(m-1)BP}{T} + C_R, \end{aligned} \quad (40)$$

where C_R is the rotational heat capacity.

Values of E(gas) for various isotopes are in Table 8. Note that at about 30 K, the negative (1-m)BP term in Eq. (39) becomes large enough to offset the steadily increasing (3RT)/2 term. In effect, the non-ideal gas energy makes vaporization a slightly less energetic process.

Table 8. Internal energies of the saturated hydrogens. E (gas) and E (solid/liquid) are thermal, with some rotational energy in the case of DT. $E_{s,v}$ is the energy of sublimation or vaporization. ϕ_T is the binding energy and ψ_T the classical well depth. DT and T_2 are estimates. All rotational energy for D_2 and T_2 is to be accounted for separately, as it is insulated from the above energies. nH_2 has $E_{s,v}$ values about 10 J/mole larger than those for $J=0$ H_2 . The small quadrupolar energies for solid D_2 and T_2 are not included.

Isotope	Phase	Temp (K)	Energies (J/mole)				
			E (gas)	E (solid /liquid)	$E_{s,v}$	$-\phi_T$	$-\psi_T$
$J=0$ H_2	Solid	0	0	0	728	-728	-1733
		13.81			909	-741	-1726
	Liquid	13.81	168	15	795	-627	-1754
		20	215	132	752	-537	-1625
		25	222	230	658	-436	-1487
		30	200	341	442	-242	-1228
D_2	Solid	0	0	0	1137	-1137	-2096
		18.7			1309	-1085	-2041
	Liquid	18.7	224	61	1127	-903	-2053
		25	262	258	1021	-759	-1915
		30	259	415	895	-636	-1794
				569			
DT	Solid	0	0	0	1246	-1246	-2196
		19.79			1418	-1140	-2137
	Liquid	19.79	278	118	1200	-922	-2123
		25	354	335	1117	-763	-1971
		30	379	468	969	-590	-1809
				622			
T_2	Solid	0	0	0	1347	-1347	-2297
		20.62			1516	-1270	-2231
	Liquid	20.62	246	90	1290	-1044	-2229
		25	275	323	1200	-925	-2115
		30	282	436	1060	-778	-1979
				591			

13. Translational Energies of the Solid and Liquid

I now determine the internal energies of the condensed phases. Again, I ignore the molecular vibrational energy below 30 K. There will be a small rotational energy for the heteronuclear hydrogens; that of the homonuclear hydrogens I remove to a separate category. I come, then, to the translational energy. For a solid, the molecules cannot move about freely and the translational energy is bound in the crystal lattice vibrations. For the solid, there is also a small quadrupolar energy, which depends on the concentration of $J=1$ molecules. This small energy will be calculated in Section 34. In the liquid, the molecules can flow past each other. One has a smeared-out set of lattice vibrations plus a large, new low-frequency component caused by the liquid diffusional motion. There is no quadrupolar energy, as this effect is washed out by the molecular motion.

I shall consider the translational energy of $J=0$ hydrogen. One usually is given the saturated heat capacity, C_s^t , which is close to, but not quite, the heat capacity at constant pressure, C_p . If I integrate C_s^t , thus, I do not obtain either the internal energy, E_t , or the enthalpy, H_t . The internal energy change of a process equals the heat

inflow plus the work done. When a solid or liquid absorbs heat, it expands and does work, which will then be negative. So

$$E_t = \int_0^T C_s^t dT - \int_{V(0)}^V PdV, \quad (41)$$

where 0 K is my reference point, and I will have to climb in temperature through the solid phase, cross the melting point, and climb again in the liquid. The corresponding equation for the enthalpy, H_t , is⁷⁶

$$H_t = \int_0^T C_s^t dT + \int_0^P VdP. \quad (42)$$

At the triple point, the energy of fusion, E_f , is related to the heat of fusion, H_f , by

$$E_f = H_f - P [V(\text{liquid}) - V(\text{solid})]. \quad (43)$$

One may equate E_f and H_f with negligible error.

FIG. 5. Saturated translational heat capacity divided by temperature cubed of the solid $J=0$ hydrogens: H_2 , hydrogen deuteride (HD), and D_2 . High points at 3 K are due to small amounts of $J=1$ hydrogen.

The integral of PdV is the work performed by the solid or liquid expanding against its own vapor pressure. It is typically small. For $J=0$ H_2 at 30 K, the work is only 4.3 J/mole referenced to 0 K. The change in PV from 0 K is 30.7 J/mole, so

$$\int_0^{P(T)} VdP = \{PV(T) - PV(0)\} - \int_{V(0)}^{V(T)} PdV \quad (44)$$

or 26.4 J/mole. The P - V corrections are, thus, small compared with the energy tied up in the C_s^t integral.

I shall now consider the experimental solid C_s^t data for $J=0$ hydrogen. The data, summarized in Fig. 5, is for $H_2^{2.77-80}$, $HD^{2.81,82}$, and $D_2^{2.38,79,83}$. The ordinate is plotted in units of C_s^t/T^3 , which is expected to be a constant at low temperatures in the Debye theory of lattice vibrations.⁸⁴ The cliff at 3 K is to be ignored — it is caused by small amounts of $J=1$ hydrogen. The remaining plot is not truly constant but forms a gentle peak at about 12 K. The Debye approximation, however, begins to falter at about 10 K, and hydrogen, as you shall see later, does not have a true Debye vibrational spectrum anyway. The scatter of data is considerable, and I simplify the results to

$$C_s^t(\text{solid}) \approx \begin{cases} 1.7 \times 10^{-3} T^3, & H_2 \\ 2.0 \times 10^{-3} T^3, & \text{other isotopes} \end{cases} \quad (45)$$

The units of C_s^t are J/mole-K. There is not enough data to explain the possible isotopic differences, and I have no choice but to simply extend the D_2 data to DT and T_2 . This does not take account of the radiation damage caused by the tritium beta particle. Quite possibly, the energy stored in radiation-induced defects will cause a negative C_s^t , i.e., energy will be released upon heating the sample. Such measurements would also have to account for the constant heat of radioactive decay of 1.95 W/mole T_2 .^{85,86} Equation (45) may be integrated to give the approximate translational internal energy, E_t . The PdV corrections are small compared with the uncertainty of Eq. (45). A more accurate fit of the C_s^t data is available.⁸⁷

I now proceed to C_s^t data for the saturated liquid. Measurements have been taken for $H_2^{77,88-90}$, $HD^{2.91}$, and $D_2^{92,93}$, and the results are summarized in Fig. 6. The HD data points contain equilibrium rotational heat capacity; the line below represents C_s^t . The H_2 and D_2 curves cross because each is climbing toward its critical point. The $J=0$ H_2 C_s^t curve to 30 K is quite steep and cannot be represented in a simple equation. The D_2 data may be represented by

$$C_s^t(D_2 \text{ liquid}) \approx 1.40 T^{0.933} \quad (46)$$

I shall extrapolate this down to the triple point and up to 30 K. I would expect the DT and T_2 curves to be slightly higher with the crossover points well above 30 K. For the triple point to 30 K range, then, I shall estimate C_s^t for

FIG. 6. Saturated translational heat capacity, C_s^t , of the liquid $J=0$ hydrogens: H_2 , HD , and D_2 . The lines depict C_s^t . For HD , the rotational heat capacity (as calculated in Section 33) must be subtracted from the equilibrium data. No correction is needed for H_2 ; only 0.3 J/mole-K need be subtracted for nD_2 at 28 K.

liquid DT and T_2 by multiplying the 1.40 amplitude of Eq. (46) by the ratio of the triple point temperatures. I then obtain amplitudes of 1.485 and 1.544 for DT and T_2 . I integrate Eq. (46) to obtain the translational energy, E_t , for D_2 , and by extrapolation, DT and T_2 . The rotational energy of DT is so small it is swallowed by the errors of extrapolation.

14. Debye Temperature and Zero Point Energy

A quantum mechanical harmonic oscillator at 0 K is not at rest but continues to vibrate with a zero point energy. The hydrogens, as seen from the parameter Λ_{eff}^* , have a considerable quantum mechanical component.

They possess, in fact, two zero point energies, which can become confused. Each diatomic molecule has a zero point energy of molecular vibration. This energy determines the low temperature equilibrium of the chemical reaction of D_2 and T_2 to DT . This is not the energy I am concerned with. Instead, I am interested in the zero point energy of a molecule vibrating in its position in the crystal or liquid lattice. In the Debye theory, the crystal lattice has the zero point energy,

$$E_Z = \frac{9}{8} R \Theta_D, \quad (47)$$

where Θ_D is the Debye temperature — a parameter that incorporates the thermodynamics of the lattice.⁹⁴ E_Z is a

large repulsive energy — on the order of a thousand J/mole, which compares to the heat of vaporization. The size of E_z is enough to make a molecule in the solid or liquid ride halfway up in the classical potential well. One must obtain, then, some measure of the size of E_z .

An early attempt to calculate E_z for solid hydrogen postulated an inverse dependence on the volume. This gave bad agreement with Θ_D , by means of Eq. (47).⁹⁵ The use of the inverse volume squared gives much better results, but the true situation is more complicated. I shall not seek a definite volume dependence for E_z but just employ Eq. (47) with the Θ_D value available at that temperature. It is true, too, that solid hydrogen is not a real Debye solid. Methods are being devised to calculate E_z for more realistic lattice spectra,⁹⁶ but I shall not investigate this complex area here.

I am concerned, then, with Θ_D and how best to get it. Also, I am concerned with the low energy acoustic vibrational branch, for which there is no electric charge separation between neighboring parts of the waves. These vibrations are thermally excited and do not respond to the electric dipole moment of the electromagnetic radiation. In the Debye theory, the spectrum of lattice vibrational frequencies, or density of modes, $D(\nu)$, is

$$D(\nu) = \frac{2V\nu^2}{U^3}, \quad (48)$$

where ν is the frequency in Hz, V the molar volume, and U the average sound velocity. In the Debye theory, U is constant. I wish to integrate Eq. (48) with respect to frequency to obtain Avogadro's Number of modes — one for each molecule. To obtain this finite answer, I integrate from zero frequency to a finite cut-off frequency, ν_D . By the Boltzmann relation, $h\nu_D = k\Theta_D$, I convert to the Debye temperature. Figure 7 shows the Debye distribution, $D(\nu)$, with its high frequency cut-off. The integral of Eq. (48) is

$$\Theta_D = \left(\frac{h}{k}\right) \left(\frac{3N_0}{4\pi V}\right)^{1/3} U, \quad (49)$$

where h is Planck's constant and k is Boltzmann's constant.⁹⁷ Θ_D describes the highest frequency vibration, whose wavelength is on the order of the intermolecular distance. The cut-off occurs because the crystal is not a continuum but is made of discrete molecules. Θ_D can be used with less validity for the liquid as well.

FIG. 7. Density of lattice vibrational modes for solid H_2 . I assumed a Debye temperature of 108 K.

I must now determine which Θ_D to use, as they come from three sources: heat capacities, volumes and sound velocities, and infrared spectra. Most of the older heat capacity data were for the saturated solid, which required a difficult compressibility correction to extract Θ_D . Recently, however, Swenson has measured the heat capacity of low $J=0$ H_2 at six constant volumes from 16.2 to 22.8 $\mu(m)^3/mole$.⁵⁵ If I extrapolate to the saturated volumes, I obtain Θ_D values of about 125 K at 0 K and 99 K at the triple point. The Debye temperature obtained from C_V declines markedly with temperature.

The density-sound velocity determination is defined by Eq. (49). For solid H_2 , it predicts Θ_D values of 108 K at 0 K and 104 K at the triple point. The third method is to measure the Q_Q -to- Q_R distance in the infrared spectrum, as shown in Fig. 8: The Q_Q peak represents a pure vibration-rotation transition; the Q_R peak also incorporates the crystal lattice vibrations. The infrared value of Θ_D for H_2 at 1.8 K is 106 to 109 K.⁹⁸ Comparable D_2 spectra show that Θ_D will decline only 3 to 4 degrees as the sample is warmed to the triple point.⁹⁹ Θ_D , then, does not change to a large extent when warmed, as seen in the latter two methods. In fact, it remains about the same even when the sample is melted.

FIG. 8. Pressure-induced infrared spectrum of solid and liquid D_2 . The Q_Q peak is a pure molecular vibration-rotation line. The Q_R is the same plus the addition of the lattice vibrational spectrum. The $Q_R - Q_Q$ difference is an approximate measure of the Debye temperature.

One must make a decision as to which Θ_D to use. The difference amounts to about 30 K in Θ_D or almost 300 J/mole in the zero point energy. For the calculations in the next section, I shall select the density-sound velocity-derived values. This method, and the infrared as well, both sample the entire lattice spectrum to yield some sort of averaged number. The heat capacity measurement sees just the first portion of $D(\nu)$, because the temperature is always quite a bit less than Θ_D . Figure 7 shows that the actual density-of-modes is climbing more slowly at first than is the Debye density-of-modes.¹⁰⁰

Experimentally, there is less heat capacity than expected, and Θ_D is apparently higher. As the two density-of-modes become comparable at higher temperatures, extra heat capacity has apparently been added and Θ_D drops.

I shall calculate Θ_D from Eq. (49), using densities from Sections 10 and 11 and sound velocities from Section 16. Table 9 summarizes molar volumes, average sound velocities, Debye temperatures, and zero point energies for four solid and liquid isotopes.

15. Binding Energies and the Potential Well

I now proceed to the potential diagram for the solid and liquid (Fig. 9), which shows the internal energy of a molecule under the influence of its neighbors. Binding occurs for negative internal energies; the gas exists at positive energies.

The binding energy, ϕ_T , is found from

$$-\phi_T = E_{s,v} - E(\text{gas}). \quad (50)$$

All quantities are inherently positive, and the minus sign is added to the left-hand side to make the binding energy

FIG. 9. Potential well for solid and liquid hydrogen.

Table 9. Deviation of the zero point energy of the lattice, E_z , as derived from the Debye temperature, Θ_D , which is obtained from average sound velocities and molar volumes. DT and T_2 are estimates.

Isotope	Phase	Temp (K)	Molar volume $\mu(\text{m}^3)/\text{mole}$	Average sound velocity (m/s)	Debye temp (K)	E_z (J/mole)
$J=0 \text{ H}_2$	Solid	0	23.14	1220	107.5	1005
		13.81	23.31	1180	103.7	970
	Liquid	13.81	26.19	1259	106.4	995
		20	28.37	1114	91.7	858
		25	31.26	953	75.9	710
		30	37.38	694	52.1	487
D_2	Solid	0	19.95	1108	102.5	959
		18.7	20.48	1043	95.7	895
	Liquid	18.7	23.16	1083	95.4	892
		25	25.28	926	79.2	741
		30	27.97	762	63.0	589
DT	Solid	0	19.30	1086	101.6	950
		19.79	19.94	1015	93.9	879
	Liquid	19.79	22.59	1043	92.6	866
		25	24.29	913	79.1	740
		30	26.66	759	63.8	597
T_2	Solid	0	18.74	1075	101.6	950
		20.62	19.44	998	93.2	871
	Liquid	20.62	22.06	1030	92.2	862
		25	23.45	919	80.6	754
		30	25.68	766	65.2	610

negative. The energy of sublimation or vaporization, $E_{s,v}$, can be calculated from vapor-pressure derived heats, $H_{s,v}$, minus the pressure times the volume change in going from the gas to the condensed phase. This is, for the liquid

$$E_V = \frac{P^s}{\rho} \left[1 - \frac{\rho}{\rho_L} \right] \left\{ T \frac{d \ln P^s}{dT} - 1 \right\}, \quad (51)$$

with a comparable equation for the solid. I combine all the numbers to this point to calculate the binding energies listed in Table 8.

I now return to the potential diagram (Fig. 9) to observe the solid or liquid riding on its cushion of thermal and zero point energy. Note that

$$-\psi_T = -[\phi_T + E_z + E(\text{solid/liquid})], \quad (52)$$

where, again, a minus sign is added to insure that ψ_T is negative. ψ_T is the deep, classical potential well. It is not quite the potential energy that the hydrogen would have if the zero point energy did not exist, because E_z inflates the material to a larger volume. The calculated values of

ψ_T also appear in Table 8. The values for $J=0 \text{ H}_2$ may be used for $n\text{H}_2$ by adding about 10 J/mole to $E_{s,v}$, which

FIG. 10. Portions of the ψ_T potential wells for the condensed hydrogens. ψ_T is the binding energy less the zero point and thermal solid/liquid energies. Deuterium tritide (DT) and T_2 are complete estimates.

will deepen the well slightly. Note that the binding energy is less for liquid DT at 30 K than for D_2 or T_2 . This is caused by DT's equilibrium rotational energy. Recall that the others may possess large amounts of rotational energy, but it cannot be added to the potential diagram.

The binding energy, ϕ_T , will vary considerably across the isotopes, because of the differences in E_z . But the classical potential, ψ_T , as a function of volume, may be a constant for all isotopes. In Fig. 10, this is so, at least for the limited data range. There is one curve for the solid and another for the liquid.

IV. OTHER SATURATED PROPERTIES

16. Sound Velocity in the Solid and Liquid

Sound velocities are a major entree to Debye temperatures and zero point energies. Two major studies have been carried out on solid hydrogen. The first is on single-crystal H_2 and D_2 .^{101,102} These were grown under 4- to 20-MPa (40- to 200-atm) pressures, and I have extrapolated the 4-K sound velocities on the normal isotopes to zero pressure to estimate the saturated 0 K values. The sound velocity-temperature data for the $J=0$ isotopes are measured from 6.5 to 10 MPa (65 to 100 atm), and I assume the same functional behavior at zero pressure. One may, in this way, obtain sound velocities along the saturation curve. I use an empirical equation for the directionally-averaged sound velocity in the saturated solid:

$$U(\text{solid}) = A - BT^3, \quad (53)$$

where A and B are constants, and the temperature range is 0 K to the triple point. Equation (53) may be used for both the longitudinal (subscript l) and transverse (t) velocities.* Table 10 lists the constants for H_2 and D_2 . I have also estimated the constants for DT and T_2 by power fits to the triple point temperatures, Θ_1 .

The second study concerns polycrystalline nH_2 ¹⁰³ and nD_2 .¹⁰⁴ The results are comparable, but U changes more drastically with temperature than T^3 . However, the

data are sparse and already rounded off, so that I have not used this study. Table 10 is used to construct the solid sound velocities in the potential well calculations of Section 15. To obtain the average sound velocity, U, for these calculations, I combine the single longitudinal mode with the two transverse modes according to¹⁰²

$$\frac{1}{U^3} = \frac{1}{3} \left[\frac{1}{U_l^3} + \frac{2}{U_t^3} \right]. \quad (54)$$

I next represent the liquid sound velocity with the empirical equation

$$U(\text{liquid}) = A - BT^2, \quad (55)$$

where the constants are in Table 10. Of the available $J=0$ H_2 and nH_2 data,¹⁰⁵⁻¹⁰⁷ my preferred reference fits Eq. (55) to within 0.5% from 14.5 to 25 K.¹⁰⁵ It deviates at higher temperatures from the quadratic form. The nD_2 data include points at 19 and 20 K¹⁰⁴ plus the region 25 to 30 K.¹⁰⁷ Equation (55) may be used for nD_2 from 19 to 30 K to better than 0.65%. No DT or T_2 data have been measured, and I estimate the Table 10 constants from triple point temperature power fits.

I also include the sound velocity-liquid density formula

$$U(\text{liquid}) = A + B\rho_L, \quad (56)$$

where the constants are in Table 10. Equation (56) fits to 0.5% from 15 to 30 K for H_2 and D_2 .

Table 10. Sound velocity in saturated liquid and solid hydrogen. The solid equation may be used from 0 K to the triple points. The liquid T^2 equation may be used from the triple points to 25 K for $J=0$ H_2 and nH_2 and to 30 K for the others. The liquid density equation may be used from the triple points to 30 K. All DT and T_2 data are estimates.

Isotope	Solid				Liquid			
	$U = A - BT^3$				$U = A - BT^2$		$U = A + B\rho_L$	
	A(l) (m/s)	A(t) (m/s)	B(l) (m/s-K ³)	B(t) (m/s-K ³)	A (m/s)	B (m/s-K ²)	A (m/s)	B (m ⁴ /s-mole)
$J=0$ H_2	1880	1100	7.0(-3)	14.6(-3)	1387.3	0.6787	-627.6	0.0494
nH_2					1397.8	0.6820	-616.5	0.0492
D_2	1700	1000	6.2(-3)	9.5(-3)	1274.6	0.5475	-782.7	0.0432
DT	1670	980	6.1(-3)	8.7(-3)	1251.8	0.5244	-820.2	0.0421
T_2	1645	970	6.0(-3)	8.3(-3)	1236.5	0.5094	-846.6	0.0414

*These are directions relative to the sound wavefront propagating through the crystal. I again assume an averaging of direction. Both U_l and U_g would further be functions of the specific direction in a single crystal.

17. Solid Thermal Conductivity

A solid's thermal conductivity is the first property encountered here that is an extreme function of the mole fraction of $J=1$ hydrogen. Perhaps it should be included under rotational phenomena, but it is too basic for applied work to be so hidden away. Figure 11 summarizes the experimental situation for H_2 ^{108,109} and HD .¹¹⁰ The thermal conductivity is, below 1 K, as poor as that of room temperature air. It rises four orders of magnitude to a peak at 4 K; then it slowly descends to a limiting value comparable to room temperature glass or water. It is the peak height that is so sensitive to the $J=1$ concentration, $c(1)$. For nH_2 [$c(1) = 0.75$], there will be no mountainous peak, just a gradual rise to the high temperature limiting value. For 0.002 and 0.005 $J=1$ H_2 , the thermal conductivity is better than that for room temperature iron. What makes the thermal conductivity so unusual is that it diverges as $c(1)$ gets smaller. All of the highest peaks represent samples that one would call "pure" $J=0$ hydrogen for any other property. Solid D_2 values of 0.31 to 0.38 W/m-K have been measured from 16.3 to 17.7 K.¹¹¹

The peak is the result of two competing mechanisms. At low temperatures, the lattice vibrational waves, or phonons, are few and unlikely then to meet one another. They scatter from impurity atoms, $J=1$ hydrogen molecules, dislocations, grain boundaries, and crystal edges. Solid thermal conductivity is the most sensitive known measure of the total quality of a hydrogen crystal. From the kinetic theory of gases, I borrow a mean free path equation for the phonons, now treated as though they are particles:

$$K = \frac{1}{3} C_s^t \rho_s U \lambda \quad (57)$$

K is the thermal conductivity, C_s^t the saturated translational heat capacity, ρ_s the solid density, U the average velocity, and λ the phonon mean free path.¹¹² For crystals of lowest $c(1)$,

$$K_Q [c(1) \sim 0] \approx 8T^3 \quad (58)$$

K_Q now refers to the low temperature mechanism, where λ becomes the crystal size, ℓ . The only quantity that changes rapidly with temperature is C_s^t , which increases as T^3 , according to the Debye theory.¹¹² This is what makes the low temperature thermal conductivity rise so quickly, as seen in Fig. 11. When I evaluate the numerical coefficient in Eq. (58) for ℓ , I find to my surprise that

the crystal size is only 2×10^{-4} m. This amazed the original researchers, who swore that their 10^{-2} m-long, optically clear crystals were single.^{108,109} It appears, however, that their crystals have invisible internal boundaries off which the phonons scatter. These boundaries may be associated with the residual $J=1$ molecules but no one can be sure. A truly perfect crystal should have a 4-K thermal conductivity almost two orders of magnitude higher than the maximum in Fig. 11. This has not been achieved, despite recent efforts in single crystal growth.¹¹³ One may say, then, that solid thermal conductivity offers the best definition as to how good a single crystal really is.

The introduction of $J=1$ molecules drastically reduces the thermal conductivity. For an arbitrary $c(1)$, low temperature thermal conductivity becomes

$$K_Q \approx \frac{1.9 \times 10^{-3} T^3}{[c(1) + (7 \times 10^{-4})]^{1.15}} \quad (59)$$

I have fitted Eq. (59) to the preferred data source.¹⁰⁸ [Almost order-of-magnitude differences in K_Q exist for a given $c(1)$ in Fig. 11. This is not surprising, as K_Q is a most sensitive function of the exact history of the crystal growth.] The coefficient " 7×10^{-4} " is added to the denominator of Eq. (59) to fit it to Eq. (58). This coefficient is effectively the "zero" $c(1)$ value in the actual experiments. The crystallite size then becomes

$$\ell \approx \frac{3.9 \times 10^{-8}}{[c(1) + (7 \times 10^{-4})]^{1.15}} \quad (60)$$

For nH_2 [$c(1) = 0.75$], ℓ becomes 5×10^{-8} m, or one hundred intermolecular distances. It will remain fairly constant with temperature.

As heat is added to the sample, ever more phonons are formed, until they collide, mostly with each other. This is the Umklapp (or U-) mechanism, which retains the T^3 term in the thermal conductivity. This function is overshadowed by a new exponential term:

$$K_U \approx A T^3 \exp\left(-\frac{\Theta_D}{2T}\right) \quad (61)$$

where A is a constant and Θ_D is the Debye temperature. The exponential term makes K_U decrease with increasing temperature, and one descends from the 4-K peak.^{112,114}

FIG. 11. Measured thermal conductivity of the solid hydrogens. The numbers indicate the mole fraction of $J=1$ hydrogen in the otherwise $J=0$ solid. Two competing mechanisms cause the extraordinary 4-K peak.

I take from Table 9 an average Θ_D value of 106 K for solid H_2 , and

$$K_U \approx 10^{-5} T^3 \exp\left(\frac{53}{T}\right), \quad (62)$$

This mechanism brings the overall thermal conductivity to about 1 W/m-K at 14 K, no matter what the $c(1)$ value. One may use Eq. (57) to obtain the corresponding phonon mean free path, λ_U :

$$\lambda_U \approx (3 \times 10^{-10}) \exp\left(\frac{53}{T}\right). \quad (63)$$

At 14 K, λ_U will be 1.4×10^{-8} m or 30 intermolecular distances.

In the 4 to 10 K region, one must combine the two mechanisms to get the overall thermal conductivity, K :

$$\frac{1}{K} = \frac{1}{K_d} + \frac{1}{K_U}. \quad (64)$$

The equations above are based on H_2 data, although the HD and D_2 data agree. It is almost a complete guess what the thermal conductivity will be for a solid D_2 -DT- T_2 mixture. Both D_2 and T_2 may possess a large fraction of $J=1$ molecules, but small crystallites are probable just from the mixture itself. In my infrared work, I have not been able to obtain good spectra of solid (saturated) 50% D_2 -50% T below 18 K. At lower temperatures, the beam scatters from the crystallites that remain no matter how many annealing attempts are made.¹¹ I speculate that fresh, solid D-T will have a thermal conductivity like that of 0.72 $J=1$ H_2 , or about 0.2 W/m-K at 4.2 K. The thermal conductivity must decrease with time, as radiation damage attacks the solid. I fantasize a 4.2 K value of 0.03 W/m-K after one day and 10^{-3} W/m-K after a week.^{12,13,*} One supposes that fresh D-T would show the one W/m-K value near the triple point, but it might degrade an order of magnitude with radiation damage. This lower limit of 0.1 W/m-K at 18 K is suggested by reducing λ_U to a few intermolecular distances.

The thermal diffusivity, D_s , is used in time-dependent thermal problems. It is defined by¹¹⁵

$$D_s = \frac{K}{C_s^t \rho_s} = \frac{1}{3} U \lambda. \quad (65)$$

For a pure crystal, as the temperature falls, C_s^t gets small, and D_s will be huge — perhaps 10^{-1} to 10^{-2} m²/s. As the temperature increases, λ decreases because of the exponential term of Eq. (63). At the triple point, D_s may be as low as 10^{-6} m²/s. The effects of isotopic mixing may lower the 4-K value of D_s to perhaps 10^{-4} m²/s, and eventually, even to 10^{-6} m²/s. Even these guesses use C_s^t values as described for unirradiated hydrogen. These will certainly change as well under the damaging effects of the radiation.

For future fusion engineering, thermal conductivity is probably the single most important cryogenic property to be measured.

18. Liquid Thermal Conductivity

Liquid thermal conductivity is represented by only two experiments on H_2 ^{116,117} and D_2 .¹¹⁸ The data, shown in Fig. 12, are, mercifully, not a function of the $J=1$ molecular concentration. There is, however, a 22% difference between the two sets of H_2 data. The higher points, labeled "two-phase," in Fig. 12, represent data measured with liquid and vapor in equilibrium on the saturation line.^{116,118} The lower points are labeled "one-phase" in Fig. 12. These are derived by measuring K as a function of pressure for just the liquid phase and then extrapolating to the saturation pressure. If one experimentally drops to the saturation curve, the thermal conductivity suddenly increases. This is attributed to two-phase convection and vaporization effects. The one-phase data then represent the "true" thermal conductivity of the saturated liquid.¹¹⁷ But the two-phase data are probably better to use for actual work on the saturation curve, where one will have to live with whatever convection effects occur.

The two-phase data, however, are not measured to a high enough temperature to note the peak observed in the one-phase experiment. (There is no physical explanation at present for the 17- to 23-K portion.) I shall extrapolate my data by placing a gentle peak on top of the two-phase data. For two-phase liquid H_2 , I extrapolate to:

$$K(H_2) \approx 0.125 \cos [4.6(T - 23)] , \quad (66)$$

where the bracket of the cosine is in degrees. For D_2 , I move the peak up in temperature by the ratio of the

*I have recently measured a crude value of 0.028 W/m-K at about 10 K for frozen T_2 several hours old.

FIG. 12. Liquid thermal conductivity of H₂ and D₂. I extrapolated the lower H₂ data from pressurized-liquid experiments; they probably represent the true liquid thermal conductivity. The higher points are actually taken on the saturation curve, and they contain unknown two-phase effects. In an engineering sense, the higher data probably is "more real." Equations (66) and (67) are extrapolations.

critical points (from Table 1). I then fit the D₂ data to obtain

$$K(D_2) \approx 0.135 \cos [3.0(T - 27)] \quad (67)$$

These may be extended from the triple points to 30 K with no guarantees outside the measured ranges of data. Equation (67) can be used for liquid DT as well. Tritium self-heating is likely to produce more of the unknown two-phase effects, and K may well be larger.

If I extrapolate Eq. (63) for the phonon mean free path in the solid, I obtain 1.1×10^{-8} m at 15 K and 1.8×10^{-9} m at 30 K. If I use Eq. (57) with actual liquid-H₂ data for thermal conductivity, translational heat capacity, and sound velocity, I calculate phonon mean free

paths of 4.6×10^{-10} m and 3.4×10^{-10} m at 15 and 30 K. Note the inherent difference between the solid and the liquid. Because of diffusional motion, the liquid possesses a small (one intermolecular distance) and constant phonon mean free path.

19. Liquid Surface Tension, Viscosity, and Self-Diffusion

The liquid-vapor equilibrium line reaches out into the fluid phase space like a pier. Only on this slender thread occurs the liquid phase; distinguished from the fluid phase around it by its possession of a surface. The liquid's capacity to pull this surface taut is the surface tension, γ .

For nH_2 , one finds that γ decreases linearly with temperature, and one may describe it with the empirical equation

$$\gamma = A - BT, \quad (68)$$

where A and B are constants. The surface tension is zero at the critical point. From Eq. (68), one would expect the critical temperature to equal A/B , and it is close (e.g., 31.9 K for nH_2 compared with the 33.19-K critical temperature). The deviation from linearity occurs in the last few degrees below the critical point.¹¹⁹ Table 11 lists the constants A and B for nH_2 . The 14.7- to 25-K equation fits the data to $\pm 0.5\%$; the equation to 30 K has a 1% error at 20 and 26 K and 5% at 30 K. HD and nD_2 have also been measured, but over a much narrower temperature range; they exhibit the same linear temperature behavior.¹²⁰ The surface tension is unusual in that it appears to be a good function of molecular weight (ignoring possible differences between HT and D_2). I have used this functionality to estimate the DT and T_2 values. For mixtures, the measured surface tension is slightly less than that calculated from mole fractions. The deviation is a maximum of 4% for H_2 - D_2 and 1-1/2% for HD- D_2 at 20 K.^{120,121} For D_2 -DT- T_2 , such a correction should be less than 1%.

Viscosity is a property of both the liquid and fluid phases, but I shall consider here its saturated liquid value only. Table 12 lists data points over almost the entire temperature range. The viscosity rises so steeply as one decreases the temperature to the triple point that no simple function will suffice. The preferred source shows that the nH_2 viscosity is 1 to 3% higher than that of $J=0$

Table 11. Liquid surface tension of some of the hydrogen isotopes. DT and T_2 are estimated. N/m may be converted to dyne/cm by ignoring the 10^{-3} factor.

Isotope	Surface tension ($\times 10^{-3}$ N/m)		Value at triple point	Measured temp range (K)
	$\gamma = A - BT$			
	A	B		
nH ₂	5.38	0.170	3.01	14.7-25
nH ₂	5.336	0.1673	3.00	14.7-30
HD	6.53	0.188	3.41	16.3-20.5
nD ₂	7.90	0.218	3.82	18.8-20.5
DT	9.15	0.242	4.36	Est
T ₂	10.4	0.267	4.89	Est

H_2 .¹²² I have not used an added source with three isotopes at once.¹²³ The nH_2 data here is probably 3 to 8% below the actual values.

It is impossible to accurately extrapolate liquid viscosities for DT and T_2 . This is because the liquid viscosity diverges on an isothermal plot, a rare occurrence in the hydrogen family. If I nevertheless extrapolate the viscosity as a function of the triple point temperatures, I obtain the lower estimates of Table 12; using molecular weights, I obtain the upper values. The differences amount to as much as 20%. The viscosity is also somewhat decreased in a liquid mixture from the additive pure component values. The effect is a maximum of 12% for H_2 - D_2 and 5% for HD- D_2 . For D_2 -DT- T_2 , one might expect a maximum effect of perhaps 2%.¹²⁴

Table 12. Liquid viscosities of the saturated hydrogens. For DT and T_2 , estimates are uncertain because the isothermal viscosity diverges as one proceeds from H_2 to T_2 . A Pa-s may be converted to poise by multiplying by 10.

Temp (K)	Liquid viscosity (10^{-5} Pa-s)						
	$J=0 H_2^{122}$	nH_2^{122}	nH_2^{123}	HD ¹²³	nD_2^{123}	DT ^a	T_2^a
Triple point	2.567 ^a	2.596 ^a	2.39 ^a	3.38	4.30 ^a	4.5-5.1	4.8-6.2
14	2.507	2.543	2.38	—	—	—	—
16	1.975	2.039	1.88	—	—	—	—
18	1.605	1.656	1.54	2.84	—	—	—
20	1.354	1.392	1.31	2.31	3.68	4.4-5.0	—
22	1.161	1.187	1.14	2.00	3.18	3.8-4.3	4.4-5.7
24	1.008	1.026	0.98	1.80	2.76	3.4-3.9	3.9-5.1
26	0.872	0.890	0.86	1.56	2.46	3.0-3.4	3.4-4.5
28	0.752	—	0.74	1.38	2.21	2.7-3.1	3.1-4.2
30	0.649	—	0.62	1.20	1.98	2.4-2.9	2.9-3.9

^aMy estimate.

Liquid H₂ and D₂ are quite mobile, as shown by their large self-diffusion coefficients (in m²/s):¹²⁵

$$D_1 (14 \text{ to } 21.5 \text{ K}) = 8.58 \times 10^{-8} \exp \left(\frac{-44.8}{T} \right) \quad (69)$$

and

$$D_4 (18.2 \text{ to } 24.1 \text{ K}) = 5.70 \times 10^{-8} \exp \left(\frac{-54.00}{T} \right). \quad (70)$$

H₂ is considerably slowed down by being placed in a 50–50 solution with D₂. The H₂ now diffuses at the Eq. (70) D₂ rate.¹²⁵ Liquid DT should be just slightly less mobile than liquid D₂.

20. Solid Self-Diffusion and Quantum Corresponding States

One would expect molecular diffusion to be slower in the solid than in the liquid, and indeed it is. The measured self-diffusion coefficients, D (in m²/s), for three non-tritiated isotopes^{126,127} are

$$D_1 (10 \text{ to } 14 \text{ K}) = 1.4 \times 10^{-7} \exp \left[-\frac{1590}{RT} \right], \quad (71)$$

$$D_2 (13.8 \text{ to } 16 \text{ K}) = 1.7 \times 10^{-5} \exp \left[-\frac{2510}{RT} \right], \quad (72)$$

$$D_4 (9 \text{ to } 17 \text{ K}) = 4 \times 10^{-8} \exp \left[-\frac{2295}{RT} \right]. \quad (73)$$

The HD data are clearly out of line with that of the other two isotopes. There is no way to know if this is a property of the heteronuclear isotopes or an error caused by measurement over too small a temperature range. The measured ranges of the diffusion coefficients above are 2–1/3, 1–2/3, and 7 decades for H₂, HD, and D₂.

To better estimate the solid diffusion coefficients of DT and T₂, I shall turn to the quantum theory of corresponding states.²¹ Each chemical element possesses a characteristic Lennard–Jones potential energy well, which describes the basic attractive and repulsive forces that two like molecules exert on each other. The Lennard–Jones potential energy function, ϕ_{LJ} , is

$$\phi_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (74)$$

where r is the intermolecular distance and ϵ and σ are constants. The potential energy is zero at infinite separation of the molecules. It becomes negative for binding and has a maximum depth, ϵ (J/mole). This occurs at the intermolecular distance $2^{1/6}\sigma$ (m). The potential energy becomes zero again at the closer intermolecular distance σ . It is positive for closer distances as the molecules repel each other. The potential energy diagram in Fig. 9 looks quite similar, except that is for the liquid and solid. Figure 9 is the sum of Lennard–Jones potentials of many pairs of molecules at various distances. The resulting summed binding energy is considerably deeper than ϵ .

For each chemical element, one has the energy, ϵ , and the distance, σ . Isotopic differences can be added with the molecular weight, M . These three variables may be manipulated about to give a dimensionless set of pressure, volume, and temperature variables. These reduced variables, P^* , V^* , and T^* , are

$$P^* = \frac{N_0 \sigma^3}{\epsilon} P, \quad (75)$$

$$V^* = \frac{V}{N_0 \sigma^3}, \quad (76)$$

and

$$T^* = \frac{RT}{\epsilon}, \quad (77)$$

where N_0 is Avogadro's Number and R the gas constant. I also define the quantum parameter

$$\Lambda^* = \frac{N_0 h}{\sigma \sqrt{M\epsilon}} \quad (78)$$

This is the only dimensionless combination of Planck's constant and the other variables. Λ^* is roughly the ratio of the wave function length to the classical particle diameter. It tells how quantum-mechanical the molecule is. It varies from zero for a totally classical molecule to 3.08 for He^3 , which possesses quantum properties to the largest degree.

Equation (78), however, gives D_2 and HT the same Λ^* value. This cannot be so, for they differ in their isothermal vapor pressures.¹⁹ I, therefore, correct Λ^* for the molecular wobble caused by the difference in atomic weights. For DT , with atoms of weight M_D and M_T , I obtain the corrected parameters, Λ_{eff}^* , where¹²⁸

$$\Lambda_{\text{eff}}^* = \left\{ 1 + \frac{1}{6} \frac{(M_D - M_T)^2}{M_D M_T} \right\}^{1/2} \Lambda^* \quad (79)$$

I now have a set of four reduced variables: P^* , V^* , T^* , and Λ_{eff}^* for each isotope of each element. These variables are much like the reduced variables based on the critical point values, to which they may easily be related (except for Λ_{eff}^*).

I now combine my constants to define a dimensionless diffusion coefficient, D^* . The only way to change the real diffusion coefficient, in m^2/s , to a dimensionless coefficient is by the combination

$$D^* = \frac{1}{\sigma} \sqrt{\frac{M}{\epsilon}} D \quad (80)$$

I now plot D^* vs $1/T^*$ and expect an exponential dependence. The resulting lines for different substances should vary only as a function of Λ_{eff}^* .

I have plotted D^* vs $1/T^*$ for the hydrogens and rare gases in Fig. 13. For all the hydrogens, I have used $\epsilon = 307.6 \text{ J/mole}$ and $\sigma = 2.928 \times 10^{-10} \text{ m}$.²¹ Experiment shows the Lennard-Jones potential does not quite hold. More careful values are for H_2 and D_2 : $\epsilon = 305$ and 293 J/mole ; $\sigma = 2.964 \times 10^{-10}$ and $2.958 \times 10^{-10} \text{ m}$.²³ In Fig. 13, I have included the experimentally measured diffusion coefficients for He^3 ,¹²⁹ Ar ,^{130,131} Kr ,^{132,133} and Xe ,¹³⁴ plus their Lennard-Jones parameters.^{135,136} The rare-gas Λ_{eff}^* lines in Fig. 13 are out of sequence, probably because of the error in combining the different sources for a property so difficult to accurately measure. I note, however, that the position for the Λ_{eff}^* value of DT and T_2 is relatively well-defined. One may estimate the solid DT and T_2 self-diffusion coefficients with some confidence, and one obtains;

FIG. 13. Comparative self-diffusion coefficients for the solid hydrogens and rare gases. The comparison is in terms of dimensionless reduced diffusion and temperature variables from the quantum mechanical theory of corresponding states. The numbers refer to the quantum parameter, Λ_{eff}^* .

$$D_{s,6} \approx \frac{5 \times 10^{-7}}{\sqrt{M}} \exp \left[-\frac{2800}{RT} \right] \quad (81)$$

where the appropriate molecular weight, M , is substituted.

The power of the theory of corresponding states is evident in Eq. (81). It has three drawbacks, however: (a) an enormous amount of data has to be obtained, (b) the functionality with Λ_{eff}^* is essentially empirical, and (c) one cannot treat mixtures very well. Most mixture theories combine constants in a single manner regardless of variable composition.²¹ However, linear combinations of $(\Lambda_{\text{eff}}^*)^2$ values have been tried for the hydrogens.²⁰

21. Refractive Index of All Phases

I have previously remarked that liquid and solid are quite transparent and not easy to see. This indicates a refractive index near one, and I shall summarize the data, which is virtually all for yellow light at $0.546 \mu\text{m}$.

Once again, H₂ data lead the field. All liquid and 30-to-100-K gas data may be condensed into a simple equation.⁵⁰

$$N(0.5462 \mu\text{m}) = 1 + (3.15 \times 10^{-6}) \rho \quad (82)$$

N is the refractive index and ρ the density (mole/m³). Equation (82) reproduces the H₂ data to less than 1.5% error.

The above equation also fits 0.5462- μm liquid D₂ data. These values were actually measured at other optical frequencies and adjusted to 0.5462 μm .¹³⁷ No solid data exist for any isotope.

Equation (82) is a reasonable estimating procedure for all hydrogen isotopes in all phases. It will probably be accurate to a few percent. For 4.2-K solid nH₂ (density 44 360 mole/m³), I estimate the refractive index to be 1.137. This is very nearly one, as I expected. For solid DT at 4 K (estimated density 51 810 mole/m³), N is estimated to be 1.163. However, optical clarity could be a property directly influenced by the tritium radiation. It is conceivable that point defects may form with absorption in the visible spectrum. The more likely optical problem is simply the poor crystallization that occurs in the solid D₂-DT-T₂ mixture. The presence of composition gradients and crystallites may seriously scatter a light beam, although the inherent refractive index may not be affected.

22. Mechanical Properties of the Solid

Solid hydrogen is not a strong material at any temperature. The best study has been carried out on polycrystalline rods of D₂ under tension; i.e., the ends of the rod are pulled apart until the sample either necks down or breaks.¹³⁸ Table 13 shows the results in terms of the end-point stress and strain for each behavior region. Stress is the pressure pulling the rod; strain is the fractional elongation of the rod.¹³⁹ Behavior, as the pressure increases, may be separated into the elastic, elasto-plastic, and massive failure regions. In the elastic region, the sample returns to its original length if the pressure is removed. At the yield point, the sample moves into the elasto-plastic region, where deformation is continuous but the sample does not recover. At the necking point, the sample undergoes massive failure, where pressure produces uncontrollable necking or the rod breaks.¹⁴⁰

Table 13 shows that the elastic region is small. It extends to only 0.1 to 0.2% elongation. The stresses involved are also low—only 0.09 to 0.42 MPa (0.9 to 4.2 atm). The stress divided by the strain is Young's Modulus. The elasto-plastic region is also narrow, as it extends only to 0.5% elongation at 1.4 K and to 2% at

Table 13. Mechanical properties of polycrystalline D₂ under tension. At 1.4 to 4.2 K, the solid is brittle and shatters under massive failure. At 16 K, the solid is ductile and necks to large deformations. MPa may be converted to atm by multiplying by 9.87.

Temp (K)	Elastic yield point		Elasto-plastic necking point		Last measurement in massive failure	
	Stress (MPa)	Strain	Stress (MPa)	Strain	Stress (MPa)	Strain
1.4	0.42	0.001	>0.55	>0.005	0.42	0.006
4.2	0.30	0.001	>0.53	>0.008	0.52	0.010
8.0	0.20	0.0015	0.48	0.012	0.44	0.030
11.6	0.17	0.0015	0.46	0.014	0.42	0.062
15.6	0.12	0.002	>0.29	>0.020	0.28	0.130
16.4	0.09	0.002	>0.23	>0.020	0.21	0.223

16 K. The stresses are again a few MPa (several atm). Stress divided by strain is the coefficient of hardening in this region. The final two columns in Table 13 represent the last readings taken in the experiment. At 4.2 K, the sample stretched to 1% elongation before shattering from the cold-induced brittleness. The 16-K samples continue to neck down to large elongations. Just under the triple point, solid D₂ flows easily. Figure 14 shows a

FIG. 14. Solid D₂ being extruded just below its triple point, illustrating the softness of the material in this temperature range.

1-mm diameter solid D_2 rod being extruded through an orifice in the top plate.¹⁴¹ It is being pushed by the weight of an 18-in. pencil-sized plastic plunger above it. The D_2 is so soft that it is continuously extruded at about 10 mm/min. Light entering the observation ports continuously sublimates away the tip of the extruded D_2 .

Similar results have been seen in solid H_2 , where the presence of $J=1$ molecules is shown to cause hardening.¹⁴² Samples of 0.2% $J=1$ H_2 are super-soft in their deformation. Unfortunately, no one has tried an H_2 - D_2 mixture to see what effect the isotopic mixture has on mechanical properties. One may expect increased

stress values for the mixture D_2 -DT- T_2 . These will increase with time as radiation damage hardens the crystal.

Little can be said about the properties of solid hydrogen under a shear stress. Soviet researchers¹³⁸ calculated a shear modulus for unrestrained solid D_2 from the tension data. The calculated shear moduli are about 40% of the Young's Modulus; i.e., one would expect a few tenths of an MPa (a few atm) to cause large shear deformations. Some widely varying data are available on shear stresses in the restrained solid under pressure.^{143,144}

V. PROPERTIES OFF THE SATURATION LINE

23. The Melting Curve

I have previously considered the two saturation lines that stem from the triple point. The third such line is the melting curve, which marks the boundary of the solid and fluid phases. Melting is a first-order transition, with a volume discontinuity between the phases. It is conceivable that high pressures might squeeze hydrogen to a single phase. However, the melting curve is still there at 164 K and 1.9 GPa (19 kbar).¹⁵

The melting curve data have recently been augmented by work by Liebenberg¹⁵ and Swenson.⁵⁵ A smoothed set of pressure, temperature, and volume points for nH_2 , nD_2 , and nT_2 appear in Table 14.^{15,55,57,145-148,*}

In the region just above the triple point, detailed measurements have been made only on H_2 . To 23 K, the melting pressure, P_m , is given by¹⁴⁶

$$P_m(H_2, \text{MPa}) = 3.001803 (T_m - \Theta_1) + 0.1153599 \\ \times (T_m - \Theta_1)^2 - 1.245979 \\ \times 10^{-3} (T_m - \Theta_1)^3, \quad (83)$$

where T_m is the melting temperature and Θ_1 the triple point temperature (multiply MPa by 9.8692 to convert to atmospheres). Most of the data exists for $J=0$ H_2 ($\Theta_1 = 13.81$) but Eq. (83) works as well for nH_2 ($\Theta_1 = 13.956$).

At any point on the melting curve, the Clausius-Clapeyron equation is

$$\frac{dP_m}{dT_m} = \frac{H_f}{T_m \Delta V_m}, \quad (84)$$

where H_f is the heat of fusion and ΔV_m the volume difference between the solid and the liquid at temperature T_m .³⁶ For $J=0$ H_2 from the triple point to 22.6 K,

*Two Simon's equations, $P_m = A + BT_m^b$, have been meshed together in the 20 to 30 K region with a power fit. The volumes are smoothed with the equation, $V_m = A + B \ln T_m$. The volume difference D_2 , ΔV_m , is smoothed with a power fit with temperature.^{145,148} The subscript "m" indicates pressures and volumes on the melting curve.

Eq. (84) has been used to calculate the heat of fusion, which is:

$$H_f(H_2) = 117.3 + 1.823 P_m, \quad (85)$$

where P_m is in MPa.^{149,150} The constant 117.3 J/mole is the triple point (nearly zero pressure) heat of fusion. One may take the data of Table 14 to create equations useful to 160 K:

$$H_f(nH_2) \approx 117 + 7.4 (T_m - 14.0) \quad (86)$$

and

$$H_f(nD_2) \approx 197 + 7.6 (T_m - 18.7). \quad (87)$$

I have used Eq. (86) to calculate ΔV_m and, finally, $V(\text{liquid})$ for nH_2 from 24 to 60 K. For nD_2 , I estimate $V(\text{solid})$ using the high pressure data plus the triple point value of $20.48 \mu(\text{m}^3)/\text{mole}$. Equation (87) is used to generate $V(\text{liquid})$ values, which are smoothed somewhat to the $23.16\text{-}\mu(\text{m}^3)/\text{mole}$ triple point value. These volumes are also included in Table 14.

A solid-solid transformation has been reported hanging like a limpet on the solid side of the H_2 melting curve. The first work showed strange volume anomalies,¹⁵¹⁻¹⁵³ and a later x-ray study showed a face-centered cubic (fcc) structure instead of the expected hexagonal close-packed (hcp) one.¹⁵⁴ The region under study is from 15 K (3 MPa) to 19 K (20 MPa) on the melting curve. Its depth is perhaps one degree into the solid region.¹⁵³ All of these results have recently been called into question,¹⁵⁵ and further studies will be necessary to confirm the reported transformation.

24. The Solid Under Pressure

I shall make a brief foray to a few thousand MPa (tens of kbars) in the solid phase. This is "low pressure" at a time when shock wave work is pushing into the megabar region. However, any engineering application of frozen hydrogen, except pellet ablation in plasmas, is not apt to require unusually high pressures.

The most frequented path in this region of phase space is the 4.2-K isotherm, which has been measured three separate times.¹⁵⁵⁻¹⁵⁹ The pressure-volume relation

Table 14. Smoothed melting line data for nH₂, nD₂, and nT₂. MPa may be converted to atm by multiplying by 9.87 and to kbars by multiplying by 10⁻². The volume units of μ(m³)/mole and cc/mole are the same.

T _m (K)	nH ₂			nD ₂			nT ₂
	P _m (MPa)	V(solid) [μ(m ³)/mole]	V(liquid) [μ(m ³)/mole]	P _m (MPa)	V(solid) [μ(m ³)/mole]	V(liquid) [μ(m ³)/mole]	P _m (MPa)
14	0.13	23.23	26.01	—	—	—	—
16	6.61	22.65	25.01	—	—	—	—
18	13.9	22.08	24.13	—	—	—	—
20	22.1	21.52	23.34	5.0	20.14 ^a	22.48 ^a	—
22	31.0	20.95	22.63	13.9	19.70 ^a	21.84 ^a	6.1
24	40.2	20.39	22.05 ^a	23.4	19.31 ^a	21.29 ^a	15.9
26	50.2	20.05	21.58 ^a	33.7	18.94 ^a	20.78 ^a	26.4
28	60.9	19.67	21.10 ^a	44.5	18.60 ^a	20.32 ^a	37.5
30	72.2	19.31	20.71 ^a	56.0	18.28 ^a	19.89 ^a	49.2
40	141	17.80	18.84 ^a	124	16.97 ^a	18.20 ^a	117
50	218	16.64	17.56 ^a	205	15.94 ^a	16.94 ^a	199
60	308	15.69	16.49 ^a	297	15.11 ^a	15.96 ^a	294
70	409	14.89	15.62	401	14.35	15.14	—
80	521	14.25	14.93	515	13.75	14.47	—
90	644	13.69	14.31	640	13.23	13.88	—
100	777	13.18	13.76	774	12.76	13.36	—
120	1073	12.31	12.81	1070	11.95	12.45	—
140	1408	11.58	12.01	1400	11.26	11.68	—
160	1778	10.94	11.31	1770	10.66	11.01	—

^aCalculated values.

to 2800 MPa (28 kbars) is described by the Birch relation:

$$P(4.2\text{-K solid}) = Y^5 [A(Y^2 - 1) + B(Y^2 - 1)^2] \quad (88)$$

where

$$Y = \left(\frac{V}{V_0} \right)^{-1/3} \quad (89)$$

and where A and B are constants determined in the static high pressure experiment. The most recent experiment has given special attention to the low-pressures, and the resulting constants are: J=0 H₂, A = 278.68 MPa, B = 633.44 MPa; J=0 D₂, A = 476.65 MPa, and B = 1010.10 MPa. The values of V₀ do not come from these experiments, but from calculations of Section 11. It seems strange that V₀ is not as well known as the high pressure constants A and B. The values of V₀ to be used are, once again: J=0 H₂ — 23.14 ± 0.08 μ(m³)/mole and J=0 D₂ — 19.95 ± 0.05 μ(m³)/mole.^{158,159}

I turn to the corresponding Debye temperatures, Θ_D. These are obtained for H₂ from the heat capacity at constant volume. The H₂ samples contain variable percents of J=1 molecules — always less than 10%. The rotational contributions are removed, and the data extrapolated to 0 K. For volumes of 22.8 to 16.2 μ(m³)/mole (to 240 MPa or 2.4 kbars) I have⁵⁵

$$\Theta_D(H_2, T=0) \simeq -188.0 + \frac{7148}{V} \quad (90)$$

Note that Θ_D increases as the pressure decreases the volume and stiffens the crystal lattice. At the volume on the saturation curve, V₀, I obtain Θ_D(T = 0) = 121 K. There is an abundance of data in this reference spanning the solid phase clear to the melting line.⁵⁵

There is a second source of Θ_D data: to 1100 MPa (11 kbars) at 4.2 K.¹⁶⁰ Recall from Section 14 that the splitting between the Q_Q and Q_R infrared peaks is a measure of Θ_D. Under pressure, the Q_Q peak remains fixed, but the Q_R peak, which incorporates the crystal lattice vibrations, moves to higher frequencies. I combine the infrared data with volume to obtain

$$\Theta_D(H_2, 4.2\text{ K}) \simeq -212.3 + \frac{7387}{V} \quad (91)$$

which yields a saturation volume value of 107 K for Θ_D . Recall from Section 14 that Θ_D values vary depending on how they are measured. I, thus, expect differences between Eqs. (90) and (91).

There is no data for DT. I have previously estimated Θ_D to be about 101 K at 4.2 K and 19.30 $\mu(\text{m}^3)/\text{mole}$. The melting curve data show the rate of increase of Θ_D with decreasing volume to be about 3% more for D_2 than H_2 . The heavier isotope has less zero point energy, is less compressible, and, thus, its crystal lattice stiffens more readily. I estimate, then:

$$\Theta_D (\text{DT}, 4.2 \text{ K}) \simeq -298 + \frac{7700}{V} \quad (92)$$

For completeness, I mention a low pressure shock wave experiment, which starts with 5 K solid H_2 . The P-V-T values obtained are 236 MPa, 17.10 $\mu(\text{m}^3)/\text{mole}$, and 38 K; 626 MPa, 15.23 $\mu(\text{m}^3)/\text{mole}$, and 72 K.¹⁶¹ The Hugoniot, therefore, lies wholly within the solid region. In a shock wave experiment, one measures the velocities of two waves. Their velocities may be related simply to the pressure, volume, and energy transferred into the sample.¹⁶² However, a complete model is required to extract to the temperature and internal energy. To construct the model requires knowledge of precisely these two variables. Thus, shock wave experiments are never as definitive as the static high pressure work. However, this Hugoniot crosses a solid region where no other data exists.

25. The Liquid Under Pressure

I have previously considered the liquid as existing on just the narrow two-phase line. I here broaden the term to include the fluid in the triangular niche between the solid and the gas in the phase diagram, as illustrated in Fig. 15. Although there is no liquid surface, the internal energy is negative, and the fluid is in a bound state. Within this region of negative energy one thinks of the fluid as a liquid. As temperature increases, one moves into the fluid region without binding.

My concern here is cryogenic, but the most important sources of higher temperature fluid data should be listed: the second to sixth virial coefficients of H_2 and D_2 from 98 K up and to pressures of about 100 MPa (1000 atm).⁴⁷ This classic work is so generally useful in the hydrogen field that I list the 98- to 298-K data in Appendix D. A large amount of data to 35 MPa (350 atm — line a in Fig. 15) has been taken by the National Bureau of Standards (NBS) at Boulder, Colorado.¹⁶³ The raw data was not published but was immediately

FIG. 15. Lines of constant internal energy for liquid and fluid $J=0 \text{ H}_2$ in the vicinity of the triple point (TP) and critical point (CP). The H_2 is bound as a liquid or solid for negative energy values. The internal energy to line a is from experimental data; to line b, it is extrapolated.

incorporated into a computer code.^{42,164,165} The code has been extrapolated to 100 MPa (1000 atm — line b), and the internal energies in Fig. 15 are taken from these results. The code explicitly deals with $J=0 \text{ H}_2$ but it has been modified for $n\text{H}_2$. The code is presented in a long tabular format.⁴ A smaller code for D_2 to 10 MPa (100 atm) is also available.⁶ Recently, Liebenberg has studied $n\text{H}_2$ and $n\text{D}_2$ from 200 to 2000 MPa (2 to 20 kbars) at 75 to 300 K.¹⁶⁶⁻¹⁶⁹ He has extrapolated his work to include $n\text{T}_2$.¹⁷⁰ His model cannot be accurately extrapolated below 77 K because of the perturbing influence of the critical point.¹⁷¹

I now return to the liquid. From the large tables available from the NBS code,⁴ I shall consider the smaller region above 21 K from the saturation pressure to 15 MPa (150 atm). This region has been measured and documented in detail for $n\text{H}_2$.^{172,173} The data is taken at almost constant volume (isochores).

At a given volume, there is the linear relation

$$P(\text{liquid}) = A + BT \quad (93)$$

The same behavior has been noted in much less detail for $n\text{D}_2$ to 10 MPa (100 atm).^{2,174} Table 15 lists the constants A and B as well as the extrapolated temperatures on the liquid-gas and melting lines.

There is also a Hugoniot that crosses the fluid region with a number of low pressure points,¹⁷⁵ as listed in Table 16. In addition to temperature, the internal energy has also been calculated. Although parts of the model used are included in the reference, the actual detailed computer code is not available in the open literature. The Hugoniot agrees only to within 10 to 25% with the NBS $J=0 \text{ H}_2$ code. The shock wave experiment

Table 15. Constant-volume pressure-volume-temperature equations from 21 K and above the saturation pressure. The upper pressure for $n\text{H}_2$ is 15 MPa; for $n\text{D}_2$, 10 MPa. The last column shows the projection of the constant-volume lines back on the liquid-vapor curve.

$P(\text{MPa}) = A + BT$							
$n\text{H}_2$				$n\text{D}_2$			
Volume [$\mu(\text{m}^3)/\text{mole}$]	A (MPa)	B (MPa/K)	2-phase temp (K)	Volume [$\mu(\text{m}^3)/\text{mole}$]	A (MPa)	B (MPa/K)	2-phase temp (K)
26	-12.9	0.976	14.05 ^a	23	-27.2	1.49	— ^a
27	-15.3	0.926	16.84	24	-30.4	1.40	21.56
28	-16.6	0.863	19.41	25	-30.5	1.27	24.32
29	-17.1	0.808	21.53	26	-30.6	1.17	26.62
30	-17.4	0.759	23.34	27	-29.3	1.04	28.47
31	-17.3	0.712	24.70	28	-28.2	0.963	30.00
32	-17.0	0.670	25.94	29	-27.0	0.882	31.31
34	-16.0	0.595	27.88	30	-24.8	0.790	32.36
36	-14.9	0.531	29.32	31	-24.2	0.750	33.22
38	-13.6	0.476	30.31	32	-21.8	0.669	34.07
44	-10.4	0.360	32.10				
50	-8.32	0.290	32.76				

^aA projection back to the melting curve.

is done on normal hydrogen, however, and a more detailed analysis of the coupling of the lattice and rotational energies under pressure might resolve the difference. Finally, the Hugoniot is not an adiabat. The adiabat corresponding to the same starting conditions will be at 2 to 5% lower pressure for a given volume.

Table 16. Shock wave Hugoniot data for hydrogen (probably normal). The internal energy and temperature values are the results of a detailed code.

Pressure (MPa)	Volume [$\mu(\text{m}^3)/\text{mole}$]	Internal energy (J/mole)	Temp (K)
0.10	28.40	-531	20.5
3.93	27.34	-529	21
14.56	25.44	-510	23
28.49	23.96	-467	26
66.4	21.65	-303	36
220.4	18.60	549	84
246.8	18.42	700	91
464.3	16.79	2164	148
816.3	15.34	4800	235
1295	14.01	8781	354
1333	14.06	9030	363
1907	12.82	14330	514
2657	11.79	21540	716
3546	10.89	30510	969
3950	10.51	34790	1084

26. Kinetic Gas Data Below 30 K

In the pressure-temperature diagram (Fig. 3), the bottom, low pressure phase is that of the gas. I shall again limit the temperatures to below 30 K to relieve the difficulties of wandering far from perfect gas behavior. At low temperatures, a gas becomes surprisingly dense, and there are enough deviations to consider as it is. I shall consider only the kinetic region, for which the molecule mean free path is less than the dimensions of the apparatus. This excludes the high vacuum region at all temperatures, including the saturated vapor pressures at low temperatures.

From kinetic gas theory, one may calculate the mean free path, λ — the mean distance a molecule moves between collisions with other molecules.

For a perfect gas,

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_0 P} \quad (94)$$

where N_0 is Avogadro's Number and d is the molecular diameter.^{176,177} For hydrogen, I take the value 2.2×10^{-10} m,¹⁷⁷ and obtain

$$\lambda \approx 6.4 \times 10^{-5} \left(\frac{T}{P} \right) \quad (95)$$

where P is in Pa. Millimeter sizes are typical in experimental equipment. For λ equal to 1 mm, I obtain a pressure of 1.3 Pa (0.002 Torr) at 20 K. The kinetic theory might apply to a pressure this low once the gas is in position in the sample chamber. There is usually a long fill tube, however, and thermal transpiration effects will drastically slow filling at 1 Pa. Higher pressures are needed to insure a kinetic flow down thin tubes.¹⁷⁸

The keystone property in the kinetic theory of gases is the viscosity, η , which for a perfect gas should be

$$\eta = \frac{\sqrt{RTM}}{\pi^{3/2} N_0 d^2} \quad (96)$$

The temperature and molecular weight, M , are both expected to show a square root dependence.^{176,177} This is almost true at room temperature,¹⁷⁹ but at 30 K, it is not, and one needs recourse to experiment. Unfortunately, most of the low temperature data are for the pressurized fluid.¹²² The lesser amount of low pressure data, taken from 0.33 to 13 kPa (2.5 to 100 Torr), is in Table 17.¹⁸⁰⁻¹⁸³ Below 30 K, the powers of the temperature for H_2 , HD, and D_2 are 0.97, 0.98, and 1.12. The NBS code for $J=0$ H_2 extrapolates itself into this region, and it displays an exponent of 0.97.⁴ I next consider the power displayed by the molecular weight at constant temperature for the three isotopes. At 14.4 (two isotopes only),

Table 17. Experimental low pressure viscosities for H_2 , HD, and D_2 from 14 to 30 K. The pressures vary from 0.33 kPa (2.5 Torr) to 13.3 kPa (100 Torr). All numbers are rounded off to three significant digits. Pa-s may be changed to poise by multiplying by 10.

H_2		HD		D_2	
Temp (K)	Viscosity (10^{-6} Pa-s)	Temp (K)	Viscosity (10^{-6} Pa-s)	Temp (K)	Viscosity (10^{-6} Pa-s)
14.4	{ 0.789 0.79	14.1	0.818	14.3	0.913
14.5	0.751	14.4	{ 0.880 0.895	14.4	1.00
16.0	0.860	15.5	0.905	15.5	0.992
17.0	0.881	17.0	1.00	17.0	1.13
18.8	1.00	18.7	1.12	18.7	1.23
20.3	1.08	20.3	1.22	20.3	1.34
20.4	{ 1.10 1.13	20.4	{ 1.20 1.26	20.4	{ 1.33 1.39
20.5	1.05		1.27	25.2	1.72
27.4	1.46	26.1	1.58	26.2	1.78
28.9	1.51	32.6	2.01	30.3	2.05
29.2	1.55				

20, and 30 K, the exponents are 0.27, 0.32 to 0.36, and 0.39. These, too, are less than the predicted value of 0.50. So the viscosity's behavior deviates significantly from that predicted by the kinetic theory. These deviations will be reflected in all other properties closely allied with viscosity. I empirically describe the gas viscosity below 30 K with this equation:

$$\eta_i (\leq 30 \text{ K}) \approx 4.20 \times 10^{-7} M_i^{1/3} T \quad (97)$$

You may use Eq. (97) for DT and T_2 predictions.

The next property to consider is the gaseous diffusion coefficient, D_{ij} , where i and j refer to hydrogen isotopes. If i and j are different, one has a mutual diffusion coefficient; if they are the same, one has a self-diffusion coefficient. One may relate the diffusion coefficients, pressures, and molecular weights of different combinations. To convert the D_2 - T_2 coefficient, D_{46} , to the H_2 self-diffusion coefficient, D_{11} , use¹⁸⁴

$$D_{11} P_{11} \sqrt{\frac{M_1}{2}} \approx D_{46} P_{46} \sqrt{\frac{M_4 M_6}{M_4 + M_6}} \quad (98)$$

P_{11} is the H_2 pressure; P_{46} is the total pressure of the D_2 - T_2 mixture; and M_i is the molecular weight of the i^{th} isotope. The validity of this transformation has been demonstrated to a few percent at 195 and 273 K with H_2 - T_2 , D_2 - T_2 , H_2 -HT, and D_2 -HT.¹⁸⁵ There is only a single measured diffusion coefficient below 30 K.¹⁸⁶ It is taken for the pair H_2 and D_2 , but one may use Eq. (98) to convert it to the customary H_2 - H_2 coefficient, D_{11} . For D_{11} at 1 Pa and at 20.4 K, one has 0.0826 m^2/s . I empirically describe D_{11} by

$$D_{11} (\leq 30 \text{ K}) \approx \frac{2 \times 10^{-4} T^2}{P_1} \quad (99)$$

The quadratic temperature dependence is also seen in six data points taken from 55 to 90 K, but the coefficient is 20% larger.^{186,187}

For a mixture of the gases i and j , at a pressure P_{ij} , and with molecular weights M_i and M_j , I write the mutual diffusion coefficient, D_{ij} (in m^2/s):

$$D_{ij} (\leq 30 \text{ K}) \approx \frac{6.4 \times 10^{-6} T^2}{P_{ij}} \sqrt{\frac{M_i + M_j}{M_i M_j}} \quad (100)$$

The properties described so far may all be related by the dimensionless Schmidt coefficient, S . From the kinetic theory of a perfect gas, S is

$$S = \frac{\eta RT}{PDM} \quad (101)$$

For a perfect gas, S should be exactly one.¹⁸⁸ The single diffusion coefficient at 20.4 K yields an S_1 value (for H_2) of 1.10, but, because of the uncertainty in D , this may be as much as 20% too high, as the 55 to 90 K values are 0.75 to 0.83. However, the various gas equations above may be combined to obtain this rough description of S :

$$S_i \approx 0.39 M_i^{-1/6} \quad (102)$$

S_5 for DT will be 0.86 that of S_1 for H_2 .

Next I move to the heat capacity at constant volume, C_v , which is almost constant below 30 K for the low pressure gas. The values are in Table 18.^{2,4,189,190} These are calculated from partition functions, but they are nevertheless acceptable. No one has done low pressure heat capacity work since validating the partition functions over forty years ago.¹⁹¹ The heat capacities increase slightly with temperature as rotational energy is acquired. Table 18 assumes that DT instantly absorbs this energy and adjusts itself to the equilibrium form. The table also assumes that only $J=0$ to 2 transitions can occur in nH_2 , nD_2 , and nT_2 . This two-level jump is quite large compared with 30-K thermal energy. Only the T_2 , with the lowest lying rotational levels, shows much effect.

I arrive next at a more difficult property — the gaseous thermal conductivity, K . This property is a direct derivative of the viscosity by way of the Eucken constant, E , which is defined by

$$E = \frac{KM}{\eta C_v} \quad (103)$$

From perfect-gas kinetic theory, one may relate E to C_v and the heat capacity at constant pressure, C_p ,¹⁹²

$$E = \frac{9}{4} \frac{C_p}{C_v} - \frac{5}{4} \quad (104)$$

Below 30 K, the heat capacity is almost all translational, and C_p/C_v is about 5/3. In this case, one expects a constant E value of 2.50 for H_2 , D_2 , and T_2 . DT, however, has increasing amounts of rotational heat capacity as the temperature rises. At 30 K, C_p/C_v is 1.39 and E drops to 1.87. If I combine Eqs. (96), (103), and (104), I expect the thermal conductivity for a perfect gas to be

$$K = \frac{C_v}{\pi^{3/2} N_0 d^2} \left\{ \frac{9 C_p}{4 C_v} - \frac{5}{4} \right\} \sqrt{\frac{RT}{M}} \quad (105)$$

There are two experimental sources of low pressure data (Table 19) taken at about 4 kPa (30 Torr).^{193,194*} The power of the temperature is 1.02 for H_2 and 1.36 for D_2 — as compared with 0.50 in Eq. (105). The power of the molecular weight is about -0.82 as compared with -0.50 in Eq. (105). These differences reflect the deviations initially seen in the viscosity. I shall assume that thermal conductivity has the same power of the temperature as does the viscosity, i.e., one. This means I do not accept the temperature dependence of the D_2 data. I represent the thermal conductivity data of Table 19 by

$$K (\leq 30 \text{ K}) \approx 4.6 \times 10^{-6} M_i^{-5/6} T \quad (106)$$

Previous equations may be combined to yield an Eucken constant with no temperature dependence:

$$E_i \approx 0.878 M_i^{-1/6} \quad (107)$$

Table 18. Zero-pressure heat capacities at constant volume, C_v , for four hydrogen isotopes.

Temp (K)	Heat capacity, (J/mole-K)			
	nH_2	nD_2	(e)DT	nT_2
10	12.47	12.48	13.46	12.47
15			17.06	12.48
20			20.16	12.61
25			21.42	12.97
30		12.53	21.59	13.64

*The data contain one oddity. At 24 K, the thermal conductivity is an extreme function of pressure as though the sample were moving from the kinetic to the high vacuum region.¹⁹³ Since the smallest dimension is 10^{-4} m in a static experiment, this effect occurs at a hundred-times higher pressure than expected.

Table 19. Experimental low pressure gaseous thermal conductivities of H₂ and D₂. The pressure is about 4 kPa (30 Torr). Interpolated viscosity data is added and the Eucken constant calculated.

Isotope	Temp (K)	Thermal conductivity (W/m-K)	Viscosity (10 ⁻⁶ Pa-s)	Eucken constant
H ₂	14.6	0.0115	0.775	2.40
	15.0	0.0120	0.797	2.44
	15.1	0.0121	0.802	2.44
	17.5	0.0141	0.929	2.46
	19.1	0.0154	1.01	2.47
	19.3	0.0157	1.02	2.49
	20.1	0.0162	1.07	2.45
	20.7	0.0172	1.10	2.53
	24.0	0.0190	1.27	2.42
D ₂	14.9	0.00640	0.995	2.08
	15.1	0.00657	1.01	2.10
	16.5	0.00757	1.10	2.22
	18.5	0.00874	1.24	2.28
	19.9	0.00950	1.33	2.31

The molecular weight dependence is the same for both the Eucken and Schmidt constants. Equation (107) predicts 2.47 for H₂ and 2.20 for D₂ — in agreement with the calculated points of Table 19. Equation (107) assumes a heat capacity of 12.47 J/mole-K; it will be slightly higher, as listed in Table 18.

So far, only the diffusion coefficient can be used at various pressures. The other properties are all low pressure values for comparison with perfect gas theory. The quantities η , C_v , and K all increase as the pressure isothermally rises and the gas deviates more from ideal behavior. The increases are ever steeper as the pressure increases. To simplify this complicated situation for easy use, refer to Fig. 16. Here, as a function of pressure, I plot the ratio of K and η at that pressure divided by the "zero pressure" values. The maximum correction is about 1.55 for the thermal conductivity at 30 K. The source of Fig. 16 is the $J=0$ H₂ code constructed by the NBS.⁴ Figure 16 is, therefore, an extrapolation of their higher pressure fluid data. The viscosity curves may be used for C_v as well, with little error. No comparable curves are available for the other isotopes, but I feel that Fig. 16 can be used unchanged for them with little error. The corrections will not be as large, anyway, because the heavier isotopes isothermally liquefy at lower pressures.

I end this chapter with the sound velocity, U . For H₂, I have

$$U \simeq \left\{ \frac{5RT}{3M} - (6.85 \times 10^7) \frac{P^{1.10}}{T^2} \right\}^{1/2}, \quad (108)$$

where the pressure is in MPa. For D₂, I use a coefficient of 5.5×10^7 in the second term. For DT I estimate 4.8×10^7 . The first term on the right in Eq. (108) is the zero pressure expression from kinetic theory.¹⁹⁵ The second term is an empirical correction for non-ideality. Equation (108) is formed partly from the NBS code for $J=0$ H₂, which extends to 0.8 MPa (8 atm) at 30 K.⁴ It is also derived from a small amount of under-30-K gas data, which has been taken for H₂ and D₂ between 18.9 and 20.4 K and from 0.01 to 0.1 MPa (75 to 760 Torr).^{196,197} The data are quite scattered, and it is not possible to accurately determine the functionality of the non-ideal term.

27. Hydrogen-Helium Mixtures

Many years from now, the helium-3-deuterium (He³-D) mixture may be used as the preferred nuclear

FIG. 16. Pressure corrections to the zero-pressure values of gaseous thermal conductivity and viscosity. The zero values, as determined from Eqs. (97) and (106), should be multiplied by the ratio. Use the viscosity curves for correcting the heat capacity, C_v . Although derived for $J=0$ H₂, this may be applied to all isotopes.

FIG. 17. Pressure-temperature phases of $n\text{H}_2$ -helium-4 (He^4). The numbers are the mole fraction of He^4 dissolved in liquid $n\text{H}_2$, x_{He} . The pure- $n\text{H}_2$ diagram forms the reference plane. One may imagine the various x_{He} lines telescoping behind the plane of the paper to form an ascending two-phase fluid surface. The three-phase line is to the left.

fuel to provide electrically charged particles by means of Eq. (4). However, the major importance of He^3 today is as the daughter of tritium. Every 24 h, one tritium atom out of 6500 turns into He^3 . Several-months-old D-T gas can contain percent amounts of He^3 . After clean-up with powdered uranium, 0.1% He^3 remains. Less He^3 remains after passage through a palladium thimble, but how much is unknown. He^3 , then, must really be considered as a true partner in the D-T phase diagram.

At the hydrogen triple point, helium is a gas far above its critical point [5.20 K for helium-4 (He^4) and

3.32 K for He^3].¹⁹⁸ The phase diagram is, thus, easier to understand if one ventures just a small distance from pure hydrogen. Figure 17¹⁹⁹ shows the phase diagram for the most studied system, He^4 dissolved in $n\text{H}_2$. Note that the $n\text{H}_2$ melting line climbs almost vertically on the left, and the $n\text{H}_2$ liquid-vapor line gently curves upward at the bottom to the critical point. One may think of the pure $n\text{H}_2$ lines as lying in the plane of Fig. 17 while the H_2 -He data lie in constant He-composition planes telescoping beyond. The higher the liquid mole fraction of He, x_{He} , the farther away its pressure-temperature

plane. You see, then, that you are looking up a valley, bounded on the left by the steep three-phase cliff. Above the $n\text{H}_2$ critical point, where x_{He} is 0.06, the valley disappears.

The steeply rising valley floor in Fig. 17 is a two-phase surface. By analogy with the $n\text{H}_2$ liquid-vapor curve, one may visualize the He gas dissolving in the liquid hydrogen. Its solubility is not great, and a large helium partial pressure is needed to force the system up the valley. Most of the He remains in the gas phase. As one moves farther away from pure hydrogen, the distinction between liquid and gas begins to break down. One finds the liquid becoming the hydrogen-rich fluid.²⁰⁰ The upper valley, then, is a two-fluid surface. On the cliff to the right, one can barely distinguish the pure $n\text{H}_2$ melting curve and the $n\text{H}_2$ -He⁴ three-phase line. From our perspective in Fig. 17, they appear to overlies one another. Actually, they intersect only at the pure- $n\text{H}_2$ triple point, and they diverge from one another rapidly in the direction of composition. The cliff is the solid phase. No measurements have been taken there, and the extent of solid-solid phase separation is unknown.

The three-phase line for $n\text{H}_2$ -He⁴ has been measured to quite high pressures — the data appear in Table 20.²⁰⁰ At higher pressures, temperatures, and mole fractions of helium, the three-phase line appears at much lower isobaric temperatures than the $n\text{H}_2$ melting curve. At 938 MPa (9.4 kbars), these temperatures are 100 and 109 K. One may think of the He as depressing the H_2 freezing point, in a manner analogous to salt in water.

Let me further consider liquid hydrogen with small amounts of dissolved helium, which I describe by

$$y_i P = \alpha_i x_i P_i^s, \quad (109)$$

where y_i is the gas phase mole fraction of isotope i , P the total pressure (of all components), x_i the liquid mole fraction, and P_i^s the pure-component vapor pressure.²⁰¹ All other factors are compressed into the coefficient α_i . It will be 1 for a perfect solution, and Eq. (109) reduces to Raoult's law. For hydrogen-helium mixtures, α_i will be much larger than 1. Helium will be hotter than its critical point at my temperatures of interest, and this forces me to employ a dubious pseudo-vapor pressure for helium in Eq. (109). The total vapor pressure of the mixture is

$$P = \sum_i \alpha_i x_i P_i^s, \quad (110)$$

where I sum over the hydrogen and helium isotopes.

I shall investigate the hydrogen component first, using the pair $n\text{D}_2$ -He³, which is the closest to the

Table 20. The three-phase line for $n\text{H}_2$ -He⁴ mixtures. Two phases are fluid—one rich in H_2 (liquid) and the other in He⁴ (gas). The third phase is an H_2 -rich solid. There are no studies as to possible phase separation in the solid. MPa may be converted to atm by multiplying by 9.87 and to kbars by multiplying by 10^{-2} .

Temp (K)	Pressure (MPa)	He mole fraction	
		x_{He} in liquid or H_2 -rich fluid	y_{He} in gas or He-rich fluid
13.956	0.000	0.000	0.000
14.02	0.235	0.001	0.936
14.10	0.526	0.002	0.966
14.44	1.73	0.005	—
15.52	5.67	0.0118	—
16.09	7.54	0.0149	—
16.82	10.37	0.0187	—
27.18	63.7	0.0532	0.973
29.00	75.5	0.0610	0.969
34.95	117.9	0.0824	0.968
38.88	149.3	0.0939	0.957
61.50	378.9	0.1445	0.911
77.61	591.2	0.1655	0.905
84.82	698.4	0.1756	0.895
100.00	937.7	0.1870	0.896

DT-He³ combination. Hiza has recently studied the properties of He³ in liquid $n\text{D}_2$ from 20 to 30 K and from 0.35 to 1.8 MPa (3.5 to 18 atm).²⁰² I empirically fit the D_2 data to the equation:

$$\alpha_4 \approx 1 + AP^b, \quad (111)$$

where P is in MPa. The constants are in Table 21. The effects of the non-ideal solution behavior are greater

Table 21. Constants for the non-ideal mixtures coefficient, α_4 , for $n\text{D}_2$ -He³ mixtures. The pressure, P , is in MPa.

Temp (K)	$\alpha_4 \approx 1 + AP^b$	
	A	b
20	0.589	1.038
22	0.484	1.103
24	0.406	1.122
26	0.346	1.245
28	0.300	1.231
30	0.230	1.549

FIG. 18. Henry's Law constant, k , for the system $n\text{H}_2\text{-He}^1$. This quantity is an inseparable combination of the pure-component vapor pressure and non-ideal mixing effects. It may be used to calculate He^1 solubilities in liquid $n\text{H}_2$.

at lower temperatures. At 20 K and a pressure of 1.67 MPa, α_4 reaches a value of two. I may now calculate the mole fraction of $n\text{D}_2$ in the gas phase, y_4 , using

$$y_4 \sim \frac{\alpha_4 P_4^s}{P} \quad (112)$$

where I have set x_4 equal to 1. The P_4^s value may be obtained from Section 5.

Next, I consider He^3 . The quantity measured by experimental apparatus is $(y_{\text{He}}P/x_{\text{He}})$ which is equivalent to Henry's constant, k , at low pressure approaching infinite dilution.²⁰³ This quantity is independent of pres-

sure in the range studied. Hiza had displayed it in the exponential form

$$k(\text{He}^3 \text{ in } n\text{D}_2) \approx 0.594 \exp \frac{1120}{RT}, \quad (113)$$

where k is a pressure in MPa and the 1120 J/mole is a measure of the heat of solution of the He^3 in the liquid $n\text{D}_2$.²⁰⁴ Notice from Eq. (113) that k gets larger with decreasing temperature, which is the opposite expected from the pure-component vapor pressure, P_{He}^s .

The constant α relates the two ($k = \alpha_{\text{He}} P_{\text{He}}^s$), and its behavior with helium must be overwhelming. I shall try to estimate it, even though the helium is above its critical point. I first require some real liquid line data. For pure He^3 from 2.0 to 3.32 K, the vapor pressure is^{198,205}

$$\ln P_{\text{He}}^s \approx 0.45929 - \frac{8.8355}{T}. \quad (114)$$

I extrapolate Eq. (114) to obtain pseudo-vapor pressures of 1.0 MPa at 20 K and 1.2 MPa at 30 K. From Eq. (113), I then calculate α_{He} values of 500 at 20 K and 44 at 30 K! This is the source of the temperature dependence in Eq. (113).

One may use the Henry's law constant, k , to calculate He solubility in the liquid, x_{He} . This is

$$x_{\text{He}} = \frac{P - \alpha_4 P_4^s}{k}. \quad (115)$$

For He^3 in $n\text{D}_2$ at 20 K, I calculate a solubility of 1.4×10^{-4} mole fraction with a 0.1 MPa (1 atm) total pressure. If the total pressure increases to 2 MPa (20 atm), x_{He}

increases to 4×10^{-3} . The He^3 is also more soluble at higher temperatures. At 30 K and 2 MPa, x_{He} becomes 0.024.

Hiza has also studied other combinations of isotopes. He finds, for the range 20 to 30 K

$$k(\text{He}^4 \text{ in } n\text{D}_2) \approx 0.410 \exp \left(\frac{1150}{RT} \right), \quad (116)$$

$$k(\text{He}^3 \text{ in } n\text{H}_2) \approx 0.314 \exp \left(\frac{995}{RT} \right), \quad (117)$$

and

$$k(\text{He}^4 \text{ in } n\text{H}_2) \approx 0.568 \exp \left(\frac{840}{RT} \right), \quad (118)$$

where k is in MPa.²⁰³ The data possess enough scatter so the various isotopic combinations cannot be compared too closely. However, it is true that helium is more soluble in H_2 than in D_2 . The solubility of the two He isotopes in a given liquid hydrogen isotope is similar.

I have noted that k is independent of pressure within 20 to 30 K and up to 1.8 MPa.²⁰² The pair $n\text{H}_2\text{--He}^4$ has been further studied to 15.5 K and to 3.5 MPa.^{199,202} The data in Fig. 18 show us that k indeed increases with pressure, as expected, and that the pressure dependence becomes larger at lower temperatures.

He^3 in the DT system has not yet been studied, although work is proceeding on He^3 in T_2 .²⁰⁶ One could adjust Eq. (113) to represent the larger mass of DT, which would render He^3 less soluble. However, there remains the question of whether additional He^3 can be bound in liquid DT following some sort of radiation-induced reaction. Indeed, not all the He^3 formed by tritium decay outgases from a sample of unrefluxing liquid tritium. The reason for this fascinating effect is unknown but Sherman et al.²⁰⁷ have postulated the formation of the exotic molecule helium tritide.

VI. MIXTURES OF HYDROGENS

28. Raoult's Law and D-T Fractionation

The hydrogen isotopes are miscible in the liquid and probably in the solid down to 4 K. Most work has been done with H_2 and D_2 , and the most dissimilar pair, H_2 and T_2 , has not been studied. Early Soviet work indicated possible phase separation in the 4.2-K solid;^{208,209} but despite some lingering doubts,²¹⁰ no phase separation is now expected down to about 3 K.²¹¹⁻²¹³

The solution of hydrogen isotopes are close to being ideal; i.e., they almost obey Raoult's law, which for isotope i is

$$y_i P_I = x_i P_i^S, \quad (119)$$

where y_i is the gas mole fraction of component i , P_I the total solution vapor pressure, x_i the liquid mole fraction of i , and P_i^S the liquid pure-component vapor pressure.

The left side of Eq. (119) is the partial vapor pressure of i . One may think of the right side as being a partial "liquid pressure" of i . Summing the partial pressures provides the total vapor pressure

$$P_I = \sum_{i=1}^6 x_i P_i^S, \quad (120)$$

where I sum here over the six hydrogens. The subscript "I" on the vapor pressure indicates the ideal solution value. These equations also hold for the solid, where I denote the pure-component vapor pressure as Q_i^S . When solid, liquid, and vapor are in equilibrium, I expect

$$x_i P_i^S = s_i Q_i^S, \quad (121)$$

where s_i is the mole fraction of isotope i in the solid. I use both saturated liquid and solid vapor pressures at the same temperature, even though one of them will be extrapolated beyond its physical region of existence. For example, an H_2 - D_2 three-phase solution will lie between the pure-component triple points of 13.81 K for eH_2 and 18.7 K for D_2 . The solid solution will contain H_2 above 13.8 K; the liquid will contain D_2 below 18.7 K. When I extrapolate the vapor pressure equations derived in Sections 5 and 6 of this report, my extrapolations add errors that cannot presently be evaluated. The use of two different vapor pressure equations at once has led me to the two distinct terms P_i^S and Q_i^S .

Figure 19 shows the phase diagram for the two components eH_2 and eD_2 .²¹⁴ The horizontal plane contains temperature and composition, and the vertical di-

rection represents pressure. On the near face of the cube is the pressure-temperature diagram of pure eH_2 ; on the far wall is the same for eD_2 . The letters S, L, and G refer to the solid, liquid, and gas phases. High in the phase diagram are two isobaric cuts, one for the solid-liquid and the other for the liquid-gas. Each cut has the shape of a banana; each side of the banana represents a phase. The banana, pointed at each end, is tilted with respect to temperature because it takes a higher temperature to get the same vapor pressure from eD_2 than it does for eH_2 . The tie-line is a straight, isothermal connection across the banana. The two phases are now connected by the tie-line and the compositions related to each other. Isobaric bananas may also be drawn for the solid-gas equilibrium, although these are not shown in Fig. 19.

The foci of Fig. 19 are the two pure-component triple points. Connected to each is an end of the three-phase banana. This banana bows upward to a pressure maximum at about 20% H_2 -80% D_2 . The outer lines of the banana represent the solid and gas, and the liquid line runs almost exactly down the center of the banana. If you ignore pressure for a moment, and draw a line between the two triple point temperatures, you shall find that the liquid line lies only 0.05 K above this. A tie-line is again an isothermal cut across the banana, but now three phases are linked by it. The liquid line, however, is especially useful because of its nearly straight course between the triple points. It allows me to estimate the temperature of first freezing of a hydrogen solution, Θ , which is

$$\Theta(\text{first freeze}) \simeq \sum_i x_i \Theta_i, \quad (19)$$

where Θ_i is the triple point temperature of isotope i .

The D_2 -DT- T_2 mixture extends to three components; six if all hydrogen impurities are considered. All Raoult's law equations hold for multicomponent systems without change. There are two differences, however. First the bananas need not be pointed at the ends — a banana can simply be bitten off at the edge of the phase diagram. Secondly, it is not obvious where to draw the tie-line connecting the various phases. There may be no unique isothermal path, and the components may be reacting toward a different chemical equilibrium.

The Clausius-Clapeyron equation [Eq. (22)] also has a multicomponent form. For an ideal solution where the vapor obeys the perfect-gas law, the Clausius-Clapeyron equation becomes

$$\left(\frac{\partial \ell_n P}{\partial T} \right)_{x_i} = \frac{1}{RT^2} \sum_i y_i H_{vi} \quad (122)$$

FIG. 19. Pressure-temperature phases of the binary system $J=0$ H_2 and $J=0$ D_2 . S, L, and G refer to solid, liquid, and gas phases.

The partial derivative on the left is for constant liquid mole fractions. On the right, the overall heat of vaporization is the sum of the individual heats, H_{vi} , times the vapor phase mole fractions.^{215,216}

The practical reason for caring that D-T is really a three-component solution has to do with fractionation effects. In the three-phase region at about 20 K, chemically equilibrated liquid D_2 -DT- T_2 with 50% D and 50% T will disproportionate to 58% D in the vapor and 48% D in the solid. This occurs because D_2 is slightly more volatile than DT, which is more volatile than T_2 . Two degrees of temperature separate the three pure-component triple points. The effect above is not great but it is cumulative. As freezing continues, the liquid becomes richer in D and the three-phase temperature falls. The result is a layered solid, with enough variety of composition to be renamed a mixture.

To prevent fractionation, one must freeze a liquid D-T layer of thickness, ℓ , in a time, t , so short that no appreciable liquid diffusion can take place across the layer. The diffusion coefficient, D , of liquid D_2 is quite large — about $2 \times 10^{-9} \text{ m}^2/\text{s}$.¹²⁵ The time to freeze must be less than²¹⁷

$$t \lesssim \frac{\ell^2}{\pi^2 D} \quad (123)$$

For a 1- μm liquid layer, I must freeze faster than 50 μs ; for a 1-mm layer, I have 50 s.

At low temperatures, D_2 is relatively much more volatile than T_2 . At 4.2 K, the 50% D-50% T solid has 95 to 99% D in the vapor phase. The solid will absorb stray radiation, sublime, and refreeze in unknown compositions on walls of slightly different temperatures. This migration of the solid is easily noted in a cryostat observation port, which is itself the source of the stimulating radiation.

29. Non-Ideal Solution Theory for the Hydrogens

Solutions of hydrogen isotopes do not quite obey the ideal form of Raoult's law given in Section 28. Neither does one have to capitulate by falling back to Henry's law constants, as I did in considering the dissimilar pair of hydrogen and helium. The following theory has been constructed by Sherwood to be as simple as possible and yet provide an adequate description of the hydrogen isotopes.²¹⁶ I expand Raoult's law to the more complicated form

$$\phi_i y_i P = \gamma_i x_i f_i^s \quad (124)$$

I have added two adjustment parameters: the fugacity coefficient, ϕ_i , and the activity coefficient, γ_i . The pure-component vapor pressure has become a fugacity, and I shall have to readjust it to get back my pressures.²¹⁸

I first consider ϕ_i , the correction for vapor-phase non-ideality. For a mixed vapor of components i and j , I employ just the cross-term second virial coefficient, B_{ij} . The non-ideal gas equation has the form

$$PV \simeq RT + B_{ij}P \quad (125)$$

I relate B_{ij} to the pure component coefficients, B_i and B_j , by the arithmetic average

$$B_{ij} \simeq \sum_{i=1} \sum_{j=1} y_i y_j \left[\frac{B_i + B_j}{2} \right] \quad (126)$$

I calculate the fugacity coefficient from

$$\phi_i = \exp \left\{ \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V_T}{\partial n_i} \right)_{T,P,n_j} - \frac{RT}{P} \right] dP \right\}, \quad (127)$$

which includes the partial derivative of volume with respect to the number of moles of i .²¹⁹ I use Eqs. (125) and (126), carry through a lengthy partial differentiation, and finally integrate Eq. (127) assuming B not to be a function of pressure. I finally obtain²¹⁸

$$\phi_i \simeq \exp \left(\frac{B_i P}{RT} \right) \quad (128)$$

Now I move to the liquid side of Eq. (124). To evaluate the pure-component fugacity, f_i^s , I momentarily reconsider Eq. (124) for a pure component. Then x_i , y_i , and γ_i are all one. I combine this with Eq. (128) and substitute back into Eq. (124) to obtain²¹⁸

$$f_i^s \simeq P_i^s \exp \left(\frac{B_i P_i^s}{RT} \right) \quad (129)$$

The activity coefficient represents the mixing of the liquids and is related to the partial molal-excess Gibbs free energy of mixing, $\bar{G}_i^E$, by²¹⁸

$$\gamma_i = \exp \left(\frac{\bar{G}_i^E}{RT} \right) \quad (130)$$

I combine Eqs. (124), (128), (129), and (130) and sum to obtain the total pressure

$$P \simeq \sum_i x_i P_i^s \exp \left[\frac{B_i (P_i^s - P) + \bar{G}_i^E}{RT} \right] \quad (131)$$

For an ideal solution, the exponential terms equal one and I arrive at Raoult's law.

I now obtain the free energy of mixing by a variant of Wohl's method.²²⁰ I have, for simplicity, assumed the hydrogen isotopes to be close enough in molar volume that mole fractions can be used. I expand the total Gibbs excess free energy of mixing in the quadratic form

$$G^E = \frac{1}{2} \sum_i \sum_j x_i x_j A_{ij} \quad (A_{ij} = 0, i = j), \quad (132)$$

where A_{ij} is a binary-mixing parameter. The derivative with respect to the composition of i yields, after some manipulation, the partial molal quantity

$$\bar{G}_i^E = \sum_j x_j A_{ij} - G^E \quad (133)$$

For two components ($D_2 = 4$, $T_2 = 6$), the above reduces to

$$\bar{G}_4^E = x_6^2 A_{46} \quad (134)$$

Recall that

$$G^E = \sum_i x_i \bar{G}_i^E \quad (135)$$

which for a binary mixture becomes

$$G^E = x_4 x_6 A_{46} \quad (136)$$

One sees that A_{46} is four times the excess free energy for a mixture of 50% D–50% T.

For three components (add DT = 5):

$$\bar{G}_4^E = x_5(1 - x_4)A_{45} + x_6(1 - x_4)A_{46} - x_5 x_6 A_{56} \quad (137)$$

and

$$G^E = x_4 x_5 A_{45} + x_4 x_6 A_{46} + x_5 x_6 A_{56} \quad (138)$$

The A_{ij} parameters are all different, and one loses the simple physical relationship with G^E in Eq. (136). If the A_{ij} of Eqs. (136) and (138) were all the same, one would find G^E increasing by 4/3 as one goes from 50% D_2 –50% T_2 to 33% D_2 –33% DT–33% T_2 .

There is hydrogen present in stainless steel, and this emerges to add H_2 , HD, and HT impurities to the extent of 1 to 2 mole% in all D–T. One should describe all six isotopes of hydrogen, but this would result in a model of enormous complexity. Instead, I lump the three H impurities into either HD or HT, according to whether there is more D or more T in the mixture. For HD, D_2 , DT, and T_2 (isotopes 2, 4, 5, and 6), I have the four-component equations

$$\bar{G}_2^E = 1 - 2x_2 + \xi \quad (139)$$

$$\bar{G}_4^E = x_5 A_{45} + x_6 A_{46} + \xi \quad (140)$$

$$\bar{G}_5^E = x_4 A_{45} + x_6 A_{56} + \xi \quad (141)$$

and

$$\bar{G}_6^E = x_4 A_{46} + x_5 A_{56} + \xi \quad (142)$$

where

$$\xi = x_2^2 A_{25} - (x_4 x_5 A_{45} + x_4 x_6 A_{46} + x_5 x_6 A_{56}) \quad (143)$$

I now return to consider the deviation of the real total pressure, P , from that calculated using Raoult's law in its perfect form, P_I . I define the percent deviation, I , as

$$I = (100) \left(\frac{P - P_I}{P_I} \right) \quad (144)$$

I substitute from Eqs. (120) and (131); and I further make the assumption that the e^x term of Eq. (131) may be replaced by $(1+x)$ for small derivations from Raoult's law. Then

$$I \approx 100 \sum_i \left(\frac{x_i P_i^s}{P_I} \right) \left[\frac{B_i (P_i^s - P) + \bar{G}_i^E}{RT} \right] \quad (145)$$

Eq. (145) allows me to directly compare the portion of non-ideal solution due to the non-ideality of the gas (the B_i term) and that part due to liquid mixing ($\bar{G}_i^E$). The full exponential mixes the two mechanisms together and makes comparison more difficult. One may also note that $(x_i P_i^s / P_I)$ is the Raoult's law gas mole fraction,

which will be close to the real value. Note, then, that I is a function of y_i for both mechanisms. A plot of I against x_i , which is usually done for binary systems, will display a peak skewed toward the heavier isotope.

Finally, note that Scatchard-Hildebrand theory seeks to develop $\bar{G}_i^E$ in terms of measurable energies and volumes according to

$$\bar{G}_i^E = V_i \sum_j \Phi_j^2 \left[\left(\frac{E_v}{V} \right)_i^{1/2} - \left(\frac{E_v}{V} \right)_j^{1/2} \right]^2, \quad (146)$$

where V_i is the molar volume, Φ_j the volume fraction, and $E_v(i)$ the pure-component energy of vaporization.^{221,222,*} This is not expected to work near the critical point, and it does not for almost the entire liquid hydrogen range. This is probably caused by the large zero point energies, which greatly reduce the energies of vaporization from the classically expected values. In any case, the failure of Scatchard-Hildebrand theory leads to the more general Wohl representation.

30. Binary-Mixing Parameters

You have seen in the previous section that the mixture theory evolves into a set of binary-mixing parameters, A_{ij} . These must be obtained experimentally. Only two extensive sources of data exist. The first covers the nH_2 - nD_2 and nH_2 -HD liquid-vapor equilibrium from 18 to 28 K.²²³ I use only their boiling point data for which the liquid mole fractions are given. They list only total pressures, so the temperatures must be found by reiterating with the pure-component vapor pressure equations until the proper Raoult's law pressure is obtained. I then calculate A_{14} (H_2 - D_2) and A_{12} (H_2 -HD). The second reference, which is for the boiling points of eH_2 - eD_2 solutions from 14 to 20 K, gives all the needed temperatures and pressures.²²⁴ I have plotted all values in Fig. 20.

Note from Fig. 20 that A_{14} is 2.5 to 3 times as large as A_{24} . One would expect larger effects for isotopes with larger property differences. Second, the A_{ij} parameters increase rapidly as the temperature falls. This is the phenomenon that makes the measured derivation from Raoult's law, I_m , increase in the same way. I take the approximate description of Eq. (145) for the 30% H_2 -70% D_2 solution.^{223,224} As shown in Fig. 21, note that the derivation due to gas non-ideality is constant at about -1% from 17 to 27 K. It is the liquid mixing term that dominates the overall behavior of the Raoult's law derivation.

* E_v may be derived from the heat of vaporization, H_v , by a PV adjustment similar to that of Eq. (43).

From Eq. (136), the A_{ij} parameter for a binary solution is just four times G^E . From Fig. 20, I obtain a 50% H_2 -50% D_2 value of 20 K of 7.4 J/mole, which may be compared with calculated values ranging from 4.6 to 8.4 J/mole.^{22,223,225,226} The actual measured heat of mixing is 12.1 to 13.0 J/mole—about 70% higher than G^E .^{225,226} One sees, then, that the hydrogen isotopes do not form regular solutions, with a zero entropy of mixing.²²⁷ For H_2 -HD, I compare the Fig. 20 value of 2.6 J/mole at 20 K with calculated values of 2.1 to 2.6 J/mole.^{208,210,211} The 20-K heat of mixing is 4.9 J/mole.²¹¹ Thus A_{ij} may indeed be equated with G^E , although a calculation is needed to proceed from the heat of mixing to G^E . This calculation is for the entropy term, and it requires a knowledge of compressibilities, which are not well known.

I now wish to fit the data of Fig. 20 to an empirical equation for extension to other isotropic combinations. The H_2 - D_2 data of the two references do fit together, but the slopes are quite different.^{223,224} I, nevertheless, fit the data to

$$A_{ij} \approx 1580 \left(\frac{\Theta_i - \Theta_j}{\Theta_1 - \Theta_4} \right)^{1.81} T^{-1.33}, \quad (147)$$

where Θ_i is the triple point temperature of isotope i . I relate A_{ij} to the triple point temperature differences of isotopes i and j , with the H_2 - D_2 system as the reference. A power fit for temperature is also included with the lines in Fig. 20 representing this fit. I reduce Eq. (147) to

$$A_{ij} \approx A_{ij}^0 T^{-1.33}, \quad (148)$$

where the A_{ij}^0 coefficients in J/mole are

$$\begin{aligned} A_{12}^0 &= 580, A_{13}^0 = 1060, A_{14}^0 = 1580, A_{15}^0 = 2320, A_{16}^0 = 2900, \\ A_{23}^0 &= 110, A_{24}^0 = 350, A_{25}^0 = 750, A_{26}^0 = 1120, A_{34}^0 = 90, \\ A_{35}^0 &= 350, A_{36}^0 = 620, A_{45}^0 = 120, A_{46}^0 = 300, \text{ and } A_{56}^0 \approx 60 \end{aligned}$$

I again mention that these are all estimates, except for A_{14} from 15 to 27 K and A_{24} from 19 to 27 K.

The estimates above do not predict large values for D_2 -DT- T_2 mixtures. For example, I estimate A_{46} at 25 K to be only 4.2 J/mole. The actual data is not in agreement, as it shows A_{46} values in the 10 to 20 J/mole range.^{9,10} This leads to non-idealities as large as those of H_2 - D_2 . The error bars in the D-T experiments are large, and, in my opinion, the work needs repeating.

FIG. 20. Binary-mixing parameter for H_2-D_2 (A_{14}) and H_2-HD (A_{12}). A_{ij} is related to the excess free energy of mixing and is in J/mole.

FIG. 21. Approximate Raoult's law deviation for H_2 - D_2 solutions of 0.30 to 0.70 liquid mole fraction. The observed deviation is the approximate sum of mechanisms due to liquid mixing and gas non-ideality.

31. The Chemical-Exchange Reaction

Researchers who deal with H_2 - D_2 consider this mixture to be almost indefinitely stable. To induce a reaction to form HD, a catalyst must be added. Tritium, however, carries its own catalyst—its beta particle. One may expect the exchange reaction

to take place in hours or days, with the time being a complicated function of the experimental conditions. Once one's experimental equipment has been exposed to tritium, there is never again a moment of peace. Even H_2 and D_2 will now react, catalyzed by the residual tritium from the walls of the apparatus.

It is relatively easy to estimate the limiting equilibrium concentrations of the reacted hydrogens. At high temperatures, energy will be shared equally across the four molecules of Eq. (149). There will be 25% D_2 , 50% DT, and 25% T_2 . Room temperature D-T equilibrium is close to this. At 0 K, however, the pair D_2 and T_2 has a lower molecular vibrational zero point energy than does

DT by 170 J/mole.* All of the molecules turn into D_2 and T_2 at 0 K. The 0 K energy difference is larger for the more dissimilar isotopes: 656 J/mole for H-D and 1458 J/mole for H-T.

At some given temperature, the equilibrium may be calculated from the statistical mechanical partition functions.^{189,228,229} For D_2 -DT- T_2 (isotopes 4, 5, and 6), the equilibrium constant, K_{456} , for the reaction of perfect gases is

$$K_{456} = \frac{(P_5)^2}{P_4 \cdot P_6}, \quad (150)$$

where P_i is the partial pressure of the i^{th} isotope. Table 22 offers the set of calculated equilibrium constants. Not every point is directly calculated in the 4 to 30 K range. Instead, least-squares-fitted equations are used to interpolate within given temperature ranges. For D_2 -DT- T_2 ,

$$K_{456} (4 - 15 \text{ K}) \approx 5.924 \exp \left(-\frac{168.3}{RT} \right) \quad (151)$$

and

$$K_{456} (15 - 30 \text{ K}) \approx 2.995 \exp \left(-\frac{89.96}{RT} \right) \quad (152)$$

Eq. (151) fits to $\pm 2\%$ and Eq. (152) to $\pm 1\%$. At 15 K, where they join, K_{456} should be 1.46. For these isotopes, rotational states are excited at low temperatures, thus

*This is the zero point energy of vibration of individual molecules. It is not the collective zero point energy of the liquid or solid calculated in Section 14.

Table 22. Calculated perfect gas equilibrium constants for the three hydrogen self-exchange reactions. The numbers in parentheses are exponents.

Temp (K)	D_2 -DT- T_2 K_{456}	H_2 -HT- T_2 K_{136}	H_2 -HD- D_2 K_{124}
0	0	0	0
4.2	0.048	2(-17)	4.9(-8)
6	0.20	4(-12)	1.4(-5)
8	0.47	5(-9)	3.6(-4)
10	0.78	3.8(-7)	2.6(-3)
12	1.10	6.5(-6)	9.6(-3)
15	1.46	1.1(-4)	3.6(-2)
20	1.74	2.0(-3)	0.13
25	1.94	0.011	0.29
30	2.09	0.034	0.49
50	2.57	0.24	1.34
100	3.29	0.95	2.26
200	3.69	1.95	2.90
300	3.82	2.58	3.26
∞	4.00	4.00	4.00

requiring the two equations to describe K_{456} . Table 22 also includes the equilibrium constants for H_2 -HT- T_2 :

$$K_{136} (4-30 \text{ K}) \approx 10.22 \exp \left(-\frac{1423}{RT} \right) \quad (153)$$

and for H_2 -HD- D_2 :

$$K_{124} (4-30 \text{ K}) \approx 6.785 \exp \left(-\frac{654.3}{RT} \right) \quad (154)$$

Eq. (154) fits to $\pm 3\%$ but Eq. (153) only to $\pm 35\%$. The H_2 -HT- T_2 system is extremely sensitive to temperature, and K_{136} runs over many orders of magnitude before reaching 4 K.

Once armed with equilibrium constants, I next calculate the amounts of isotopes. For the reaction of Eq. (149), I consider n_4 moles of D_2 reacting with n_6 moles of T_2 . The equilibrium mole fractions are²³⁰

$$f_4 = \frac{n_4 - \Sigma}{n_4 + n_6}, \quad (155)$$

$$f_5 = \frac{2\Sigma}{n_4 + n_6}, \quad (156)$$

and

$$f_6 = \frac{n_6 - \Sigma}{n_4 + n_6}, \quad (157)$$

where

$$\Sigma = \frac{(n_4 + n_6) - \sqrt{(n_4 - n_6)^2 + \frac{16n_4 n_6}{K_{456}}}}{2 \left[1 - \frac{4}{K_{456}} \right]} \quad (158)$$

In Table 23, I list the percents of the various equilibrated isotopes given an initial 50-50 mix of two pure hydrogens. However, an actual D-T mix always contains 1 to 3% H so the sample is really a mixture of all six isotopes. To treat all the isotopes, one must solve sets of Eqs. (155) to (158). First I solve for the most abundant trio of D_2 -DT- T_2 . If there is more D than T, I next solve the H_2 -HD- D_2 set using the D_2 concentration from the first step. I then use the calculated H_2 and T_2 concentrations to calculate H_2 -HT- T_2 , I may reiterate by rerunning the D_2 -DT- T_2 reaction using $(D_2 + DT/2)$ for D and $(T_2 + DT/2)$ for T. This is different from the first cycle in that the D and T tied up with H are excluded. Two iterations are usually sufficient for good accuracy. Three would be needed for all six isotopes in about equal abundance.

All experimental checks on whether a mixture really reaches the calculated equilibrium have been made in the gas phase by mass spectrometer. D-T mixtures in our laboratory with no more than a few tenths of a percent of air, methane, or He^3 equilibrate as expected if

Table 23. Calculated equilibrium amounts of isotopes for initial 50-50 atomic mixes. These are derived from the perfect gas equilibrium constants. D_2 -DT- T_2 changes the least at cryogenic temperatures; H_2 -HT- T_2 the most.

Temp (K)	$D_2 + T_2 \rightleftharpoons 2DT$		$H_2 + T_2 \rightleftharpoons 2HT$		$H_2 + D_2 \rightleftharpoons 2HD$	
	$D_2 = T_2$	DT	$H_2 = T_2$	HT	$H_2 = D_2$	HD
0	50.0	0	50.0	0	50.0	0
4.2	45.1	9.9	50.0	0	50.0	0
6	40.8	18.4	50.0	0	49.9	0.2
8	37.2	25.6	50.0	0	49.5	0.9
10	34.7	30.7	50.0	0	48.8	2.5
12	32.8	34.4	49.9	0.1	47.7	4.7
15	31.2	37.7	49.7	0.5	45.7	8.6
20	30.1	39.8	48.9	2.2	42.3	15.4
25	29.5	41.1	47.5	5.0	39.4	21.3
30	29.0	41.9	45.8	8.4	37.0	26.0
50	27.8	44.5	40.2	19.7	31.7	36.7
100	26.2	47.6	33.6	32.8	28.5	42.9
200	25.5	49.0	29.4	41.1	27.0	46.0
300	25.3	49.4	27.7	44.5	26.3	47.4
∞	25.0	50.0	25.0	50.0	25.0	50.0

left overnight at room temperature. So do irradiated H_2 - D_2 mixtures previously cleaned by passage through palladium.²³¹ H_2 - T_2 mixtures equilibrate at 192 and 299 K only if given the palladium treatment. At 76.7 K, not even this is enough, as shown by the assortment of experimental equilibria displayed in Fig. 22. The calculated equilibrium constant at 77 K is 0.63, which seems to be the probable limit at low pressures and low tritium concentration. The temperature of the palladium diffuser was 673 K, where the equilibrium constant is 3.5.¹⁸⁸ It appears that, for some reason, the H-T mixture never equilibrated at the higher pressures, despite two to three weeks of waiting. True equilibration of H-T can be brought about, however, with an iron-alumina catalyst.²³²

Other inhibiting behavior has been seen in H_2 - D_2 mixtures irradiated with alpha particles at room temperature and at 13 to 40 kPa (100 to 300 Torr). Here, HD formation is prevented by the presence of rare gases. Their poisoning efficiency increases with molecular weight, so helium must be present in 20% quantity to

cause an effect; whereas a trace of xenon is enough to do the same.^{233,234} This behavior illustrates the accepted mechanism of the radiation-induced reaction. The thermally-activated, uncatalyzed H_2 - D_2 reaction proceeds by the leisurely formation of atomic hydrogen.²³⁵ This is to be expected, as atomic hydrogen is the easiest species to make, requiring 0.43 MJ/mole (4.5 eV) compared with three to four times that for ion formation.²³⁶ Atomic hydrogen is not energetic enough, however, to attack the rare gases, but the ions are. Xenon is the most effective poison because it has the lowest ionization potential of the common rare earths. The radiation, therefore, breaks the molecules into ions, which then react to exchange the isotopes:

This reaction may continue many times in a chain sequence before a positive ion meets a negative one and is neutralized.

FIG. 22. Measured equilibria for H_2 -hydrogen tritide (HT)- T_2 gas at 76.7 K. The samples probably start at the 673-K equilibrium of the palladium diffuser. The higher observed values may be caused by non-perfect gas effects. The samples were stored two to three weeks in Pyrex bulbs before these measurements were taken.²³² The numbers are pressures in MPa.

There are two recently measured equilibrium constants in the low pressure regime at 4.2 K. These are $(1.5 \pm 0.2) \times 10^{-2}$ for D-T and $(2.5 \pm 0.5) \times 10^{-2}$ for H-T.³⁴ The corresponding calculated values from Table 23 are 0.048 and 2×10^{-17} . It is difficult, indeed, to confirm a true equilibrium constant under high-vacuum conditions. One may easily imagine unusual impurity effects as well in such dilute gases.

Little work has been done on reaction rates. In the gas phase, the mass spectrometer is the universal instrument for study. Six good H₂-T₂ runs exist at room temperature in Pyrex bulbs.²³⁷ The increase in the mole fraction of the HT product, f_3 , follows the equation

$$1 - \frac{f_3(t)}{f_3(\text{final})} = \exp\left(-\frac{t}{\tau}\right), \quad (160)$$

where $f_3(t)$ is the HT concentration at time t , $f_3(\text{final})$ the concentration after a long time, and τ the time constant. The initial concentration of HT is zero. It is surprising to find a first-order rate equation, when the overall reaction [Eq. (149)] is bimolecular. The reaction rate instead depends on one step of the overall process, quite possibly the chain reaction sequence [Eq. (159)]. I have also observed the exponential rate behavior in D-T and H-T mixtures.^{238,239}

The time constants for the six H₂-T₂ runs in glass²³⁷ decrease with increasing total pressure and increasing

initial tritium pressure. At a total pressure of 7.8 kPa (59 Torr), τ is 1180 min; at 53 kPa (400 Torr), τ is 375 min. These points, however, are not good enough to establish definite behavior. The researchers felt that τ should be proportional to the total pressure (although it better fits the square root) and the square root of the tritium atom concentration. No convincing theory based on a mechanism has yet appeared.

Researchers at our laboratory have recently measured some reaction rates at room temperature in stainless-steel vessels. For D₂-T₂ at 13 to 22 kPa (100 to 170 Torr) total pressure, the time constants are 35 to 70 min. For H₂-T₂, the time constants are 75 to 150 min.^{238,239} Note that these reactions are an order of magnitude faster than the first H₂-T₂ set. This probably reflects the difference between the relatively active stainless steel and the less catalytic glass walls of the reaction vessels. These reactions, then, are heterogeneous, with the wall materials, dimensions, and history of treatment all being important.

The only gaseous rate studies below room temperature are at 77 K in Pyrex bulbs.²³² The rate at 77 K is about eight times slower than at room temperature.²³⁷

The only liquid phase rate measurement is our 18 h half-time for D₂-T₂ at 21 K as measured by infrared absorption (Section 36).¹¹ This lengthy time agrees with the views of distillation researchers, who consider DT to be stable during its five-min passage through the column. They, in fact, heat the D-T mixture to room temperature to catalyze the exchange reaction.²⁴⁰

VII. ROTATIONAL EFFECTS

32. Rotational Energy Level Populations

In Part III, I calculated the various translational energies that are, in general, the more accessible ones in a hydrogen sample. All the while, I have kept an eye on the lurking rotational energies, whose effects are usually just enough to force a constant inventory. It is time now to quantify the description of the rotational energy levels.

The rotational levels are labeled with the quantum numbers, J , equal to 0, 1, 2, 3, . . . The ground state ($J=0$) has a rotational energy of zero: this is where most hydrogen molecules reside below 30 K. The first excited state ($J=1$) is the other energy level of interest at cryogenic temperatures. The $J=2$ level is very slightly populated for T_2 and DT at 30 K. The rotational energy of an arbitrary level J at low temperatures, for a perfect gas, is²⁴¹

$$E(J) = hcN_0 \left\{ \left(B_e - \frac{\alpha_e}{2} \right) J(J+1) - \left(D_e + \frac{\beta_e}{2} \right) J^2(J+1)^2 \right\}, \quad (161)$$

where B_e , α_e , D_e , and β_e are rotational constants, different for each isotope. Table 24 lists these constants for the hydrogens, with the corresponding values of $E(J=1)$ and $E(J=2)$. Hunt has smoothed the most recent high resolution data²⁴²⁻²⁴⁵ by the isotope rule²⁴⁶ to provide the most accurate and self-consistent table to date.¹¹ The constants are in the spectroscopically traditional cm^{-1} but the energies are in J/mole. Equation (161) is simplified by consideration of only the ground molecular vibrational state ($v=0$), which is by far the dominant one below room temperature.

Recall that DT, HT, and HD are expected to quickly equilibrate at a given temperature. Their partition functions are simple, as they include only the rotational levels. The fractional population in the J^{th} state of perfect gas DT, $c_5(J)$, is

$$c_5(J) = \frac{(2J+1) \exp \left[-\frac{E(J)}{RT} \right]}{\sum_{J=0}^{\infty} (2J+1) \exp \left[-\frac{E(J)}{RT} \right]}. \quad (162)$$

The numerator describes the number of molecules in the J^{th} level and the denominator the total number in all states from $J=0$ to ∞ . The sum on the bottom is the rotational partition function, Q_R . The $J=0$ term equals one no matter what the temperature. Q_R , then, is not normalized to one but will be larger, and the value will vary with temperature.

Recall from Section 2 that T_2 , D_2 , and H_2 will quickly de-excite upon cooling only within even and odd- J states. The $J=1$ state will metastably hold its energy until forced to give it up by a catalyst. This new behavior is reflected in the partition functions, which now contain locked combinations of rotational and nuclear spin states. The H and T nuclei have identical nuclear-spin quantum numbers of $1/2$, with their partition functions similar in appearance. The D nucleus has a nuclear spin of 1, with the resulting partition function unique to this isotope.

First consider T_2 and H_2 . The molecular nuclear-spin quantum number, I , will be the sums of the atomic ones, i.e., zero and 1. The magnetic field of the electrons splits these into $2I+1$ substates, one for the first and three for the second. The first is associated with the even- J rotational levels and the second with the odd- J .

Table 24. Self-consistent set of spectroscopic constants for the hydrogen isotopes. ω_e through β_e are in cm^{-1} ; $E(1)$ and $E(2)$ are in J/mole. The numbers in parentheses are exponents.

	H_2	HD	HT(est)	D_2	DT(est)	T_2 (smoothed)
ω_e	4401.213	3811.924	3594.46	3112.81	2842.30	2543.20
$\omega_e X_e$	121.336	90.711	80.45	59.66	48.96	37.74
B_e	60.853	45.638	40.579	30.442	25.376	20.319
α_e	3.0622	1.9500	1.634	1.0623	0.808	0.5785
D_e	4.666(-2)	2.6341(-2)	2.072(-2)	1.164(-2)	0.805(-2)	0.514(-2)
β_e	1.82(-3)	0.857(-3)	0.64(-3)	0.31(-3)	0.198(-3)	0.114(-3)
$E(1)$	1417.0	1067.3	950.33	715.08	597.09	478.98
$E(2)$	4237.5	3194.3	2845.0	2141.8	1788.9	1435.4

There are, thus, three times as many odd-J levels as one would have previously expected. For an odd-J level, the fraction of molecules in T_2 is

$$c_6(\text{odd} - J)$$

$$= \frac{3(2J+1) \exp \left[-\frac{E(J)}{RT} \right]}{\sum_{\text{even}-J} (2J+1) \exp \left[-\frac{E(J)}{RT} \right] + 3 \sum_{\text{odd}-J} (2J+1) \exp \left[-\frac{E(J)}{RT} \right]} \quad (163)$$

For an even-J state, take the three out of the numerator.

Each D nucleus, however, has a spin of 1. In the magnetically polarized diatomic molecule, the two spins combine to yield total spins of 0, 1, and 2 with 1, 3, and 5 magnetic substates each. The two even nuclear-spin states, 0 and 2, with a total of six substates, are associated with the even-J rotational levels. The nuclear-spin 1 state, with three magnetic substates, is associated with the odd-J rotational levels. So the even-J rotational states are weighted twice as much as the odd-J in the partition function. For an even-J level, the equilibrium population is

$$c_4(\text{even} - J)$$

$$= \frac{6(2J+1) \exp \left[-\frac{E(J)}{RT} \right]}{6 \sum_{\text{even}-J} (2J+1) \exp \left[-\frac{E(J)}{RT} \right] + 3 \sum_{\text{odd}-J} (2J+1) \exp \left[-\frac{E(J)}{RT} \right]} \quad (164)$$

D_2 is the only isotope for which the $J=0$ term of the partition function is not one — it is six.

Table 25 combines these partition functions with the spectroscopic constants of Table 24 to produce the equilibrium percents of $J=0$ and $J=1$ populations from 4.2 to 30 K. For T_2 at 30 K, one finds only 0.0068 of molecules in the $J=2$ state, which shows that one may generally neglect the second excited state.

Equations (163) and (164) represent equilibrium populations, which one is not apt to have if one just changed the temperature without a catalyst. One must now consider the metastable states, with the most likely starting point of room temperature. At 300 K, the molecules are strewn over about ten rotational levels. But it is the percent of even- and odd-J levels that I want to know. At 300 K, the fractions of even-J states are for H_2 , D_2 , and T_2 : 0.2507, 0.6667, and 0.2508.^{247,*} Upon cooling to low temperatures, almost all even-J molecules will fall into the $J=0$ state (a few to $J=2$). A large quantity of energy will be released but the percent of even-J molecules will remain the same. At 300 K, the fractions of odd-J states are for H_2 , D_2 , and T_2 : 0.7493, 0.3333, and 0.7492, and these will fall exclusively into the $J=1$ state at low temperatures. Consider nT_2 at 30 K as an example. It will contain 0.2508 $J=0$ and $J=2$ T_2 and 0.7492 $J=1$ T_2 . From Table 25, 30-K eT_2 has 0.4283 $J=0$ and 0.0068 $J=2$. This same proportion is now spread across the 0.2508 brought down from room temperature. One has, then, 0.2469 $J=0$ T_2 and 0.0039 $J=2$ T_2 . The 0.7492 $J=1$ T_2 will gradually be catalyzed by the beta particle to 0.5649 with the evolution of more heat.

*These are calculated with slightly older constants than those of Table 25.

Table 25. Fractional equilibrium rotational populations for the ground ($J=0$) and first excited state ($J=1$). The constants of Table 25 have been used in this calculation. The numbers in parentheses are exponents.

J	Temp (K)	H_2	HD	HT	D_2	DT	T_2
0	4.2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
	10	1.0000	1.0000	1.0000	0.9997	0.9977	0.9724
	15	0.9999	0.9994	0.9985	0.9952	0.9756	0.8380
	20	0.9982	0.9951	0.9902	0.9800 ^a	0.9235 ^a	0.6641 ^a
	25	0.9902	0.9826	0.9699	0.9539 ^a	0.8543 ^a	0.5254 ^a
	30	0.9702	0.9601	0.9376 ^a	0.9206 ^a	0.7827 ^a	0.4283 ^a
1	4.2	2.1(-17)	1.6(-13)	4.6(-12)	1.9(-9)	1.1(-7)	9.9(-6)
	10	3.6(-7)	8.0(-6)	3.2(-5)	0.0003	0.0023	0.0276
	15	0.0001	0.0006	0.0015	0.0048	0.0244	0.1620
	20	0.0018	0.0049	0.0098	0.0199 ^a	0.0764 ^a	0.3353 ^a
	25	0.0098	0.0174	0.0301	0.0459 ^a	0.1449 ^a	0.4720 ^a
	30	0.0298	0.0399	0.0623 ^a	0.0785 ^a	0.2143 ^a	0.5649 ^a

^aThe sum of the two populations is less than 1. The difference is the $J=2$ population, which amounts to only 0.0068 for 30-K T_2 and less for the others.

At 77.4 K, the equilibrium populations are even-J H_2 —0.5033, odd-J H_2 —0.4967; even-J D_2 —0.7749, odd-J D_2 —0.2251; and even-J T_2 —0.4095, odd-J T_2 —0.5905.²⁴⁷

Early heat capacity work showed that H_2 really does occupy the rotational states predicted by the partition function.²⁴⁸ More recent work has been done with H_2 , D_2 , and T_2 equilibrated over a wide temperature range with a cerium oxide catalyst. The H_2 , and D_2 are well behaved; the T_2 was up to 10% higher in odd-J composition than expected. It is possible that imperfect calibration was the cause.²⁴⁷

33. Rotational Energies and Heat Capacities

The perfect gas rotational energy, E_R , is given by

$$E_R = \sum_J c(J)E(J) \quad (165)$$

where $c(J)$ is the fractional population of the J^{th} level and $E(J)$ its energy. I evaluated both in the previous section. The population may be either an equilibrium or a metastable one.

The spectroscopic constants of Table 24 have been used to calculate the rotational energies listed in Table 26. These, plus the $(3/2)RT$ translational energy, give us the entire energy picture, as based on the partition-function model. One should keep track of the two energies separately because of the metastable rotational behavior. For example, at 300 K, nT_2 possesses

2427 J/mole rotational energy and 3741 J/mole translational energy. Quickly cooling to 10 K gives us 358.9 J/mole rotational energy and 125 J/mole translational energy. The rotational energy then decays to an equilibrium value of 13.2 J/mole. I assume in Table 26 that HD, HT, and DT do not remain long in metastable rotational states.

Rotational heat capacity is the derivative of E_R with respect to temperature. It is tedious to carry out the actual differentiations, so I shall use the functions

$$Q'_R = \sum_J g(J) \left[\frac{E(J)}{RT} \right] \exp \left[- \frac{E(J)}{RT} \right] \quad (166)$$

and

$$Q''_R = \sum_J g(J) \left[\frac{E(J)}{RT} \right]^2 \exp \left[- \frac{E(J)}{RT} \right] \quad (167)$$

where g_J includes $(2J+1)$ times whatever weighting factor belongs to the j^{th} state. Q'_R and Q''_R are not true derivatives of the partition function Q_R . They are simply defined to make the calculation easier. The perfect gas rotational heat capacity, C_R , is

$$C_R = R \left\{ \frac{Q_R Q''_R - (Q'_R)^2}{Q_R^2} \right\} \quad (168)$$

where R on the right side is the gas constant.²⁴⁹ For DT, HT, and HD, I use the full partition function, as all

Table 26. Perfect gas rotational energies for equilibrium and normal forms at various temperatures. The 300-K normal energy contains both rotational and molecular vibrational energies. In going from one state to another, the energies may be subtracted for the net heat in or out of the experiment. All 4.2-K equilibrium values are zero; the 4.2-K normal values for H_2 , D_2 , and T_2 are the same as those at 10 K.

		Rotational energy, E_R (J/mole)					
	Temp (K)	H_2	HD	HT	D_2	DT	T_2
Equilibrium forms	10	0.0	0.0	0.0	0.2	1.4	13.2
	15	0.1	0.6	1.4	3.4	14.6	77.6
	20	2.6	5.2	9.3	14.4	45.8	161.5
	25	13.9	18.6	28.6	33.2	87.9	229.8
	30	42.2	42.6	59.5	58.1	133.3	280.3
Normal	10	1061.8	0.0	0.0	238.3	1.4	358.9
	15	1061.8	0.6	1.4	238.3	14.6	358.9
	20	1061.8	5.2	9.3	238.5	45.8	360.2
	25	1061.8	18.6	28.6	238.7	87.9	366.0
	30	1061.8	42.6	59.5	240.4	133.3	381.3
Normal	300	2285	2326	2348	2388	2407	2427

transitions are allowed. For T_2 , D_2 , and H_2 , the $\Delta J = \pm 1$ transitions are not allowed. The only heat capacity below 30 K will come from $J=0$ to 2 transitions. Below 30 K, I have the equilibrium equations

$$C_R(D_2) \approx R \cdot \frac{180 \left[\frac{E(2)}{RT} \right]^2 \exp \left[-\frac{E(2)}{RT} \right]}{\left\{ 6 + 30 \exp \left[-\frac{E(2)}{RT} \right] \right\}^2}, \quad (169)$$

$C_R(DT)$

$$= R \cdot \frac{\left\{ 3 \left[\frac{E(1)}{RT} \right]^2 \exp \left[-\frac{E(1)}{RT} \right] + 5 \left[\frac{E(2)}{RT} \right]^2 \exp \left[-\frac{E(2)}{RT} \right] \right.}{\left. + 15 \left[\frac{E(2) - E(1)}{RT} \right]^2 \exp \left[-\frac{E(1) + E(2)}{RT} \right] \right\}}{\left\{ 1 + 3 \exp \left[-\frac{E(1)}{RT} \right] + 5 \exp \left[-\frac{E(2)}{RT} \right] \right\}^2}, \quad (170)$$

and

$$C_R(T_2) \approx R \cdot \frac{5 \left[\frac{E(2)}{RT} \right]^2 \exp \left[-\frac{E(2)}{RT} \right]}{\left\{ 1 + 5 \exp \left[-\frac{E(2)}{RT} \right] \right\}^2}. \quad (171)$$

I used the above equations with the Table 24 spectroscopic constants to derive the rotational heat capacities of Table 27. All the values are for equilibrium amounts. These may be easily modified for the normal species. For 30 K T_2 , I found in the last section that the fractions of $J=0$ molecules are 0.2469 for nT_2 and 0.4283 for eT_2 . Their ratio of 0.576 times the 4.2 J/mole-K value for eT_2 yields 2.4 J/mole-K for nT_2 . Table 27 includes the nD_2 and nT_2 values.

Table 27. Perfect gas rotational heat capacities of the hydrogen isotopes to 30 K. All 4.2-K values are zero, as are all H_2 values.

Temp (K)	Heat capacity, C_R (J/mole-K)						
	HD	HT	eD_2	nD_2	DT	eT_2	nT_2
10	0.0	0.0	0.0	0.0	1.0	0.0	0.0
15	0.4	0.7	0.0	0.0	4.5	0.1	0.0
20	1.7	2.6	0.0	0.0	7.7	0.6	0.2
25	3.7	5.1	0.1	0.1	8.9	2.0	1.0
30	5.8	7.1	0.6	0.4	9.1	4.2	2.4

34. Quadrupolar Energy and Heat Capacity

There is yet another heat capacity, which appears only in the solid at low temperatures. It arises from the $J=1$ hydrogen molecules, which possess molecular electric quadrupole moments. This interaction splits the $J=1$ levels into a set of closely spaced sublevels, whose population by thermal energy gives rise to the quadrupolar heat capacity, C_Q . C_Q will be a direct function of the $J=1$ population, $c(J)$, and it is, thus, another special aspect of rotational behavior. The shape of C_Q (ignoring a narrow peak at about 0.2 K) is a peak at about 1.7 K, which tails off slowly to higher temperatures. It is difficult to get good values for C_Q because one obtains it by subtraction of other quantities:

$$C_Q = C_s^t - C_s^t(J=0) - C_R, \quad (172)$$

where C_s^t is the total measured heat capacity for a given $c(1)$, $C_s^t(J=0)$ the crystal lattice heat capacity, and C_R the rotational heat capacity. A few nice curves for C_Q have been taken for low $J=1$ concentrations,²⁵⁰⁻²⁵² but the high-concentration data for H_2 ^{76,78} and D_2 ^{38,77,81,90,253} are less satisfactory. The H_2 data give good linear plots, but the D_2 points are quite scattered. I have empirically fitted the H_2 data, from 2 K up, to

$$C_Q \approx c(1)^{0.92} [4.20c(1)^{0.23} - 0.29T]. \quad (173)$$

This also fits the D_2 data within error and may be used for the other isotopes. Equation (173) really describes only the high temperature side of the C_Q peak. For nH_2 , with $c(1) = 0.75$ at 4 K, C_Q equals ~ 2 J/mole-K — not a large value.

The tail represented by Eq. (173) is not really supposed to be linear; it should fall as T^{-2} . This may be seen in the simplest derivation of C_Q , which employs a two-level Schottky model, with the levels separated by 4.5 K.²⁵⁴ The actual quadrupolar models are much more complicated, with four levels for two interacting $J=1$ molecules²⁵⁵ and eighteen for three.²⁵⁶

I now wish to integrate Eq. (173) to obtain the quadrupolar energy. Assume C_Q to be zero at 0 K and to rise in a straight line to the 1.7 K value of Eq. (173). Then let Eq. (173) drop to zero with increasing temperature. The quadrupolar energy, E_Q , is

$$E_Q \sim c(1)^{0.92} \left\{ c(1)^{0.23} (4.20T - 3.57) - 0.145T^2 + 2.47 \right\}. \quad (174)$$

For nH_2 [$c(1) = 0.75$], the E_Q value at 4 K is 10 J/mole; at 13.6 K, it is 20 J/mole. These energies and heat capacities, although small, should be considered for any careful thermodynamic analysis of the solid.

35. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a technique well suited to liquid and solid hydrogen. One places the sample in a large and homogeneous dc magnetic field. This field aligns a nucleus of quantum number I into the $2I + 1$ substates found as weighting functions in Section 32. A radio frequency transmitter then strikes the nuclei with a pulse of energy. The nuclei absorb the energy and leap to higher sublevels. When the pulse ends, the nuclei continue to ring at the same frequency. The ringing dies away with a relaxation time T_2 (not to be confused with tritium, T_2), which describes the loss of phase coherence between all the broadcasting nuclei. Another pulse sequence allows the measurement of the other relaxation time T_1 , which describes the loss of energy as the nuclear substates de-excite. In practice, it is easier to use electronics at a fixed frequency, ν_0 , and to vary the magnetic field, H_0 . One must be prepared, however, to compare the various frequencies used by different researchers.

The great benefit of NMR is that each isotope resonates at a different field value, H_0 , for a fixed frequency. The gyromagnetic ratio, γ , relates the field and the frequency according to²⁵⁷

$$H_0 = \frac{2\pi\nu_0}{\gamma} \quad (175)$$

The gyromagnetic ratios and H_0 values at 10 MHz are listed for H, D, T, and He^3 in Table 28.²⁵⁸ For relative NMR sensitivity, T, H, and He^3 (but not D) rank among

the best nuclei in the entire periodic table. However, their absolute sensitivity is not great, and ml-sized samples of liquid or solid are needed.

The height of the nuclear ringing, M , before the T_2 decay sets in is

$$M = \frac{N_s h^2}{6\pi kT} \gamma I(I+1) \nu_0 \quad (176)$$

where N_s is the number of nuclear spins, h is Planck's constant, and k is Boltzmann's constant.²⁵⁷ The time-zero signal height is directly proportional to the number of spins. For a constant number of spins, I shall use Eq. (176) to calculate the relative isotopic sensitivities. The nuclear spin quantum numbers for the individual H, D, T, and He^3 nuclei are 1/2, 1, 1/2, and 1/2.

Recall that the two nuclear spins of 1/2 each add up to 0 for even- J H_2 . These anti-parallel nuclei result in a total cancellation of any NMR signal. For odd- J H_2 , however, the total nuclear spin is 1, and the molecule acts like a single NMR-active unit. I shall take its relative sensitivity as 1. By comparison, note that atomic H has a sensitivity of only 0.375. In the HD or HT molecule, the H nucleus does not know of the presence of the other isotope's nucleus. It is equivalent to the atomic H case, as far as the NMR is concerned, and the relative sensitivity is 0.375. Tritium isotopes have the same behavior as those of hydrogen but have a higher sensitivity. He^3 has a spin of 1/2, and a sensitivity of 0.286 at constant frequency for the same number of spins. However, one T_2 molecule can produce two moles of He^3 atoms, so twice the signal will actually appear as the result of radioactive decay.

The D nucleus has a spin of 1, which for D_2 becomes one 0 state, three 1's, and five 2's. The 0 and 2

Table 28. Comparative nuclear magnetic-resonance data for H, D, T, and He^3 .

Nucleus looked at	Gyro-magnetic ratio, γ (MHz/T)	Magnetic field at 10 MHz (T)	Isotope	Quantum number		Relative sensitivity at constant frequency and spins
				Rotational, J	Total nuclear, I	
H	267.51	0.2349	H_2	Even	0	0.000
			H_2	Odd	1	1.000
			HD, HT	All	1/2	0.375
D	41.065	1.5301	D_2	Even	one 0 five 2	0.384
			D_2	Odd	1	0.154
			DT, HD	All	1	0.154
T	285.34	0.2202	DT, HT	All	1/2	0.400
			T_2	Even	0	0.000
			T_2	Odd	1	1.067
He^3	203.80	0.3083	He^3	None	1/2	0.286

states combine and are associated with the even- J rotational levels of D_2 . The lone $I=0$ state does not give an NMR signal, but the $I=2$ states do. The odd- J rotational states of D_2 are associated with the three $I=1$ states, and again an NMR signal appears. It is not so easy to use NMR to differentiate between the even- and odd- J populations of D_2 as it is for H_2 and T_2 .

I have noted that the height of the NMR ringing before decay is a good measure of concentration, providing standards can be made. Information is contained as well in the two relaxation times, although these relations are either empirical or extremely complex theoretically. I shall consider some of the relaxation data on cryogenic hydrogen.

H_2 gas has been studied at 20.4 K for densities, ρ , between 220 and 670 mole/m³. At a 30-MHz resonance frequency, the relaxation time for loss of energy, T_1 , has the form

$$T_1(H_2 - 20.4 \text{ K}) \approx 1.67 \times 10^{-6} [1 + 1.95c(1)] \rho \quad (177)$$

where $c(1)$ is the mole fraction of $J=1$ H_2 (all else is $J=0$).²⁵⁹ It seems surprising that T_1 increases with density and $c(1)$, because one might think that more collisions with other dipoles would cause energy to drain away faster. However, rapid motion, and even collision, serves to screen the view that one dipole has from another, and one obtains just the opposite result. A practical use for T_1 is that, once calibrated, it is a measure of gas density or pressure. The T_1 for H in HD gas has also been measured at 20.4 K. It is about 2 s, or a thousand times longer than in H_2 .²⁵⁹ This illustrates how well-insulated the nuclei are in HD, where the two nuclei do not interact to any large degree.

For saturated liquid H_2 from 14 to 21 K and $0.02 \leq c(1) \leq 0.73$, one has²⁶⁰

$$T_1(\text{liquid } H_2) \approx 10^{-3} c(1) [428 - 11.4 T] \quad (178)$$

This shows that T_1 is linear with T and $c(1)$ at least over small ranges. If I move on to lower $c(1)$ values, the T_1 behavior becomes quite complex, as shown by the far right section of Fig. 23.²⁶⁰⁻²⁶² T_1 is not only nonlinear with $c(1)$, but a reversal of its behavior with temperature occurs for almost pure $J=0$ H_2 . The internal agreement of the data is not good, but the use of the two frequencies at 15 and 30 MHz, however, is almost certainly not the cause. The relaxation time T_2 is said to be about 90% the value of T_1 .²⁶⁰ T_1 for liquid HD is about 50 s from 16.6 to 22 K.²⁶³

Relaxation times in the solid are the most complicated of all. One must be especially careful in noting the resonance frequency in the range 8 K to the triple point. This is because the molecular hopping frequency is comparable to the NMR frequency in this region and because the two interact. For example, there is a fifty-fold difference in isothermal T_1 values of solid H_2 taken at 5 and 30 MHz.²⁶⁴

T_1 for saturated hexagonal close-packed (hcp) solid H_2 is shown in the center section of Fig. 23 for 5.5 and 29 to 30 MHz.^{261,265} There is a discontinuity at the melting point and strange happenings just below. On the left side of Fig. 23 is the 4.7-MHz T_1 data for saturated hcp D_2 .²⁶⁶ One sees that it is much different — a thousand times as long. One reason is that the NMR can look at both $J=0$ and $J=1$ D_2 , and the $J=0$ molecules are expected to relax slowly. Another factor is the relative weakness of the D_2 nuclear magnetic moment. The molecular hopping affects T_1 approximately as γ^{-4} . For this reason alone, one expects T_1 for D_2 to be 2000 times as long as that for H_2 . One also expects long times for H in solid HD, and they are: 2 to 5 s at the triple point, 5 to 50 s at 10 K, and 70 to 5000 s at 4 K.²⁶³ To date, no NMR has been done on the tritiated isotopes of hydrogen. For the time T_1 , I expect T_2 to be similar to H_2 and DT to resemble HD. I cannot guess the possible effect of radiation in producing ions and free radicals that could lower T_1 . The complete unraveling of the D_2 -DT- T_2 mixture, as seen only through two signals — D and T — will be complicated.

In the gas phase, the relaxation time T_2 is expected to equal T_1 ,²⁶⁷ and it has been found to be within 20% for H_2 at 78 K.²⁶⁸ We have seen similar behavior in liquid H_2 .²⁶⁰ However, in the solid phase, T_2 shortens far below the values of T_1 . This is because the nuclear dipoles are "at rest" in the solid and can see the full force of their magnetic surroundings. These forces destroy the signal's phase coherence and leave a set of excited but disordered nuclei. In solid H_2 , from 11.5 K to the triple point, T_2 decreases exponentially with temperature, according to

$$T_2(\text{solid } H_2: 11.5 \text{ to } 14 \text{ K}) \approx \frac{3500}{c(1)} \exp \left[-\frac{200}{T} \right] \quad (179)$$

where $0.16 \leq c(1) \leq 0.75$.²⁶¹ In the solid, other $J=1$ molecules [by means of the $c(1)^{-1}$ term] are a destroying influence on phase coherence. The plunge of the time T_2 in Eq. (179) cannot go on for long, and at 4.2 K one finds decay times on the order of 10 to 50 μ s. The signals are now modulated by complex oscillations, as frozen-in nuclear dipoles see geometric patterns of neighboring forces.²⁶⁹

FIG. 23. Nuclear magnetic relaxation time, T_1 (for energy loss), for solid D_2 and H_2 and liquid H_2 . The Y-axis is the fraction of molecules in the $J=1$ state. The lines represent constant T_1 , which is labeled in seconds.

36. Collision-Induced Infrared Spectroscopy and Rotational Kinetics

A second promising technique for the study of liquid and solid hydrogen is collision-induced infrared spectroscopy. By itself, the hydrogen molecule cannot have an infrared spectrum because of the extreme symmetry of the molecule. Under the effect of neighboring hydrogen molecules, however, a weak spectrum appears—about 100 000 times weaker than the allowed lines of carbon dioxide (CO_2). The intensity of these transitions increases as the square of the density, because its very existence depends on how closely molecules approach each other.^{100,270-272}

The forces giving rise to the spectra are caused by two molecular electric moments: that of the transient electric dipole (spherically symmetric) and of the permanent electric quadrupole (asymmetric). A molecule sees these moments only fleetingly as the neighboring

molecules move by. The resulting spectral lines are wide enough to be easily seen with low resolution infrared spectroscopy. The induced transitions are not allowed and cannot have rotational quantum number J changes of $+1$ (except for the weak electric dipole transitions in the heteronuclear isotopes). Instead, the induced transitions change J by either 0 or $+2$. There are no negative changes in J at cryogenic temperatures because of the low thermal energy of the sample. These rotational changes are combined with the basic vibrational transition from the ground state (quantum number $v = 0$) to the first excited state ($v = 1$). The lines are thus seen in the near infrared portion of the spectrum.

The infrared lines are labeled by letter: Q for a $\Delta J=0$ transition and S for $\Delta J=+2$. The subscript number following the letter indicates the end-point vibrational state. Then comes a number in parentheses that indicates the starting rotational state. The transition

$$Q_1(1)T_2 + S_0(1)DT \quad ,$$

for example, means a simultaneous transition involving two molecules. The T_2 molecule undergoes a $v=0 \rightarrow 1$, $J=1 \rightarrow 1$ transition and the DT molecule a $v=0 \rightarrow 0$, $J=1 \rightarrow 3$. The $Q_1(0)$ and $Q_1(1)$ lines usually are so close together that they merge and are called Q_Q . The Q_R peak is the Q_Q peak with the addition of lattice vibrational energy.

I have recently taken the first spectrum of the fusion mixture, D_2 -DT- T_2 . It is shown in Fig. 24, and the peak line frequencies in cm^{-1} are in Table 29.

Infrared spectroscopy should be quite useful in measuring kinetic rates of chemical and rotational reactions once the various lines have been calibrated. I have used crude area plots to estimate some half-times for the conversion of $J=1$ to $J=0$ T_2 : 25 h in the 21 K liquid, about the same in the 20 K solid, but only 1 h at 4 to 5 K.¹¹ This fast rate at low temperatures is surprising, but it agrees with two other experiments.^{247,273} The cause of this rapid rate is quite possibly catalysis by about 20 ppm of atomic tritium, which is present from the radiation damage (Section 40).¹¹ The inhomogeneous magnetic field of the free electron should be effective in catalyzing the reaction by decoupling the two tritium nuclei.²⁷⁴ Possibly the atomic tritium could then wander interstitially through the crystal lattice even at 4 K. A second possible mechanism is a chain reaction between interstitial atomic tritium and a molecule, with a new atom created in the adjoining interstitial compartment. Finally, the $J=1$ states may move throughout the crystal by quantum diffusion, which does not require actual molecular motion.²⁷⁵ In this possible mechanism, the catalyst could sit motionless in the crystal and wait for the $J=1$ excitation to come to it.

Table 29. Measured peak values of the collision-induced infrared spectrum of the mixture D_2 -DT- T_2 . Samples are liquid and solid.

Transition	Frequency (cm^{-1})
T_2 Q_Q	2458
T_2 Q_R	2518
$Q_1(0,1) T_2 + S_0(0) T_2$	2576
$Q_1(0,1) T_2 + S_0(0) DT$	2607
$Q_1(0,1) T_2 + S_0(0) D_2$	2636
$Q_1(0,1) T_2 + S_0(1) T_2$	2657
$S_1(0) T_2 + S_0(0) T_2$	2694
$Q_1(0,1) T_2 + S_0(1) DT$	2708 ^a
DT Q_Q	2736
$Q_1(0,1) T_2 + S_0(1) D_2$	2756
DT Q_R	2802
$Q_1(0,1) DT + S_0(0) T_2$	2855
$Q_1(0,1) DT + S_0(0) DT$	2887
$Q_1(0,1) DT + S_0(0) D_2$	2916
$Q_1(0,1) DT + S_0(1) T_2$	2937
D_2 Q_Q^a	2986
$Q_1(0,1) DT + S_0(1) DT$	
$Q_1(0,1) DT + S_0(1) D_2$	
D_2 Q_R	3056
$Q_1(0,1) D_2 + S_0(0) T_2$	3103
$Q_1(0,1) D_2 + S_0(0) DT$	3135
$Q_1(0,1) D_2 + S_0(0) D_2$	3164
$Q_1(0,1) D_2 + S_0(1) T_2$	3186
$Q_1(0,1) D_2 + S_0(1) DT$	3230
$Q_1(0,1) D_2 + S_0(1) D_2$	3283
$S_1(0) D_2 + S_0(0) D_2$	3334

^aTransitions are referenced to 2986- cm^{-1} Q_Q line of D_2 . The line expected at 2708 cm^{-1} was not seen.

FIG. 24. Collision-induced infrared spectrum of solid 50% D-50% T (25% D_2 -50% DT-25% T_2) at 18.3 K. XY refers to the second isotope in a double transition.

VIII. EFFECTS OF TRITIUM RADIOACTIVITY

37. Tritium Radioactivity

The final part of this report concerns properties caused totally by the radioactivity of the tritium.* Tritium decays according to the reaction

where β^- is the beta particle and $\bar{\nu}$ an antineutrino. The He^3 is not left in an excited nuclear state and there are no gamma rays. The electron, in penetrating the surrounding material, produces x-rays and secondary elections. The half-life of the decay is 12.346 y.²⁷⁶ This corresponds to the fraction 1.780×10^{-9} of T nuclei decaying each second. This is also 1.072×10^{15} Bq/mole T (disintegrations/s-mole T).

The He^3 daughter nucleus carries off only about 5.3×10^{-19} J/decay (3.3 eV/decay), while the beta particle and neutrino carry off 2.970×10^{-15} J/decay (18.54 keV/decay).²⁷⁷ Any combination of shared energy is possible between the latter two particles. The neutrino barely interacts with matter, and it carries its energy out of the experiment. The beta particle, thus, has a kinetic energy distribution between zero and 18.54 keV. It is the particle that causes damage.

The mean energy of the tritium beta particle is 9.11×10^{-16} J/decay (5.69 keV/decay). The amount of heat obtained from stopping these electrons is considerable: 0.977 W/mole T.^{278,279} This heat output continues unabated as one cools to ever lower temperatures where materials have smaller heat capacities. Too large a tritiated sample will bring a cooling cryostat to a standstill. Small samples and exceptional care are required to minimize thermal gradients in a cryogenic sample so pressure and temperature measurements are significant. It is easy to imagine a sample of tritium frozen on the bottom and boiling on the top.

Figure 25^{277,280,281} shows the energy spectrum of the tritium beta particle. A straight line is used to extrapolate to zero energy. The actual measured spectrum becomes uncertain below 2×10^{-17} J/T-decay (100 eV).²⁸⁰ The spectrum peaks at about 4.3×10^{-16} J/decay (2.7 keV/decay), just below the mean energy (5.69 keV/decay). The spectrum tails off gradually so that the end-point energy is difficult to determine.²⁷⁷ For work that is not too precise, I chop the spectrum into nine

intervals, each 2-keV wide. The fractional area in each interval is, from left to right in Fig. 25 (0 to 18 keV): 0.193, 0.203, 0.186, 0.153, 0.116, 0.079, 0.045, 0.020, and 0.005. These may be used for quick integrations.

38. Electron and X-Ray Ranges in Hydrogen

Often it is desirable to estimate the range of the beta particle in the hydrogen sample. When a large number of electrons passes through a sample of thickness ℓ , the absorbed and incident energies, E' , are related by²⁸²

$$E' \text{ (absorbed)} = E' \text{ (incident)} \left[1 - \exp \left(-\frac{\ell}{\ell_\beta} \right) \right] \quad , \quad (181)$$

where ℓ_β is a penetration constant in meters that is characteristic of the sample. The constant ℓ_β may be related to the range, R_β , in kg/m², by

$$\ell_\beta = \frac{1}{\rho} \left(\frac{R_\beta}{M} \right) \quad , \quad (182)$$

where ρ is the density (mole/m³) of any phase and M the molecular weight. The range is usually listed for a given material because it is independent of density.*

Electrons in the 20-keV range lose their energy exclusively to other electrons. There is no difference in absorption between isotopes except that the electron density differs slightly with the overall density. Data on absorption in H_2 may be applied directly to the other hydrogens.

The range of tritium beta particles in H_2 gas at 298 K has been measured, and it is²⁸³

$$\frac{R_\beta}{M} \text{ (tritium betas)} = 0.226 \text{ mole/m}^2 \quad . \quad (183)$$

*Tritium is made by neutron capture on lithium-6 (Li^6) with subsequent fission. It may be purchased from the Isotopes Sales Group, Oak Ridge National Laboratory, Oak Ridge, TN 37830. Tritium costs several thousand dollars a gram. In contrast, deuterium costs about 20¢/gram from commercial sources.

*The inverse of ℓ_β is called the absorption coefficient. The inverse of R_β is called the mass absorption coefficient.

FIG. 25. Energy spectrum of the tritium beta particle. The mean and end-point energies are 5.69 and 18.54 keV. The antineutrino carries off the rest of the energy. The spectrum has been divided into nine 2-keV-wide channels. The fractional area of each is listed.

The molecular weight has been left indefinite, and Eq. (183) may be used for any isotope at any temperature. Another useful reference is an extensive code for monoenergetic electrons from 10 keV up in all the elements. For electrons in the range of 10 to 20 keV, one has²⁸⁴

$$\frac{R_{\beta}}{M} = 8.143 \times 10^{-3} E' (\text{keV})^{1.814} \text{ mole/m}^2. \quad (184)$$

One may extrapolate Eq. (184) down as far as 2 keV with reasonable accuracy. The use of the mean beta-particle energy of 5.69 keV in Eq. (184) yields 0.191 mole/m² — not too far from the result of Eq. (183). I cannot accurately integrate over the beta particle spectrum because Eq. (184) does not work at low energies.

The constant ℓ_R is the sample thickness for which 63.2% of the incident energy is absorbed. In the distance, $5\ell_R$, this increases to 99.3%. The mean beta particle is expected to have a $5\ell_R$ distance of 20 to 30 μm in liquid and solid D-T. In the saturated vapor, this

distance is about 1 mm at 30 K, 10 mm at 20 K, and 40 m at 10 K. The vapor over the solid is so diffuse that virtually every beta particle will strike the container walls.

These beta particles knock other electrons out of their atoms. The remaining electrons then cascade to the lower energy levels, emitting x-rays as they go. These x-rays are much more penetrating in hydrogen than are the beta particles. One may again use Eqs. (181) and (182), although with new constants ℓ_x and R_x . Values of R_x/M for hydrogen are in Table 30.^{285,*} If you use the 5.69-keV mean beta-particle energy, you obtain an R_x/M value of 1.2×10^4 mole/m². The nine-channel beta spectrum gives us, for hydrogen:

$$\frac{R_x}{M} (\text{tritium x-rays}) \approx 2.8 \times 10^3 \text{ mole/m}^2 \quad (185)$$

Fully 80% of this value comes from the first 0- to 2-keV channel, showing that my description is crude. The expected $5\ell_x$ distances in hydrogen are about 300 mm in the liquid and solid and many meters in the saturated vapor.

For comparison with the penetration constants for hydrogen, the corresponding ones at the mean tritium beta energy in iron, copper, and gold are: ℓ_{β} — 0.21, 0.20, and 0.17 μm ; ℓ_x — 0.65, 0.42, and 0.35 μm .^{284,285} The most troublesome x-rays are those just below the K-edges, i.e., 7 keV in iron and 9 keV in copper.

*The inverse of R_x is called the mass absorption coefficient or the x-ray cross section.

Table 30. X-ray ranges in hydrogen. Although calculated for H₂, they may be used for the other isotopes.

Energy (keV)	Range, R_x/M (10^3 mole/m ²)	Energy (keV)	Range, R_x/M (10^3 mole/m ²)
1	0.678	8	12.7
1.5	2.29	9	12.8
2	4.67	10	12.9
3	8.85	11	12.9
4	10.9	13	13.1
5	11.8	15	13.2
6	12.3	17	13.3
7	12.5	20	13.4

39. Electrical Properties

Radioactivity easily sparks the birth of electrical properties in hydrogen. In fact, background cosmic radiation may father the conductivity of pure H_2 .²⁸⁶

Most of the data in the electrical area are for the dielectric constant* of the untritiated isotopes. These samples have been considered classic dielectrics, and radiation damage, even at a low level, and has not been meshed into the analysis. A large amount of data have been taken on fluid even-J(para) H_2 from 24 to 100 K and 0.2 to 32.6 MPa at 1 KHz.²⁸⁷ The dielectric constant, K , is independent of temperature and dependent on the density, ρ . I use an empirical form of the Clausius-Mossotti equation²⁸⁸ to obtain

$$K = \frac{1 + 2\zeta\rho}{1 - \zeta\rho} \quad (186)$$

where

$$\zeta = (494010 - 0.09069\rho + 2.2630 \times 10^{-6}\rho^2)^{-1} \quad (187)$$

The density is in mole/m³; ζ has become an empirical polarizability function for the H_2 . Like the refractive index, with which K is closely related, one may use Eqs. (186) and (187) for any phase or isotope with only a small degree of error. It agrees to within a percent with measured liquid²⁸⁹⁻²⁹² and solid-under-pressure data.¹⁴⁶

There are data for liquid H_2 , HD, and D_2 over a narrow temperature range but as a function of the rotational composition.²⁸⁹⁻²⁹² These data may be described empirically by

$$K = A - BT \quad (188)$$

where A and B are constants from Table 31.

It has not been possible to take believable data on the saturated solid. In one freezing study, the dielectric constant of nH_2 rose while those of HD and nD_2 fell. The value for D_2 rose again as a gas overpressure was applied. Gaines surmised that K dropped as the crystals pulled away from the electrical plates. Overpressurizing filled in these cracks, and the crystals annealed, although they never reached the expected values.²⁹¹ This

*The dielectric constant is the ratio of the sample capacitance to that of a vacuum. It measures the capacity of the test material to store electric charge despite the driving force of the electric field.

Table 31. Dielectric constant data for saturated liquid H_2 , HD, and D_2 .

Isotope	Temp range (K)	Fraction J = 1, c(1)	K = A - BT	
			A	B (K ⁻¹)
H_2	14-20	~0	1.298	3.36×10^{-3}
		0.5 to 0.75(n)	1.300	
		0.92	1.302	
HD	17-22	(e)	1.335	3.91×10^{-3}
D_2	19-23	~0	1.358	3.96×10^{-3}
		0.33(n)	1.359	
		0.91	1.361	
DT(est.)	20-24	(e)	1.371	4.16×10^{-3}
T ₂ (est.)	21-25	0.75(n)	1.379	4.18×10^{-3}

behavior can be avoided by pressing the solid against the plates with 9 to 10 MPa (90 to 100 atm) pressure, and relative dielectric measurements have been made to 1.1 K.²⁹³ The same procedure was used to obtain J = 0 H_2 data along the melting curve from 1.4 to 32 MPa (14.4 to 22.2 K). This data is summarized by¹⁴⁶

$$K(\text{solid } H_2) = 1.2229 + 4.501 \times 10^{-3}T \quad (189)$$

It is clear that the solid must be firmly in contact with the electrical plates to get a true dielectric constant.

I now turn to the electrical conductivity of pure liquid H_2 , which is a hard insulator. At 20 K, H_2 (probably saturated) breaks down with 50% probability at 9.3 MV/m electric field. For the liquid under pressure at 20 K, I have at 70 kPa (520 Torr) — 16.3 MV/m; and at 140 to 520 kPa (1040 to 3880 Torr) — 18.5 MV/m.²⁹⁴ The dc electrical conductivity has been measured in a huge 270-pF cell under electric fields of 1 to 7 KV/m — far below breakdown. The experimental conductivity values are very small — about $10^{-17} (\Omega\text{-m})^{-1}$. As a function of electric field, E , the electrical conductivity, g , of liquid H_2 at 19.3 to 19.5 K is

$$g(\text{liquid } H_2) \approx \frac{2.8 \times 10^{-14}}{E} \quad (190)$$

This is a strange relation, for one sees the increasing electric field damping down the conductivity. For liquid 19.4-K D_2 ,

$$g(\text{liquid } D_2) \approx \frac{1.6 \times 10^{-10}}{E} \quad (191)$$

FIG. 26. Preliminary data showing the extreme electrical effects of tritium in 20-K liquid D-T. Most compositions are thought to be close to normal. At zero tritium concentration, the dielectric constant is expected to equal the 1.28 value of liquid D₂. The corresponding electrical conductivity is too small to appear on this graph.

The D₂ data, if extrapolated to zero voltage, yield a conductivity of $2 \times 10^{-13} (\Omega\text{-m})^{-1}$, instead of the expected zero. Furthermore, a comparison of Eqs. (190) and (191) discloses the surprise that D₂ possesses a 10 000 times larger conductivity than H₂. This was ascribed to a one part in 10^9 tritium impurity in D₂ while H₂ was considered pure. This offers a remarkable example of the possible effects of radioactivity on electrical properties.²⁸⁶

Figure 26 displays my preliminary data on liquid D-T at 20 K for tritium concentrations varying from 1.5 to 41 mole%.²⁹⁵ The isotopic proportions are close to those of room temperature. Equilibration to these values occurs after a few minutes, although a slight but continued drift is sometimes present. Measurements were made at 1592 Hz with a 35-pF cell and a 2-kV/m electric field maximum. Note that the dielectric constant rises from 1.5 to almost 3 and that the curve extrapolates back to the expected 1.28 value for pure D₂. Electrical conductivity rises from 10^{-8} to $10^{-7} (\Omega\text{-m})^{-1}$. This is five to six orders of magnitude greater conductivity than found in the previously described impure D₂. However, even with 40% tritium, the sample is still a soft dielectric. Also the electrical effects seem to be saturating, possibly because of quick recombination of charge carriers.

One may relate the conductivity to the carrier mobility, u , by

$$g = N_i \rho_L e [u_+ + u_-] \quad (192)$$

where N_i is the number of ion pairs per mole of liquid, ρ_L the liquid density, e the electronic charge assuming singly charged ions, and u_+ and u_- are the positive- and negative-ion mobilities.²⁹⁶ The mobilities have been measured in liquid H₂: u_+ increases from 4×10^{-7} at 15 K to $1.1 \times 10^{-6} \text{ m}^2/\text{V-s}$ at 26 K; u_- increases from 5×10^{-7} to $1 \times 10^{-6} \text{ m}^2/\text{V-s}$ over the same range.²⁹⁷ The mobilities are constant with 10 to 50 kV/m field values from 15 to 17 K.²⁹⁸ One sees, then, that the mobilities are not overly sensitive to the field and they are about the same for both ions. This means that the bare electron cannot carry the current. This is corroborated by the much larger $10^{-2} \text{ m}^2/\text{V-s}$ mobilities attributed to bare electrons in H₂ gas.²⁹⁹ The most obvious pair of carrier ions are H₂⁺ and H₂⁻, but it is thought that the real ions are even heavier than these.²⁹⁷ If I correct the 20-K liquid H₂ mobility by the inverse square root of the mass, I can calculate a maximum of about 5×10^{13} ions/mole liquid in the D-T solutions of Fig. 26. There is only about one ion for every 10^{10} molecules in 20-K liquid D-T.

There is an exotic off-shoot of the liquid H₂ electrical research: the suggestion that the heavy negative ion is an electron inside a 100- μm (10- $\text{\AA}$) bubble whose walls are kept pushed back by the electron's wave field.³⁰⁰ Positron bubbles have also been studied.³⁰¹

The overall carrier mobility has been measured in solid H₂.²⁹⁷ It is $8 \times 10^{-10} \text{ m}^2/\text{V-s}$ at 13.7 K and $4 \times 10^{-10} \text{ m}^2/\text{V-s}$ at 12.1 to 12.7 K. This is three to four orders of magnitude below the liquid mobilities.

40. Atomic Hydrogen in the Solid

The easiest way to break a hydrogen molecule is into atoms, which requires only $4.32 \times 10^5 \text{ J/mole}$ (4.476 eV). This may be compared with the $1.31 \times 10^6 \text{ J/mole}$ (13.6 eV) needed to strip the electron from atomic hydrogen or the $1.49 \times 10^6 \text{ J/mole}$ (15.42 eV) needed to form the H₂⁺ ion.³⁰² Atomic hydrogen is the smallest of all these entities, having a first-Bohr-orbit diameter of $1.1 \times 10^{-10} \text{ m}$.³⁰³ In the liquid, atomic hydrogen is so mobile that it apparently reacts almost instantly. In the solid, however, it accumulates to levels easily seen by electron spin resonance (ESR).

The first work in this area consisted of 4.2-K irradiations with 1-MeV α -rays, 40-MeV electrons, and tritium beta particles at rates of 0.013 to 1.9 W/mole. The ESR signals saturated in minutes to days at levels of 0.5 to 80 ppm of assumed atomic hydrogen.³⁰⁴⁻³⁰⁸

A more recent study consists of 160-keV electron bombardments of solid H₂.³⁰⁹ The irradiation rate is 0.015 W/mole. At 4.2 K, the ESR signal saturates at 18 ppm of assumed atomic hydrogen. When the beam is stopped, the signal decays slowly, with a half-life of

10.6 h. A more comprehensive set of measurements exists for the range 6.5 to 8.1 K. Here, the data fit an exponential inverse-temperature relationship, which, however, does not extrapolate to the 4.2-K point. The maximum mole fraction, f_H (maximum), of atomic hydrogen is found, from 6.5 to 8.1 K, to be

$$f_H(\text{maximum}) \simeq 1.8 \times 10^{-11} \exp \left[\frac{97.5}{T} \right]. \quad (193)$$

Equation (193) predicts 59 ppm at 6.5 K and 4 ppm at 8 K. If extrapolated to 4.2 K, it predicts 22% atomic hydrogen, which is clearly not so. At the H_2 triple point, Eq. (193) predicts 20 ppb as the atoms hurriedly recombine.

The 6.5- to 8.1-K work also includes the ESR signal-decay rates after turning off the electron beam. The half-life of the decay is

$$t_{1/2}(\text{atomic H}) \simeq 5.1 \times 10^{-5} \exp \left[\frac{97.5}{T} \right]. \quad (194)$$

Equation (194) yields 3 min at 6.5 K and 10 s at 8 K. It predicts 170 h at 4.2 K, compared with the actual 10.6 h—so there must be an additional low temperature mechanism. At the triple point, Eq. (194) predicts a 60-ms decay.

The 6.5- to 8.1-K decays fit the expected form for the bimolecular recombination:

$$\frac{dn_H}{dt} = kI_0 - k'n_H^2, \quad (195)$$

where I_0 is the intensity of radiation and the quadratic term is the recombination. There is a simple theory that qualitatively relates the back reaction rate, k' , to the diffusion coefficient of the atomic hydrogen in the solid.³¹⁰ I employ this and speculate onward to a hopping time of under 1 s for an atom moving from one interstitial site to another. This is a qualitative argument to suggest that atomic hydrogen could be unexpectedly mobile in the solid.

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APPENDIX A. SYMBOLS

1. Hydrogen Isotopes

I use these chemical symbols to represent the individual atoms: H, D, T, He³, and He⁴. The diatomic hydrogens are often numbered from low to high mass, according to these subscripts:

		Subscript
H ₂	hydrogen	1
HD	hydrogen deuteride	2
HT	hydrogen tritide	3
D ₂	deuterium	4
DT	deuterium tritide	5
T ₂	tritium	6

A single subscript may be used for a pure component; two or three may be used to represent mixtures or relations between isotopes. D-T is a general term for the thermonuclear fuel, which is really the mixture D₂-DT-T₂.

2. Empirical Constants

So many empirical equations are in the text that A, B, C, D, and E are always used as coefficients. They may be broken down once more with zero subscripts, e.g., B₀. The letter b is used as an exponent. The meanings should be evident from the context.

3. List of Symbols

All units are SI metric* except the spectroscopic constants (cm⁻¹), the speed of light (cm/s), and beta particle and x-ray energies (eV). Symbols listed without units are dimensionless.

A _{ij}	binary mixing parameter for isotopes i and j (J/mole)
a	lattice constant in hexagonal close-packed (hcp) crystal structure (m)
B*	second virial coefficient in terms of pressure (m ³ /mole or J/mole-Pa)
B _e	first rotational constant (cm ⁻¹)
C _P	heat capacity at constant pressure (J/mole-K)
C _Q	quadrupolar heat capacity (J/mole-K)
C _R	rotational heat capacity (J/mole-K)
C _s ^t	translational heat capacity of the saturated liquid or solid (J/mole-K)
C _V	heat capacity at constant volume (J/mole-K)
C*	third virial coefficient in terms of pressure (m ⁶ /mole-J or J/mole-Pa ²)
c	lattice constant of hcp crystal structure (m)
c	speed of light in vacuum (2.998 × 10 ¹⁰ cm/s)
c(J)	mole fraction of molecules in Jth rotational level
c(1)	mole fraction of molecules in J=1 rotational level
D	diffusion coefficient (m ² /s)
D _e	second rotational constant (cm ⁻¹)
D _s	thermal diffusivity (m ² /s)
D(ν)	Debye lattice vibration frequency spectrum (Hz ⁻¹)
d	molecular diameter (m)

*The International System of Units (Le Systeme International d'Unités), which is a rationalized selection of units from the metric system.

E	Eucken constant
E	electric field (V/m)
E	internal energy (J/mole)
E_f	energy of fusion (J/mole)
$E(J)$	energy of Jth rotational level, $J=1, 2$, etc. (J/mole)
E_R	total rotational energy (J/mole)
E_t	translational internal energy (J/mole)
E_z	zero point energy (J/mole)
E'	energy of beta particles or x-rays (J or eV per tritium decay)
e	equilibrium—precedes H_2 , D_2 , or T_2
e	electronic charge (1.602×10^{-19} C)
f_i	mole fraction ith isotope
f^s	pure-component fugacity (Pa)
G	abbreviation for gas
G^E	Gibbs excess free energy of mixing (J/mole)
$\bar{G}^E$	partial molal excess free energy of mixing (J/mole)
g	electrical conductivity ($[\Omega\text{-m}]^{-1}$)
$g(J)$	weighting factor for the Jth level in the rotational partition function
H	enthalpy (J/mole)
H_f	heat of fusion (J/mole)
H_s	heat of sublimation (J/mole)
H_t	translational enthalpy (J/mole)
H_v	heat of vaporization (J/mole)
H_0	magnetic field (T)
h	Planck's constant (6.626×10^{-34} J-s)
I	nuclear-spin quantum number
I	% deviation of a mixture from ideal Raoult's law behavior
J	molecular rotational quantum number
K	dielectric constant
K	thermal conductivity (W/m-K)
K_{ijk}	chemical equilibrium constant for the reaction of isotopes i, j, and k
K_q	thermal conductivity caused by low temperature mechanism (W/m-K)
K_U	thermal conductivity caused by higher temperature Umklapp mechanism (W/m-K)
k	Boltzmann's constant (1.381×10^{-23} J/K)
k, k(j in i)	Henry's Law constant for a dilute solution of j in i
k, k'	kinetic rate constants (mole/s; $[\text{mole}\cdot\text{s}]^{-1}$)
L	abbreviation for liquid
ℓ	thickness or size of a sample (m)
ℓ_x	penetration constant for an x-ray (m)
ℓ_β	penetration constant for a beta particle (m)
M	atomic or molecular weight (kg/mole)
M	nuclear magnetization (T/m ³)
N	refractive index
N_i	electrical carrier density (ion pairs/m ³)
N_s	nuclear-spin density (total nuclear spins/m ³)
N_0	Avogadro's Number (6.022×10^{23} molecules/mole)
n	moles of material
n	normal, precedes H_2 , D_2 , or T_2
n	neutron
o	ortho, precedes H_2 , D_2 , or T_2
P	total pressure (Pa)
P_i	total pressure of an ideal solution (Pa)
P_m	melting pressure (Pa)
P^s	saturated pure-component liquid-gas vapor pressure (Pa)
P^*	reduced pressure in quantum corresponding states

p	para, precedes H ₂ , D ₂ , or T ₂
P	proton
Q	$\Delta J = 0$ infrared line (with various additional notations, cm ⁻¹)
Q _R	rotational partition function
Q' _R	algorithm corresponding to first derivative of Q _R
Q'' _R	algorithm corresponding to second derivative of Q _R
Q ^s	saturated pure-component solid-gas vapor pressure (Pa)
R	gas constant (8.314 J/mole-K)
R _x	range of an x-ray (kg/m ²)
R _β	range of a beta particle (kg/m ²)
r	intermolecular distance (m)
S	abbreviation for solid or saturated
S	$\Delta J = +2$ infrared line (with various additional notations, cm ⁻¹)
S	Schmidt constant
s _i	mole fraction of i in a solid mixture
T	temperature (K)
T _m	melting temperature (K)
T ₁ , T ₂	nuclear magnetic relaxation times (s)
T*	reduced temperature in quantum corresponding states
t	time(s)
t _{1/2}	time for a reaction to precede half-way (s)
U	sound velocity averaged over sample direction (m/s)
U	abbreviation for Umklapp—high temperature thermal-conductivity mechanism
U _l	longitudinal sound velocity (m/s)
U _t	transverse sound velocity (m/s)
u ₊ , u ₋	ion mobilities (m ² /V-s)
V	volume (m ³ /mole)
V _m	volume at the melting point (m ³ /mole)
ΔV _m	volume change at the melting point (m ³ /mole)
V ₀	volume at zero pressure (m ³ /mole)
V*	reduced volume in quantum corresponding states
v	molecular vibrational quantum number
x _i	mole fraction of i in liquid mixture
Y	internal variable in describing 4 K isotherm
y _i	mole fraction of i in gas mixture
z	gas compressibility
α _e	rotational correction term (cm ⁻¹)
α _i	non-ideal term for solutions
β _e	rotational correction term (cm ⁻¹)
β	beta particle
γ	liquid-vapor surface tension (N/m)
γ	nuclear gyromagnetic ratio (Hz/T)
γ _i	activity coefficient for solutions
ε	Lennard-Jones potential well depth constant (J/mole)
ζ	internal parameter in dielectric constant formula (m ³ /mole)
η	viscosity (Pa-s)
Θ	first freezing point of a mixture (K)
Θ _D	Debye temperature (K)
Θ _i	triple point temperature of pure component i (K)
Λ*	quantum parameter in quantum corresponding states
Λ _{eff} *	corrected quantum parameter
λ	mean free path (m)
λ _U	phonon mean free path, Umklapp process (m)
μ _{ij}	reduced molecular weight (kg/mole)
ν	frequency (Hz or cm ⁻¹)

$\bar{\nu}$	antineutrino
ν_0	nuclear resonance frequency (Hz)
ξ	internal parameter in mixture theory (J/mole)
ρ	gas density (mole/m ³)
ρ_L	liquid density (mole/m ³)
ρ_s	solid density (mole/m ³)
Σ	internal parameter in calculating chemical reaction equilibria
σ	Lennard-Jones intermolecular distance constant (m)
τ	time constant (s)
Φ_i	volume fraction
ϕ_{LJ}	Lennard-Jones potential energy function (J/mole)
ϕ_T	liquid or solid binding energy (J/mole)
χ_{ijk}	constant in rule of the geometric mean
ψ_T	classical potential energy for liquid or solid (J/mole)
ω_e	molecular harmonic vibration frequency (cm ⁻¹)
$\omega_e\chi_e$	anharmonic correction term (cm ⁻¹)

APPENDIX B. USEFUL DIMENSIONAL RELATIONS

$$J = \text{Pa} \cdot \text{m}^3 = \text{N} \cdot \text{m} = \text{kg} \left(\frac{\text{m}}{\text{s}} \right)^2 = \text{C} \cdot \text{V} = \text{F} \cdot \text{V}^2 = \text{T}^2 \quad (196)$$

$$\text{N} = \text{Pa} \cdot \text{m}^2 = \frac{\text{kg} \cdot \text{m}}{\text{s}^2} = \frac{\text{C} \cdot \text{V}}{\text{m}} \quad (197)$$

$$\text{kg} = \text{Pa} \cdot \text{m} \cdot \text{s}^2 = \frac{\text{J} \cdot \text{s}^2}{\text{m}^2} = \frac{\text{C} \cdot \text{V} \cdot \text{s}^2}{\text{m}^2} = \frac{\text{V}^2 \cdot \text{s}^3}{\Omega \cdot \text{m}^2} \quad (198)$$

$$\text{C} = \text{A} \cdot \text{s} = \frac{\text{V} \cdot \text{s}}{\Omega} = \text{F} \cdot \text{V} = \frac{\text{m}^2 \cdot \text{kg}}{\text{V} \cdot \text{s}^2} \quad (199)$$

A = ampere (electric current)

C = coulomb (electric charge)

F = farad (capacitance)

J = joule (energy)

kg = kilogram (mass)

m = meter (distance)

N = newton (force)

Pa = pascal (pressure)

s = second (time)

T = tesla (magnetic induction)

V = volt (electrical potential)

Ω = ohm (electrical resistance)

Planck's constant, h (J-s), and Boltzmann's constant, k (J/K), are per molecule, atom, ion, or spin, although the definitions do not say so. The two constants may be related to the most important per-mole (gas) constant, R (J/mole-K) by

$$N_0 h \nu = RT \quad (200)$$

and

$$k N_0 = R \quad (201)$$

where N_0 is Avogadro's Number (molecules/mole), ν the frequency (Hz), and T the temperature (K).

APPENDIX C. VAPOR PRESSURE TABLES FOR SATURATED nH₂, nD₂, DT, AND nT₂

Tables 32 to 35 have calculated values for four isotopes for the solid from 4.2 to 21 K and the liquid from 14 to 30 K. The liquid and solid curves have been extrapolated beyond their triple points to provide data for mixture analyses. The quantities calculated are solid vapor pressure— Q^s ; liquid vapor pressure— P^s ; gas density— ρ ; gas compressibility— z ; solid density— ρ_s ; liquid density— ρ_L ; heat of sublimation— H_s ; and heat of vaporization— H_v . All quantities are for the pure components.

These tables comprise hybrid data. The liquid vapor pressures come from the most accurate equations for nH₂ [Eq. (8)²⁵], nD₂ [Eq. (9)²⁶], and nT₂ [Eq. (10)²⁶]. All other vapor pressures are from the three-constant equations of Table 3. The gas densities come from applying the virial coefficients of Table 4 with Eq. (29). When the densities are extrapolated to the triple points, they will not quite agree with the $z(1 - \rho/\rho_L)$ values of Table 2. This is because of the reiteration inherent in these calculations. One needs ρ to calculate heats and vapor pressure constants to start with. All liquid and solid densities excepting three are from Tables 5 and 7. The 26-, 28-, and 30-K liquid nH₂ points deviate too much from the Table 5 formula; the actual data are used.⁴⁹

The heats of sublimation and vaporization are calculated from Eq. (23), using the three-constant equations in all cases. This provides good agreement with these values and those of the triple point in Table 2. The problem is that the four-constant vapor pressure equations are sensitive to variations in H_v because of variations in ρ . And ρ is just not that well known because of uncertainties in the virial coefficients. Virtually all published heats are calculated from the Clausius-Clapeyron equation using these virial coefficients. All such heats may be off 1 to 2% for H₂ and D₂.

Table 32. Saturated, pure-component properties of nH₂.

Solid, temp (K)	Q^s (Pa)	Q^s (Torr)	ρ (mole/m ³)	z	ρ_s (mole/m ³)	H_s (J/mole)
4.2	1.3(-4)	9.7(-7)	3.7(-6)	1.0000	43360	823
6	1.8(-1)	1.3(-3)	3.6(-3)	1.0000	43360	863
8	1.5(1)	1.1(-1)	2.3(-1)	0.9999	43340	908
10	2.4(2)	1.8	2.9	0.9988	43300	952
12	1.72(3)	1.29(1)	1.73(1)	0.9945	43210	993
14	7.41(3)	5.55(1)	6.47(1)	0.9836	43020	1025
16	2.33(4)	1.74(2)	1.82(2)	0.962	42700	1043
18	5.88(4)	4.41(2)	4.25(2)	0.925	42170	1039
20	1.27(5)	9.56(2)	8.81(2)	0.867	41360	1002
21	1.79(5)	1.34(3)	1.24(3)	0.828	40820	966

Liquid, temp (K)	P^s (Pa)	P^s (Torr)	ρ (mole/m ³)	z	ρ_L (mole/m ³)	H_v (J/mole)
14	7.38(3)	5.54(1)	6.45(1)	0.9837	38280	908
16	2.04(4)	1.53(2)	1.59(2)	0.9669	37430	922
18	4.60(4)	3.45(2)	3.26(2)	0.9426	36460	926
20	8.99(4)	6.74(2)	5.94(2)	0.9109	35380	917
22	1.58(5)	1.19(3)	9.92(2)	0.8711	34190	894
24	2.57(5)	1.93(3)	1.57(3)	0.8222	32890	853
26	3.93(5)	2.95(3)	2.38(3)	0.764	31270	792
28	5.73(5)	4.30(3)	3.56(3)	0.691	29350	702
30	8.04(5)	6.03(3)	5.40(3)	0.597	26890	567

Table 33. Saturated, pure-component properties of nD₂.

Solid, temp (K)	Q ^s (Pa)	Q ^s (Torr)	ρ (mole/m ³)	z	ρ_s (mole/m ³)	H _s (J/mole)
4.2	5.6(-9)	4.2(-11)	1.6(-10)	1.0000	50120	1219
6	2.2(-4)	1.7(-6)	4.4(-6)	1.0000	50120	1254
8	1.3(-1)	9.8(-4)	2.0(-3)	1.0000	50100	1293
10	6.7	5.1(-2)	8.1(-2)	1.0000	50070	1332
12	1.0(2)	7.6(-1)	1.0	0.9996	49980	1370
14	7.36(2)	5.52	6.34	0.9979	49820	1406
16	3.41(3)	2.56(1)	2.58(1)	0.9932	49530	1438
18	1.16(4)	8.71(1)	7.89(1)	0.9828	49060	1459
20	3.18(4)	2.38(2)	1.98(2)	0.9635	48330	1464
21	4.93(4)	3.70(2)	2.97(2)	0.950	47840	1459

Liquid, temp (K)	P ^s (Pa)	P ^s (Torr)	ρ (mole/m ³)	z	ρ_l (mole/m ³)	H _v (J/mole)
14	9.99(2)	7.49	8.61	0.9972	45200	1241
16	4.07(3)	3.06(1)	3.08(1)	0.9918	44410	1257
18	1.22(4)	9.13(1)	8.30(1)	0.9819	43520	1265
20	2.93(4)	2.20(2)	1.82(2)	0.9666	42520	1265
22	6.05(4)	4.54(2)	3.50(2)	0.9452	41420	1253
24	1.11(5)	8.36(2)	6.06(2)	0.9181	40210	1230
26	1.89(5)	1.41(3)	9.90(2)	0.8835	38890	1191
28	2.99(5)	2.24(3)	1.52(3)	0.843	37470	1138
30	4.50(5)	3.37(3)	2.27(3)	0.795	35950	1065

Table 34. Saturated, pure-component properties of DT. All values are estimates.

Solid, temp (K)	Q ^s (Pa)	Q ^s (Torr)	ρ (mole/m ³)	z	ρ_s (mole/m ³)	H _s (J/mole)
4.2	3.6(-10)	2.7(-12)	1.0(-11)	1.0000	51810	1326
6	3.6(-5)	2.7(-7)	7.2(-7)	1.0000	51810	1360
8	3.6(-2)	2.7(-4)	5.4(-4)	1.0000	51800	1398
10	2.6	1.9(-2)	3.1(-2)	1.0000	51760	1436
12	4.7(1)	3.5(-1)	4.7(-1)	0.9998	51680	1473
14	3.98(2)	2.99	3.42	0.9988	51520	1509
16	2.06(3)	1.54(1)	1.56(1)	0.9957	51240	1542
18	7.62(3)	5.72(1)	5.15(1)	0.9883	50790	1567
20	2.23(4)	1.67(2)	1.38(2)	0.9738	50080	1578
21	3.56(4)	2.67(2)	2.12(2)	0.963	49620	1576

Liquid, temp (K)	P ^s (Pa)	P ^s (Torr)	ρ (mole/m ³)	z	ρ_l (mole/m ³)	H _v (J/mole)
14	6.42(2)	4.82	5.53	0.9981	46870	1345
16	2.75(3)	2.07(1)	2.08(1)	0.9942	46080	1356
18	8.67(3)	6.50(1)	5.87(1)	0.9866	45170	1362
20	2.20(4)	1.65(2)	1.36(2)	0.9742	44160	1359
22	4.74(4)	3.56(2)	2.71(2)	0.9563	43040	1347
24	9.08(4)	6.81(2)	4.88(2)	0.9323	41820	1322
26	1.58(5)	1.19(3)	8.10(2)	0.9025	40490	1284
28	2.57(5)	1.93(3)	1.28(3)	0.866	39050	1231
30	3.92(5)	2.94(3)	1.91(3)	0.824	37510	1163

Table 35. Saturated, pure-component properties of T₂. There is considerable uncertainty, and the solid below 14 K is an estimate.

Solid, temp (K)	Q ^s (Pa)	Q ^s (Torr)	ρ (mole/m ³)	z	ρ_s (mole/m ³)	H _s (J/mole)
4.2	2.9(-11)	2.2(-13)	8.3(-13)	1.0000	53360	1424
6	6.7(-6)	5.0(-8)	1.3(-7)	1.0000	53360	1458
8	1.1(-2)	8.2(-5)	1.7(-4)	1.0000	53340	1495
10	1.0	7.7(-3)	1.2(-2)	1.0000	53310	1532
12	2.3(1)	1.7(-1)	2.3(-1)	0.9999	53230	1569
14	2.22(2)	1.67	1.91	0.9993	53080	1605
16	1.27(3)	9.53	9.57	0.9972	52820	1638
18	5.09(3)	3.81(1)	3.43(1)	0.9919	52380	1665
20	1.58(4)	1.19(2)	9.69(1)	0.9809	51710	1681
21	2.59(4)	1.94(2)	1.52(2)	0.9725	51270	1683
Liquid, temp (K)	P ^s (Pa)	P ^s (Torr)	ρ (mole/m ³)	z	ρ_L (mole/m ³)	H _v (J/mole)
14	3.51(2)	2.63	3.02	0.9989	48410	1448
16	1.74(3)	1.31(1)	1.31(1)	0.9962	47610	1456
18	6.07(3)	4.55(1)	4.10(1)	0.9903	46690	1458
20	1.65(4)	1.24(2)	1.01(2)	0.9801	45670	1453
22	3.74(4)	2.80(2)	2.12(2)	0.9649	44540	1438
24	7.41(4)	5.56(2)	3.93(2)	0.9443	43300	1412
26	1.33(5)	9.95(2)	6.70(2)	0.9180	41960	1374
28	2.19(5)	1.65(3)	1.06(3)	0.887	40510	1324
30	3.41(5)	2.56(3)	1.61(3)	0.850	38950	1258

APPENDIX D. VIRIAL COEFFICIENTS OF H₂ AND D₂ FROM 98 TO 298 K

In considering pathways from room temperature to the cryogenic region, it is useful to have a set of virial coefficients. These, which are probably for the normal isotopes, have been the standards for years.⁴⁷ Gas compressibility, z , is related to the density, ρ , with the five virial coefficients B through F, listed in Table 36. Their relation is

$$z = 1 + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 \quad (202)$$

The maximum densities measured at 98 and 298 K are H₂—26 500 and 43 000 mole/m³ and D₂—8400 and 42 400 mole/m³.

Table 36. Virial coefficients of H₂ and D₂ gas from 98 to 298 K.

Temp (K)	B [10 ⁻⁵ (m ³ /mole)]		C [10 ⁻¹⁰ (m ³ /mole) ²]		D [10 ⁻¹⁵ (m ³ /mole) ³]		E [10 ⁻²⁰ (m ³ /mole) ⁴]		F [10 ⁻²⁵ (m ³ /mole) ⁵]	
	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂	H ₂	D ₂
98.16	-0.29906	-0.43448	5.03458	4.25758	7.51362	24.2546	3.8874	-126.6710	54.1053	—
103.16	-0.15966	-0.28599	5.10983	4.48042	5.12807	18.2310	15.7212	-93.73892	30.7317	—
113.16	0.07955	-0.009125	5.06752	3.49567	3.52305	31.9890	22.6597	-169.2355	13.6984	—
123.16	0.26774	0.18464	5.18964	4.93907	1.05937	-1.01444	31.5880	35.9715	-4.0397	-17.6643
138.16	0.50328	0.44284	5.16816	4.62942	0.89635	0.21294	39.0242	31.4034	-21.7302	-17.5408
153.16	0.69831	0.63963	4.80826	4.50080	0.81548	-0.27742	31.6628	34.2609	-17.5284	-27.9690
173.16	0.89279	0.83860	4.59101	4.38969	0.99970	-0.71394	29.2629	34.9068	-19.4499	-33.5857
198.16	1.07932	1.01634	4.14392	4.42298	3.34677	-2.94798	17.7765	42.7920	-8.32862	-49.0880
223.16	1.20576	1.15249	4.05426	4.10775	2.62979	-0.64636	18.2742	30.2213	-12.4319	-32.9063
248.16	1.30263	1.24530	3.87764	4.18576	3.03919	-2.70357	14.0341	36.8939	-8.24532	-44.7292
273.16	1.37412	1.33190	3.88772	3.63241	1.49980	2.43004	17.5923	11.7947	-13.5976	-7.35615
298.16	1.43843	1.39378	3.56368	3.49277	3.38041	2.76355	9.24918	8.97856	-4.75941	-4.82367