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"STUDIES OF THE THERMAL AND OPTICAL RESPONSES OF H ATOMS IN SOLID H_2"

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"STUDIES OF THE THERMAL AND OPTICAL RESPONSES OF H ATOMS IN SOLID H_2"

ABSTRACT

The following is THE FINAL TECHNICAL REPORT to NASA for the grant " STUDIES OF THE THERMAL AND OPTICAL RESPONSES OF H ATOMS IN SOLID H_2". The principal investigators on this project at the University of Hawaii were Dr. James R. Gaines, Professor of Physics (an experimentalist) and Dr. Chester Vause III, an Associate Professor of Physics (a theorist). Other key scientific personnel included Dr. Yi Song, an Assistant Researcher in Physics and Materials Science, and a graduate research assistant. It was the goal of this research project to model both the storage of energy in solid hydrogen in the form of atoms and the conversion of this stored energy into other forms of useful energy.

The basic ideas of rocket propulsion originate in classical physics and they remain unchanged. To escape a strong gravitational field, the "burn time" must be minimized but in negligible force fields, the burn time is unimportant and only the relative masses of rocket to fuel determine a specific exhaust velocity. It is in this latter case that low mass fuels such as hydrogen become very important. The burning of hydrogen in oxygen is a "benchmark" fuel today providing a specific impulse of 400 seconds or better. More exotic fuels will be needed for many of the interesting explorations of the future but they still must have large energy releases per unit mass. It is in this context that propulsion based on hydrogen atom recombination receives attention and these studies will serve as engineering guides.

I. INTRODUCTION

The following is the Final Technical Report to NASA for the grant entitled "Studies of the Thermal and Optical Response of H Atoms in Solid Hydrogen" with Drs. James R. Gaines and Chester A. Vause, III, as principal investigators. The report is divided into the following sections: (II) Previous Experiments and Models; (III) The New Model; and (IV) Conclusions.

II. PREVIOUS EXPERIMENTS AND MODELS

2.A Experimental Background

Hydrogen solid hosts containing tritium such as T_2, DT, HT, or even H_2, HD, and D_2 doped with some amount of T_2 display very interesting thermal and optical properties at low temperatures. It is known that these solids can store hydrogen atoms but how many of these metastable excitations can exist at any given temperature is still unknown. The atoms stored have their origin in the ß-decay of the tritium nucleus. In the gas phase, one ß-decay produces about 800 atoms but this number could be different in the solid.

Experiments on such solids have revealed many interesting phenomena and the solids themselves are intrinsically interesting because they represent potential energy storage systems, possibly for space propulsion, and also represent the cryogenic fuel for inertial confinement fusion experiments. To date, there has been little theoretical development of this subject. Rosen and Zeleznik did treat theoretically the unusual thermal responses observed by Webeler on H_2 containing 1% (or less) T_2.

Atoms produced and trapped in solid hydrogen hosts have been studied by a variety of techniques but our detailed knowledge is still quite fragmented. Admittedly, the experiments have all been complicated but just a few clear results have been established for a system that has the potential for storing large quantities of energy (in the form of atoms).

Leach and Fitzsimmons produced atoms of hydrogen in solid molecular hydrogen by bombarding the solid with 100 keV pulsed electron beams. The electron pulses produced atoms in the solid that were then studied from the time decay of their distinctive electron paramagnetic resonance (EPR) signal. Since the signal intensity is proportional to the number of atoms, they were able to conclude that the atom density decay followed:

$$\frac{1}{n(t)} - \frac{1}{n(0)} = 2\alpha t \qquad (1)$$

From which one deduces a rate equation for the atom density

$$\frac{dn}{dt} = -2\alpha n^2 \qquad (2)$$

In addition, they found that the "recombination coefficient", 2α, was strongly temperature dependent, with an activation energy (195 K) that matched that of the self-diffusion coefficient of molecules in solid hydrogen. The lower the host temperature, the smaller the diffusion coefficient and hence the smaller the atomic recombination coefficient.

Prior to the Leach and Fitzsimmons work, Sharnoff & Pound had made a beautiful study of solid deuterium that contained nominally 1% of tritium (T_2). They also used EPR techniques to detect the D atoms produced by the tritium beta decay. Their atom density as obtained from their signal intensity grew, then saturated, then grew again all at constant temperature. One would expect that atoms, continuously produced by the beta decays, would eventually reach a maximum population where additional growth tendencies would be balanced by recombination. The atom growth curve observed by Sharnoff & Pound has never been satisfactorily explained. From Leach's work, there should be temperature dependence in both the growth curve and the final atom density due to temperature dependence of the recombination coefficient. Between 4 K and 1 K, Sharnoff and Pound did not observe any temperature dependence.

Webeler, at NASA Lewis, studied H_2 containing small amounts of T_2 but he didn't use EPR techniques. He studied the heat released when atoms recombined in the host solid and attempted to quantify "storage times" for the energy resident in the trapped atoms, again produced by the tritium beta decay. Rosen and Zeleznik provided a more detailed analysis of the Webeler experiments. We will examine Rosen's approach.

2.B. Rosen's Simplified Model

In his most general approach, Rosen treated two types of atoms, "mobile atoms" and "trapped atoms" with atom diffusion included. Mobile atoms were produced by the beta decay of tritium but these atoms could become trapped in the solid leading to the second type of atom. Either type of atom contributed to the stored energy. Diffusion was considered but then discarded because it complicated the analysis and didn't seem to be required to explain the experiments. Estimates were made of all the pertinent parameters and recombination was treated by gas-phase calculations of the cross-section leading to a temperature independent recombination coefficient ($\alpha = 1.3 \times 10^{-15}$ cm^3/s). An oversimplified version of Rosen's model, reduced to one type of atom, say the trapped atoms without diffusion, the atom density would obey a rate equation given by:

$$\frac{dn}{dt} = K - 2\alpha n^2 \qquad (3)$$

where K would represent the constant atom production from tritium beta decays. Such a rate equation would predict a steady-state atom population that would grow at lower temperatures due to the reduction in recombination.

$$n_{ss} = \sqrt{\frac{K}{2\alpha}} \qquad (4)$$

Starting from zero atom density the atom density would grow according to:

$$n(t) = n_{ss}\left[\tanh\left(\frac{t}{\tau}\right)\right] \quad \text{where } \frac{1}{\tau} = \sqrt{2\alpha K} \qquad (5)$$

Although Rosen's model is valuable in understanding the heat released in Webeler's experiments and points out the critical role of the coupling between the sample and the refrigerator, some of the parameters used there were unrealistic.

First, the recombination coefficient was directly measured by Leach where he found that $\alpha = 6.0 \times 10^{-21}$ cm^3/s at 6.75 K and rapidly decreasing with temperature. Russian data, interpreted by Souers, would lead to values of $\alpha = 1.5 \times 10^{-24}$ cm^3/s at 2 K and $\alpha = 7.5 \times 10^{-25}$ cm^3/s at 1.4 K. Therefore in the temperature range of interest in the Webeler experiments, the recombination used by Rosen differs from the estimates made in the solid state by *nine orders of magnitude.* Indeed for a recombination coefficient of the magnitude used by Rosen, the calculated atom density from the heat observed in a triggered energy release could not be established for the atom production term he used (which *was* realistic).

Secondly, Rosen estimated the volume for trapping of atoms and multiplied that volume by the beta decay rate to compare with the actual volume of the sample. Since his calculated volume per second receiving new mobile H atoms was comparable to the sample volume, he concluded that it was appropriate to consider the volumetric rate of production of mobile H to be approximately constant and uniform throughout the H_2 sample. In our new model, where the parameters are obtained from other experiments where possible, we obtain a much smaller critical volume (not a trapping volume) that leads to a fraction of the sample receiving new atoms of only about 10 PPM per second for the decay rate appropriate to pure T_2 solid! In this case, it is not appropriate to consider the atom production to be uniform and we will treat atom production differently.

We proposed a new model that was simpler in some respects but more complicated in others, than Rosen's. Our model attempts to explain the EPR experiments (that he was not addressing) and draws upon other experiments such as the measurements of the ortho-para conversion rate in solid T_2 for its parameters.

The pertinent features of this model are: (1) a new approach to atom production leads to a different time dependence of the atom density at fixed temperature; (2) a new interpretation of the EPR results is made possible; (3) the model has some predictive ability, it can give an upper bound for the maximum atom density for a specified production process; and (4) it can guide experiments attempting to make large atom densities by electron bombardment.

In the analysis of most of the experiments to date, the level of detail of the observations has not warrented using a theoretical picture with the complexity of Rosen's (i.e. two types of atoms) so previously we have treated the problem as though only one type of atom existed. In trying to reconcile the atom densities obtained from a model analysis of ortho-para conversion times in T_2 (or DT) with (i) measured atom densities in ESR experiments and (ii) the time dependence of the density after a temperature change (or heat spike), it is apparent that the single type of atom model is inadequate to explain the data.

III. THE NEW MODEL

The approach we suggest differs from that of Rosen but it also relies on there being (at least) two types of atoms. We focus on a single ß-decay and its effect on the surrounding region of the solid which due to the sudden increase of energy available to it, we term a "hotspot" or a "bubble". A more careful treatment would take into account the actual spectrum of tritium ß-decay energies but we will consider all decays to be characterized by the mean energy of 5.7 keV.

The experiments to date have been sensitive only to time scales of seconds to minutes but in a fraction of a second, all the atoms that are going to be produced due to a single ß-decay have been produced and many have had the opportunity to recombine. We think this region behaves as a bubble, that expands in time due to diffusion or hopping of the atoms (much as smoke dissipates in air) and becomes indistinguishable when the atom density in the bubble equals that of the "background". Of the atoms surviving in the bubble, some diffuse into regions where the atom density is much lower than the original atom density so that they can be detected in an ESR experiment. Atoms that escape the high density region of the hotspot do not instantly appear in the ESR signal, since they still have their ESR frequency shifted away from the detection window. They must then diffuse through real space, which amounts to a diffusion through an energy space, as their local field decreases, making them detectable.

3.A Time Dependence of the Atom Density in the Bubble

The basis for this model is a continuum approximation of the space surrounding a single beta decay event. Dr. Peter Fedders, Department of Physics, Washington University, has collaborated with us on this model development and refinement. The original model we developed was based on creation of all the atoms in a specific region (V_c) by a single beta decay with atoms either recombining in this fixed volume or subsequently diffusing out of this region into the background. While that model has interesting consequences and supports the essential conclusions of the model we present below, we believe the newer version (suggested by Fedders) is superior. Both models have the same initial assumptions, both rely on the same choice of parameters. The initial assumptions are now stated.

The beta decay event creates a large number of atoms in a local volume V_c, depositing an energy of about 5.7 keV into that volume. After that instant of creation, the atoms in that region can only decay. We use the simplest possible equation to describe that time decay.

First, we need a microscopic equation for the recombination time for the atoms including the dependence of its variables on the material properties of the host. For two atoms to recombine, they first have to hop within a nearest neighbor distance of each other and then they must recombine. This last step may be decidely nontrivial since the repulsive core for the H - H_2 potential is wider than that for the H_2 - H_2 potential. Thus there could be a substantial repulsion between atomic H nearest neighbors in the H_2 host. In any case, the average recombination time T for atoms is:

$$T = \frac{(\xi_1 \tau_h + \tau_r)}{\xi_3 c} \qquad (6)$$

where ξ_1 and ξ_3 are numerical constants, τ_r is the intrinsic recombination time for two neighboring H atoms or, more precisely, $1/\tau_r$ is the recombination rate for neighboring H atoms. The quantity τ_h is the hopping time or $1/\tau_h$ is the probability per unit time for an H atom to hop a specific neighboring site and c is the concentration or fraction of the lattice that are atoms.

An equation very much like Eqn. 6 can be derived exactly within the CPA (coherent potential approximation), which is itself exact in the low concentration limit. That is, the problem of a number of particles hopping around on a lattice with a hopping rate $1/\tau_h$ with a random concentration (c) of traps which remove the hoppers can be easily solved within the CPA. This problem differs from the present one only in that the trap itself is an atom, and the sites neighboring an atom are the trap sites. Further, the CPA shows that the recombination process as described by Eqn. 6, is a process described by only the single exponential rate. The form of Eqn. 6 can also be understood in two limiting cases. If the recombination rate is very fast (so that τ_r is very small compared to τ_h) then the recombination process depends on how long it takes for an H atom to get next to another H atom. This time is just the time of one hop times the number of hops that it takes to get next to another atom. The number of hops is just the reciprocal of the fraction of sites that contain an atom. In the other limit where the recombination rate is very slow ($\tau_r >> \tau_h$), an atom feels an average recombination rate (or inverse time) that is the nearest neighbor recombination rate time the fraction of the time that an atom has another atom as a nearest neighbor. The quantity ξ_1 is equal to Z (the coordination number or number of neighboring lattice sites) times a number of order one that is related to the tracer correlation factor. The quantity ξ_3 is also nearly equal to Z and obtains because every site neighboring an H atom is a trapping site in the sense that an atom sitting there can undergo recombination. Both of these numerical factors will be approximated by Z.

In the bubble of H atoms that we are considering there are N atoms in a volume V. Thus c, the concentration of atoms is given by the equation

$$c = \frac{N v_0}{V} \qquad (7)$$

where v_0 is the volume of a cell containing one H_2 molecule. Thus V/v_0 is the number of unit cells or H_2 molecules in the bubble. It is also convenient to define a "particle radius" associated with one molecule that is defined in the usual way as

$$r_0 = \left(\frac{3 v_0}{4\pi}\right)^{1/3} \qquad (7a)$$

The differential equation governing the decrease in the number of atoms inthe bubble is

$$\frac{dN}{dt} = -2\,\frac{N}{T} \qquad (8)$$

where the factor 2 obtains because each recombination destroys two atoms. Further, V , which appears in Eqn. 8 though the factor c in the recombination time T, depends on time. This time dependence can be well approximated by the equation

$$V(t) = \left(\frac{4\pi}{3}\right)\left[R_0 + (2Dt)^{1/2}\right]^3 \qquad (9)$$

where R_0 is the radius of the bubble at time zero and D is the diffusion coefficient for the atoms. The physics of this equation is just that for a diffusion process $x^2 = 2Dt$ and that $D = a^2Z/6\tau_h$, where a is the jump length. This length should be approximately $2r_0$. Thus we obtain

$$D = \frac{2Z(r_0)^2}{3\tau_h} \qquad (10)$$

Now Eqns. 7-9 are solved with the boundary condition the $N = N_0$ at time $t = 0$. We also wish to note that α of Eqn. 3 is given in terms of the parameters we have introduced as

$$\alpha = \frac{\nu_0}{\tau_h + \tau_r/Z} \qquad (3a)$$

Implicit in the above equations is the assumption that the initial bubble is sphercial. A few comments are in order on this approximation. First of all, the initial shape of the bubble is not vital since it will become sphercial as time evolves because of diffusion. In fact we have also performed calculations for a cylindrical geometry and get results that are very close to those for a sphere. It turns out that for a cylinder, the results are dominated by the large length. Further, since the atoms are caused by the collision of electrons (the b decay) with atoms, one would expect large angular scattering by the electron. This is in contrast to the more familiar case of charged nuclear ions scattering off of much lighter electrons. In fact the multiple Coulomb scattering for electrons in H gives an angular deviation of about 1 radian for 400 keV electrons. Further, for electrons with about 100 keV, are likely to deposit 10% of their energy behind their starting plane. Since the multiple scattering rate is proportional to some inverse power of the velocity, electrons at say 4 keV will be bouncing around almost randomly.

In writing the solution to the equations, it is useful to introduce two variables that set the scale of the evolution of the bubble. First we introduce the diffusion time td. This is the time it takes an H atom to diffuse across half of the original bubble volume and is given by the formula

$$\tau_d = \frac{(R_0)^2}{2D} \qquad (11)$$

The other useful quantity is b, the (dimensionless) number of H_2 cells across the intial bubble,

$$b = \left(\frac{V_0}{v_0}\right)^{1/3} \qquad (12)$$

The solution to Eqn. 8 can be written as

$$\frac{N}{N_0} = \frac{1}{[1 + \beta h(x)]} \qquad (13)$$

where h(x) is given by the equation

$$h(x) = \left(\frac{x}{1 + x}\right)^2 \qquad (14)$$

and β is given by

$$\beta = \left(\frac{3}{2Z}\right)\left(\frac{rN_0}{b}\right) \qquad (15)$$

and x is a measure of the dimensionless time

$$x = \sqrt{\frac{t}{\tau_d}} \qquad (16)$$

and r is a ratio of relaxation times

$$r = \frac{\tau_h}{(\tau_h + \tau_r/Z)} \qquad (17)$$

From the above equations, we can immediately deduce the effective number of atoms that each β-decay produces. At times long compared to τ_d the number density of atoms in the bubble $N(t)/N_0$, is comparable to the uniform background density. Then one can consider the bubble should merge into the uniform background and its remaining atoms will be added to the uniform background. Note that almost all of the recombination happens within several diffusion times, τ_d. The number of atoms left is given by Eqn. 13 with h(x) equal to unity. Thus we obtain the equation

$$\frac{N_{eff}}{N_0} = \frac{1}{1 + \beta} \qquad (18)$$

This analysis also yields an effective production constant for Eqn. 5. The relevant equation is

$$K_{eff} = \frac{K}{1 + \beta} \qquad (19)$$

This is the quantity that belongs in Eqn. 5 since only a fraction of the atoms survive long enough to be incorporated into the uniform background.

The dimensionless quantity β is the key parameter in the above expression. We note that it is proportional to the number of initial atoms, as one might have expected. It is, however, inversely proportional to the diameter of the initial bubble and not the bubble's volume. This is a rather weak size dependence. Thus for example, one could imagine changing N_0 or V(0) by slightly doping the H_2 and/or injecting electrons with a variety of incident energies. We see that increasing the initial bubble size but keeping the initial atom density constant can have a great effect on the fraction of atoms that recombine at short times.

We also see that the effective production constant is dependent on the material properties of the host (i.e. H, D, or T) and not just on the fraction of radioactive T atoms. Further, this constant can be temperature dependent if r is less than unity.

From numerical estimates, we use $N_0 = 1000$, $b = 27$, and $Z = 12$. This yields

$$\beta = \left(\frac{3}{24}\right)\left(\frac{1000\ r}{27}\right) = 4.63\ r \tag{20}$$

where r is given by Eqn. 17. We see that, depending on the ratio of the characteristic times, the effective number of atoms created by a single β-decay can be almost an order of magnitude less than the bare number.

There have been (informal) suggestions from time to time that some of the ESR signal from the spins associated with the H atoms are "invisible" or missing from the resonance. This could obtain if they were in regions of the H_2 that had very high spin density which would lead to a very broad ESR line. An eatimate of the fraction of spins that are in the high atom density bubbles can easily be made. Let R be the rate at which T nuclei decay and c_r be the concentration (fraction) of atoms in the sample that are T. Further, we assume that a H-bubble stays in a high density phase for a time of the order a diffusion time with N_0 atoms in it. Then, n_b, the average number of atoms per unit volume in the bubbles is given by the equation

$$n_b = c_r R \tau_d N_0 \tag{21}$$

Unfortunately, this number is vitally dependent on the diffusion time and thus on the H atomic hopping rate. However, for example, let us assume a diffusion time of 1 second which corresponds to a hopping time of 0.66 sec. For pure T_2 ($c_r = 1$), and a decay rate of 1.15×10^{14} decays per cc per sec, we get a number of spins per unit volume that are in the high density bubbles of 2.6×10^{18} per cc. This is the same as the density of spins at 100 PPM in the uniform background.

What is the characteristic lifetime of the bubbles?

To estimate this, we calculate the characteristic time t_c defined to be that time at which the atom density has fallen to 10% of its initial value (i.e. $n(t_c) = 10\%\ n_0$). We obtain this estimate by numerically solving for the ratio of the density to the initial density finding that $t_c = 1.48\ \tau_d = 67.8\ \tau_h$. Crude estimates of this atom hopping time in H_2 give the values: $\tau_h = 0.1$ s at $T = 5$ K;

τ_h = 1 s at T = 4.2 K; and τ_h = 10 s at T = 2 K. This converts to a characteristic lifetime of t_c = 6.8 s at T = 5 K; t_c = 68 s at T = 4.2 K; and t_c = 680 s at T = 2 K.

3.B. DETERMINATION OF MODEL PARAMETERS

We will use data taken from NMR determinations of the ortho to para conversion rate in pure T_2. In those experiments, the NMR signal was directly proportional to the J = 1 concentration (ortho species) with no signal contribution from the J = 0 (para) molecules. The directly measured rate was found to be very much larger than the intrinsic rate measured in either pure H_2 or D_2 and the exponential decay of the J = 1 concentration indicated that the rapid decay was caused by unpaired electron spins, not other molecules with their nuclear spins.

The rate, in contrast with those in H_2 and D_2, was found to be temperature dependent, peaking around 10 K. An earlier calculation of the ortho to para conversion in H_2 by Hardy and Berlinsky was adapted to T_2 containing unpaired electron spins (probably resident) on atoms. The peak in the rate was produced by atom motion and occurred when the atom hop frequency equaled the calculated transition probability per unit time. At temperatures below 10 K, the peak in the rate, atom hopping slows dramatically and the simple motional expression we used for the rate fails. At the lower temperatures, 6 K, the time constant for the conversion is 150 minutes in T_2 but 300 minutes in D-T (25% T_2, 25% D_2, 50 % DT); the conversion rate being inversely proportional to the beta decay rate, an effect not predicted by our earlier calculation. In addition, the ortho T_2 concentration (in pure T_2) which should be 2 x 10^{-4} according to the Boltzmann distribution, is in fact 2.3 %, one hundred times larger.

The low temperature limit of the ortho to para conversion deserves special consideration. When the atom hopping is negligible, conversion can still take place because the calculated rate is very high near an atom. If there are many atoms, each can convert all its near neighbors in about 1 second! The applicable transition probability per unit time (Ω) is

$$\Omega = z\left(0.0735\ \mathrm{s}^{-1}\right)\left(\frac{R_0}{R}\right)^{10} \qquad (22)$$

where z is the number of neighbors of the atom and R is their distance from the atom with R_0 being the nearest neighbor separation. In the above expression, for an atom at a substitutional site, z = 12, R = R_0, and Ω= 0.88 s^{-1}. For an atom in an interstitial position, although z is smaller, Ω is even larger.

As a result of a single beta decay, at low temperatures, atoms are produced in a restricted volume V_c, where they will convert all ortho molecules in their vicinity almost instantly (on the time scale of all experiments to date). With 1000 atoms produced per beta decay, it is not unreasonable that 10^4 or more ortho molecules would be converted to para in a few seconds inside V_c. We use this concept to calculate V_c from the ortho to para measured rate at low temperatures and the known beta decay rate (r_β = 1.15 x 10^{14} decays/cm^3·s in pure T_2 and half this value in D-T). This approximation should be valid until the volumes associated with different beta decays start to overlap.

We assume that a single beta decay defines a volume V_c, where all the ortho T_2 molecules are "instantly" converted to para T_2 molecules. The electron spin catalyzed conversion of ortho molecules with concentration x_1 follows:

$$x_1 = x_{10} e^{-t/\tau} \tag{23}$$

where x_{10} is the initial ortho concentration (near 75%) and τ is the measured time constant for ortho to para conversion. The fraction of the molecules converted in a time constant is:

$$\frac{x_{10} - x_1(\tau)}{\tau} = \frac{(0.632)x_{10}}{\tau} = x_{10} r_\beta V_c \tag{24}$$

Therefore taking $\tau = 150$ min. and the value of r_β given above, we find that $V_c = 6.1 \times 10^{-19}$ cm^3. In this volume, there are 2.3×10^4 T_2 molecules (with 1.75×10^4 originally being ortho T_2). It should be noted that Rosen estimated the volume obtaining "fresh hydrogen atoms" by multiplying a trapping volume by the beta decay rate and found that essentially all the Webeler sample received these fresh atoms each second, allowing him to conclude that the atom production was uniform. We can make the same type of estimate from the above equation $r_\beta V_c = 8.3 \times 10^{-5}$, for pure T_2, being four orders of magnitude samller for the Webeler experiment. Thus we can conclude that atom production is *nonumiform* and requires a different treatment.

Another method of estimating this volume is from the measured large residual ortho T_2 concentration of 2.3 % at low temperatures (with 2×10^{-4} being expected from the Boltzmann distribution). We assume the 1000 atoms recombine into molecules with 3/4 (or 375) being ortho T_2, the fraction given by the spin weight factors. Since there are 3.21×10^{22} T_2 molecules per cm^3, we have,

$$x_1(\infty) = 2.3 \times 10^{-2} = \frac{375}{(3.21 \times 10^{22})V_c} \tag{25}$$

giving $V_c = 5.1 \times 10^{-19}$ cm^3. The agreement of these two estimates is encouraging but it doesn't involve an independent concept only a different measured quantity. In this volume, 1000 atoms would represent an initial atom concentration of 6.2 %.

IV. **CONCLUSIONS**

4.A. DIFFUSION AND RECOMBINATION OF ATOMS

All the important physical quantities in the "bubble model" depend on the atom hopping time, τ_h. During the past year, we have obtained a *much* better understanding of the existing data capable of yielding the atom hopping times that are critical for our modeling of the atom production and recombination processes and we can now predict the atom hopping times as a function of temperature and relate measurements on one hydrogen isotope to measurements on another. The data in existence consisted of: (i) NMR measurements of the diffusion coefficient *of molecules* in H_2, HD, and D_2 which we had extended to D-T and T_2 along with our own measurements in HD and D_2 as checks on the earlier data; and (ii) measurements of the recombination coefficient (α) *of atoms* of H in H_2.

The problem arises when one tries to compare data taken on the different isotopes; when using the data from one isotope to predict behavior in another; or when using the data, valid for molecules, to predict the behavior of atoms. A theory of corresponding states that would contain universal behavior for the hydrogen isotopes is needed--but a conventional approach will not work because all the hydrogen isotopes have the same intermolecular potentials. *Moreover, it is not the static properties that are required but the kinetic ones such as the recombination coefficient and the diffusion coefficient, both dependent on the atom hopping time.* For instance, much of the data we needed to understand was data taken on T_2 where we required the recombination coefficient or the diffusion coefficient at low temperatures although no actual data existed but where data, to a certain extent, did exist for H_2. The simplest relationship between the recombination coefficient and the diffusion coefficient is:

$$(2\alpha) = 4\pi R_0 D(T) \tag{26}$$

where R_0, the distance within which recombination is assured, is usually taken to be the nearest neighbor distance in a solid.

The diffusion coefficient (D) for H atoms in H_2, calculated from the recombination coefficient (that had been pieced together from three sources by Clark Souers) is shown below.

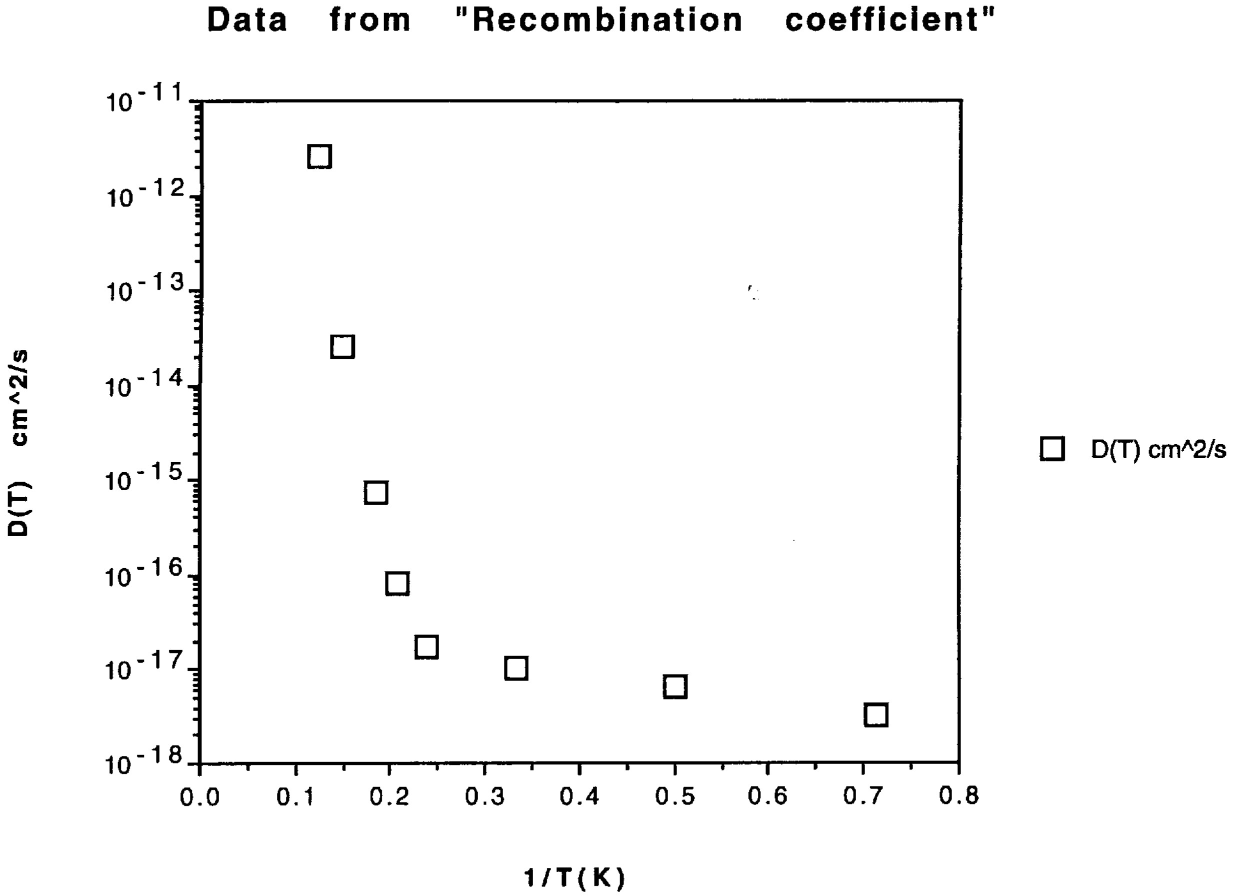

FIGURE 1

From this diffusion coefficient for atoms, one can compare with the diffusion coefficient measured for molecules by extracting the correlation time for hopping using the relationship:

$$D(T) = \frac{\langle r^2 \rangle}{6\tau} \tag{27}$$

where $<r^2>$ is the mean square hopping distance (typically an interatomic spacing). When the hopping times for atoms and molecules are calculated and compared, it is astonishing to find that at a given temperature, *they are essentially equal.* This is shown in the figure below (Fig. 2) where the lowest temperature point shown for molecules is not a measured point but was extrapolated from a theoretical fit to the high temperature data.

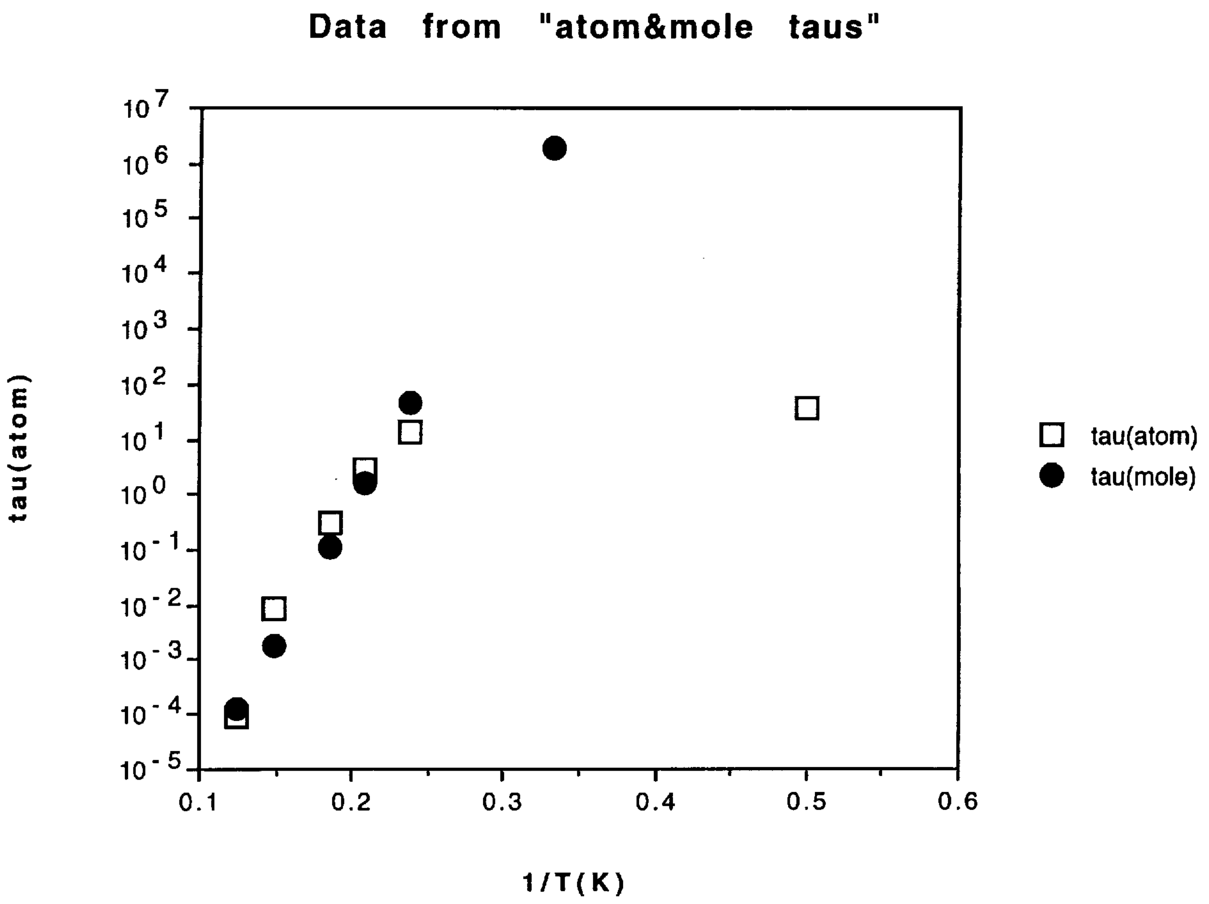

FIGURE 2

The solution to the problem arising from the application of measurements on one isotope to predicting the behavior of a different isotope came from our NMR diffusion coefficient measurements and their analysis. There we found that the diffusion coefficient, at higher temperatures, followed an Arrhenius equation:

$$D = D_0 \exp(-E_A/T) \tag{28}$$

where the activation energy E_A is expressed in degrees Kelvin. Moreover from isotope to isotope, E_A varied regularly with the isotope mass (M), increasing linearly from H_2 (M = 2) to T_2 (M = 6). The activation energy for T_2 (411 K) being roughly twice that of H_2 where E_A = 197 K. The scaling relationship for temperatures can be expressed as:

$$T^{*} = \frac{E_A(T_2)}{E_A(H_2)} T(K) = \frac{411\ K}{197\ K} T(K) \approx 2\ T(K) \tag{29}$$

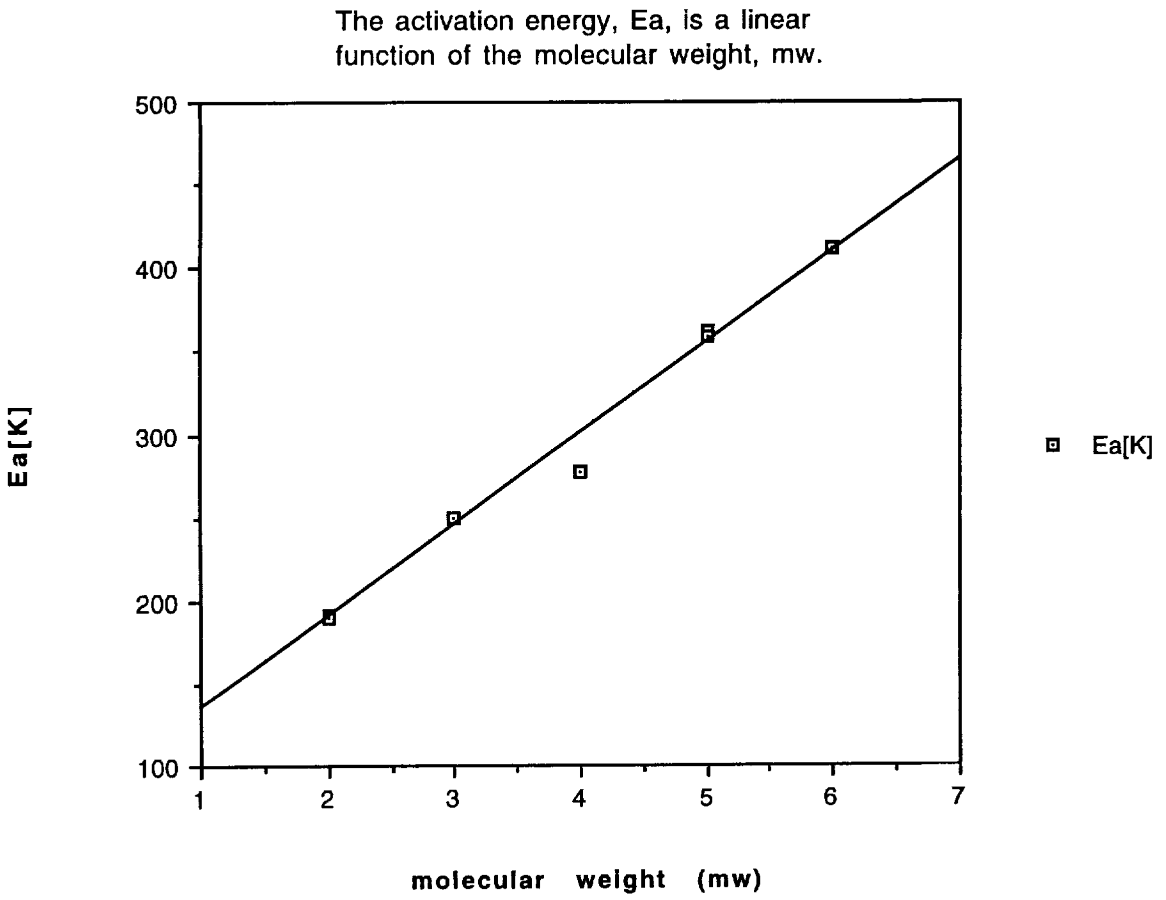

FIGURE 3

where the scaled temperature T* is related to the actual sample temperature T(K) in solid H_2.

Thus at a temperature of 8 K in solid H_2, the atoms diffuse at a rate equal to that at 16 K in T_2 so that temperatures scaling, proportional to the respective activation energies, makes it possible to compare data from different isotopes and provides the required "law of corresponding states" for the kinetic quantities . In simple terms: The result (say the diffusion coefficient) obtained for H_2 at 4 K is then valid for T_2 provided it is plotted at 8 K, the scaled temperature.

We have applied this discovery by taking the recombination coefficient values (2α) measured in H_2, scaling them for T_2 by scaling the temperature as described above, to predict the steady-state atom densities (n) that should exist in T_2 for the known production rate of atoms due to beta decays since $n^2 = K/2\alpha$. *These calculated atom densities agree very well with the atom densities deduced from the ortho to para conversion experiments.*

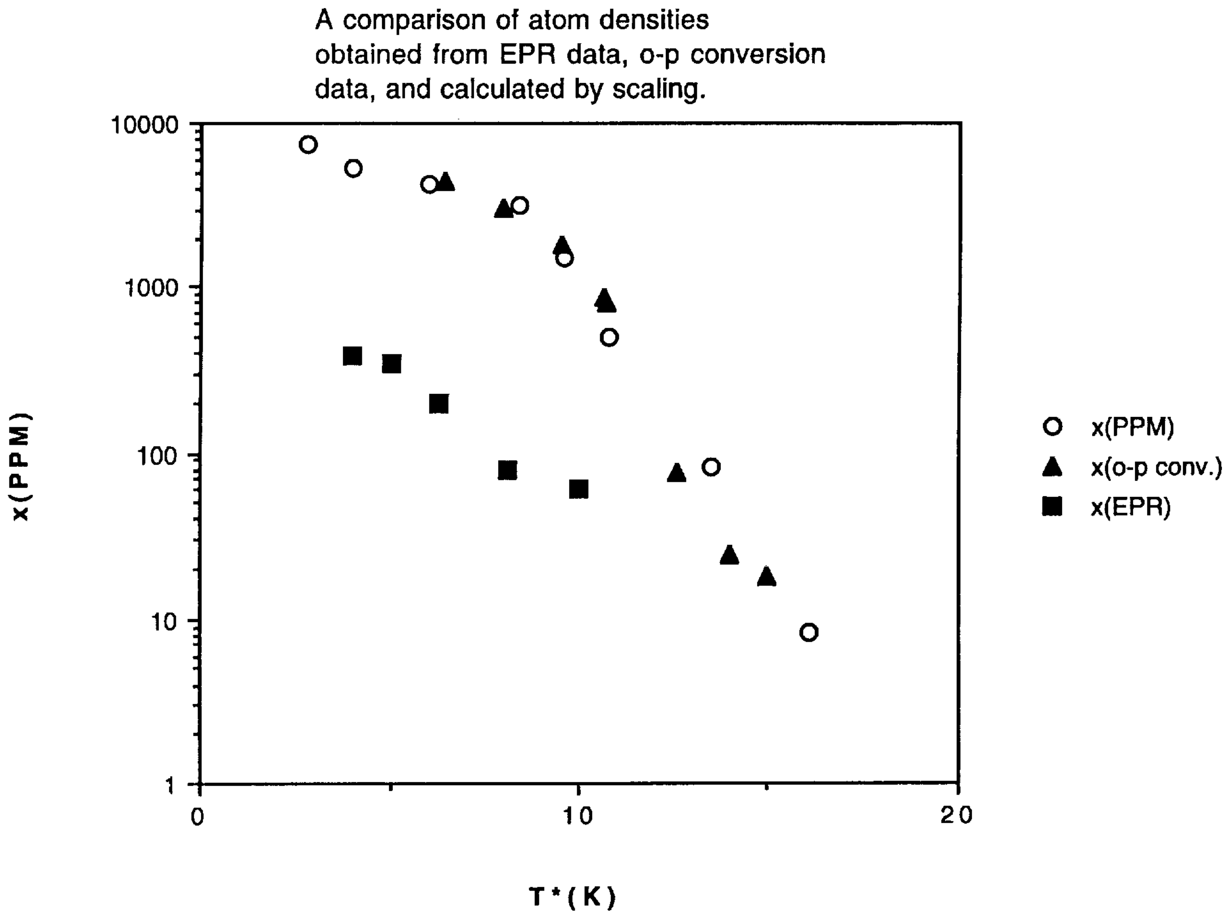

FIGURE 4

To summarize these findings: Based on Souers' tabulation of the data on the atomic recombination coefficient in H_2, we have produced a graph of the diffusion coefficient of H atoms in solid H_2 over the temperature range 1.2 K to the triple point (different from the Souers result for D(T)). The diffusion coefficient of molecules is approximately the same as that of atoms. This diffusion-temperature relationship can be scaled to predict behavior in the other isotopes, in particular, the recombination coefficient of T atoms in T_2 in low magnetic fields. *There is a "universal behavior" of atoms and molecules in the solid hydrogen isotopes for the kinetic quantities dependent on the atom hopping time.*

While the agreement between the values of atom density deduced from the ortho to para conversion work and those calculated from the known source term in solid tritium and the recombination coefficient scaled from hydrogen measurements is excellent, the actual measured values of the atom density, shown above are more than an order of magnitude lower than the other two values. This problem is discussed next.

4.B. RESOLUTION OF THE EPR SPIN COUNT PROBLEM

The only experiments that directly measure the number of atom spins are the EPR experiments. The number of atoms per unit volume gives the spin density. The spin density determined in solid T_2 by EPR is about a factor of ten lower than the spin density determined by modeling the ortho to para conversion of solid T_2 as shown in the above figure (Fig. 4).

The simple bubble model presented here predicts that (conservatively) only one-sixth of the atoms produced *could* be observed by EPR techniques so that the factor of ten difference in densities is partially resolved. A more detailed argument, given below can completely explain the observed difference in atom densities. *The atom densities deduced from the ortho to para conversion experiments are the best values to use.*

The existence of "invisible spins" near the large electron spins on atoms, while postulated first in the 60's was first demonstrated experimentally by us in our NMR experiments on D-T. The same phenomenon is at work here and can be explained qualitatively by the following argument. The second moment of a spin distribution is the starting point of all linewidth calculations. From the book by Abragham (Nuclear Magnetism, Oxford Press), we have:

$$\left\langle (\Delta\omega)^2 \right\rangle \equiv M_2 = \frac{3}{5} S(S+1)\gamma^4\hbar^2 \sum_k \frac{1}{r_{jk}{}^6} \qquad (30)$$

The lattice sum over a dilute (but not too dilute) spin system (spin S) is replaced by:

$$\sum_k \frac{1}{r_{jk}{}^6} = \frac{14.45\ (f)}{a^6} \qquad (31)$$

where the factor 14.45 comes from an HCP lattice, the factor (f) is the fraction of geometric lattice sites occupied by a spin and (a) is the nearest neighbor distance in the geometric lattice. The mean square "local field", $(\Delta H)^2$, appropriate for T_2, is given by:

$$\left\langle (\Delta H)^2 \right\rangle \equiv \frac{M_2}{\gamma^2} = \frac{3}{5} S(S+1)\left(\frac{\gamma\hbar}{a^3}\right)^2 14.45\ (f) = \frac{3}{5}\frac{3}{4}(420\ \text{gauss})^2(14.45\ f) \qquad (32)$$

For $f = .05$, $\Delta H = 240$ gauss. Various narrowing mechanisms may be operative such as "unlike spin narrowing" (see p 124 Abragham) but even this would only produce about a factor of ten reduction in width--still making the atoms inside a bubble "invisible" until the concentration drops.

This volume gives $n_0 = 1000$ atoms/(6.1×10^{-19} cm^3) = 1.64×10^{21} atoms per cm^3, representing an *initial* concentration of 5×10^4 ppm = 5%. At this density, the local magnetic field assuming uniform density of atoms would be nearly 200 gauss. The observed ESR lines are usually less than 5 gauss in width so atoms in V_c initially would be ESR "invisible".

As mentioned above, the "sphere of influence" model has been shown to be correct for nuclear spins by our earlier work. Applied to electron spins, all spins within a sphere of radius R_L will be invisible if R_L is chosen so that on the surface of the sphere, the magnetic field due to the spin at the center is equal to the "local field" in the material.

Using the above expression for the local field, one can calculate the field due to one spin by not performing the lattice sum in equation (31). Thus the local field is 282 gauss at the nearest neighbor separation, a_{nn}.

$$\Delta H_{local} \equiv (282 \text{ gauss})\left(\frac{a_{nn}}{R_L}\right)^3 \qquad (33)$$

If we use the practical criterion for the EPR experiments, namely that the local field surrounding an atom must be larger than the linewidth for spins to be invisible, and we take that field to be 10 gauss so the resonance from those spins would fall outside the detection window of the experiments, then 137 molecular sites are blocked out! This corresponds to a concentration of about 0.73 % being the observable concentration. If the bubble concentration starts out at 5%, the spins are too close together for them to be detectable by EPR techniques and only when the concentration has dropped to 0.73%, a factor of 6.8 reduction, is the EPR signal due to the spins in that bubble observable. This corresponds closely to the apparent reduction in the production term by a factor of 6. If the "field window" is taken to be 5 gauss, then 274 sites are blocked by a spin at the origin giving a factor of 13 reduction in signal or EPR atom density.

We propose to complete the modeling of the EPR experiments in this next year in order to provide unambiguous interpretations of that important data and to relate it to the other data that obtains the spin density indirectly.

4.C. THERE IS A " THERMAL PROBLEM"

The average beta particle leaves 5.7 keV in the bubble region while producing 1000 atoms. If it takes 11 eV to produce the excited molecular state that dissociates into two atoms, then 518 events are possible and 1036 atoms could be produced. As soon as the atoms have thermalized, they store 500 times 4.5 eV or 2.25 keV leaving 3.45 keV to be dissipated.

The enthalpy of T_2 has been estimated from measurements and comparison with known values for H_2 and D_2. At the *critical point*, the enthalpy is 1500 J/mol. If we use this value for the volume containing 20,000 molecules, the average molecule has 15.6 meV enthalpy at the triple point for a combined total of 311 eV. Thus, if 3450 eV is deposited into a region containing only 20,000 molecules, the region would be vaporized and a high pressure gas bubble would result.

These effects are potentially so drastic that no ordinary "heat conduction" approach will suffice to describe the conditions in the solid after local deposition of such a large amount of energy.

Spread over 20,000 molecules, only 311 eV can be absorbed to reach the critical point.

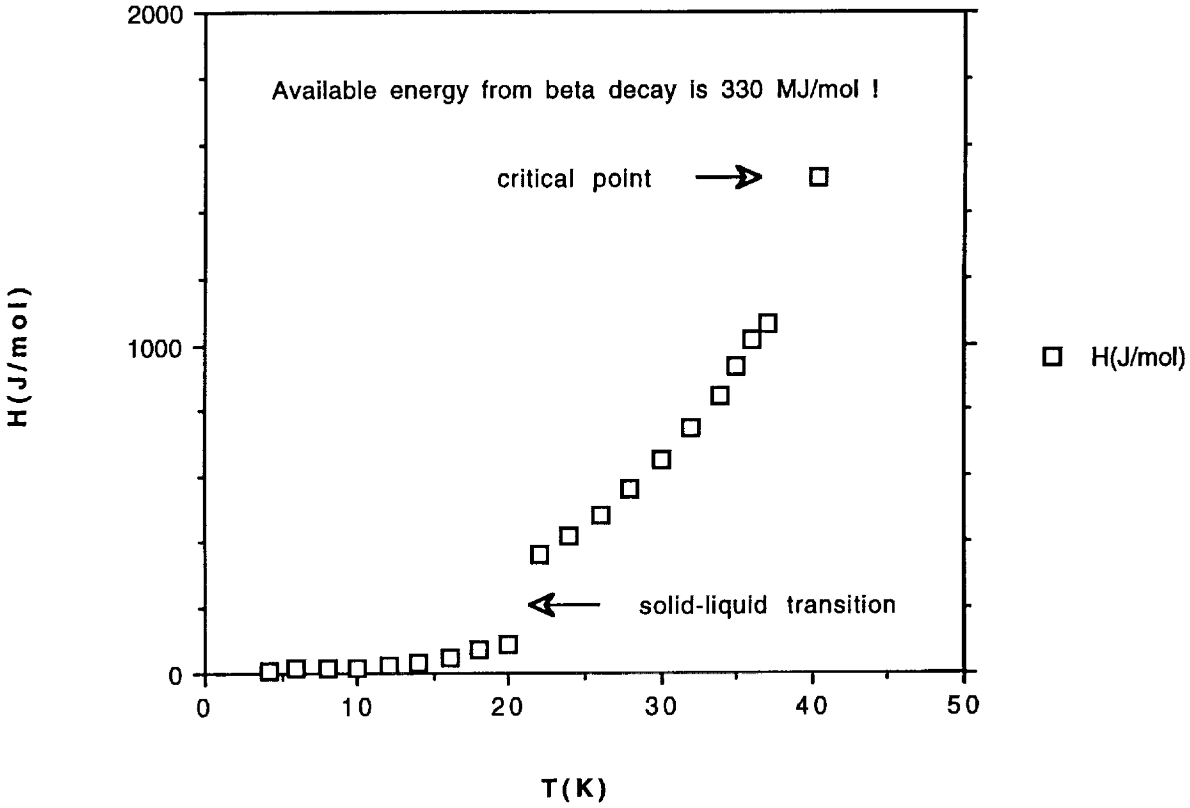

FIGURE 5

The "Classical Approach" to this problem is now discussed. When the thermal conductivity and specific heat capacity are each independent of the temperature, a difference equation for the heat flux yields the partial differential equation for the temperature as a function of space and time.

$$(\dot{Q})_{in} - (\dot{Q})_{out} = \frac{\partial E}{\partial t} = \text{time rate of energy increase} \qquad (34)$$

Writing the heat flux in terms of the thermal conductivity and the temperature gradient and the energy in terms of the specific heat capacity gives:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) = \frac{1}{\alpha}\frac{\partial T}{\partial t} \qquad (35)$$

which is the classical equation describing the temperature (T) variation along a radius in a sphere. In the above equation, α is the thermal diffusivity obtained from the thermal conductivity (κ), the specific heat capacity (C) and the density (ρ):

$$\alpha = \frac{\kappa}{C_p} \Rightarrow \frac{J/s \cdot m \cdot K}{(J/mol \cdot K)(mol/m^3)} \Rightarrow \frac{m^2}{s}$$

At 3 K in H_2, α is about 10^{-1} m^2/s making hydrogen superior to silver and gold in its thermal response but at 12 K, α is 10^{-5} m^2/s, comparable to the values of metals.

By redefining such that U = rT, the differential equation becomes:

$$\left(\frac{\partial^2 U}{\partial r^2}\right) = \frac{1}{\alpha}\frac{\partial U}{\partial t} \tag{36}$$

This is analogous to the one dimensional equation which is frequently solved as an example in a differential equations course.

If we take the boundary condition to be that the initial temperature from r = 0 to $r = R_c$ is equal to T_0 with the temperature equal to zero for all r values greater than R_c, then the temperature at all times and all r values is given by:

$$rT(r,t) \;=\; \frac{T_0}{\sqrt{4\pi\alpha t}}\int_{r\,-\,R_c}^{r} dx\ (r - x)\ e^{-\frac{x^2}{4\alpha t}} \tag{37}$$

which can be integrated to yield the expression:

$$\frac{T(r,t)}{T_0} = \frac{1}{2}\left\{\operatorname{erf}\frac{r}{\sqrt{4\alpha t}} - \operatorname{erf}\frac{r-R_c}{\sqrt{4\alpha t}}\right\} + \frac{\sqrt{4\pi\alpha t}}{2\pi r}\left\{e^{-\frac{r^2}{4\alpha t}} - e^{-\frac{(r-R_c)^2}{4\alpha t}}\right\} \tag{38}$$

where "erf x" is the error function of x.

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}}\int_0^x dz\, e^{-z^2}$$

The time scale of the problem is determined by the time required to make the arguments of the terms in the error functions and the exponentials equal to unity. For times shorter than the characteristic time (τ_c), the arguments are very large and for times longer than the characteristic times, the arguments are small.

$$1 = \frac{R_c}{\sqrt{4\alpha\tau_c}} = \frac{(52.6 \times 10^{-10} m)}{\sqrt{4(10^{-1}\ m^2/s)\tau_c}}$$

using the value of α at 3 K for H_2. This yields $\tau_c = 7 \times 10^{-17}$ s with the value increasing by 10^4 as the temperature increases to 12 K. These extremely rapid thermal relaxation times are obtained only by applying the equations to a very small volume! Thus on times scales of femtoseconds, the sample reaches equilibrium according to this calculation.

4.D. HIGH ATOM DENSITIES HAVE ALREADY BEEN ACHIEVED

The spin densities from the ortho to para conversion experiments indicate that high atom densities are possible and have already been achieved. See Fig. 4. It only remains to investigate the dependence of spin density upon magnetic field and to produce comparably high spin densities by techniques other than tritium impregnation.

4.E. A MODEL FOR THE TRANSPORT COEFFICIENTS

Our previous studies have shown that the diffusion, D_0, and bimolecular recombination, $2\alpha_0$, transport coefficients are given by the expressions

$$D_0 = a^2\,\Gamma_0(H+V \to V+H) \qquad (39)\ ,$$

and

$$2\alpha_0 = za^3\,\Gamma_0(H+H \to H_2+V) \qquad (40)$$

where a is the lattice spacing and z is the coordination number (number of nearest-neighbors) provided by the lattice of cells formed by the host material. The microscopic rates (inverse time) are

$\Gamma_0(H+V \to V+H)$	⇒	(H atom and vacancy exchange nearest-neighbor sites)
$\Gamma_0(H+H \to H_2+V)$	⇒	(nearest-neighbor H atoms recombine to form a H_2 molecule and a vacancy on same nearest-neighbor sites)

An important consequence of the above expressions for the transport coefficients is that from a fundamental point of view, $2\alpha_0$ is <u>not proportional</u> to D_0 as is usually taken to be the case. The reason for this is that the H atom-vacancy exchange is a one-body effect and the recombination is a many-body effect. It may turn out that the rates are numerically similar. If one imagines this to be the case in some temperature regime, then one obtains

$$2\alpha_0 = zaD_0\ .$$

This is the lattice analogue of the continuum "condensed phase" diffusion controlled kinetics result:

$$2\alpha_0 = 4\pi R_0 D_0\ ,$$

where R_0 is the critical spherical reaction radius. Clearly, to obtain the isotropic continuum limit from the lattice result, one makes the replacements, $z \to 4\pi$, $a \to R_0$.