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Absence of Molecular Deuterium Dissociation During Room-Temperature Permeation Into Polystyrene ICF Target Shells

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ABSTRACT

Polystyrene microshells filled with deuterium and tritium gas are important target shells for inertially confined fusion (ICF) and are particularly promising for targets containing spin-polarized hydrogens fuels. A currently active approach to the latter uses polarized D in HD, in a method which requires preservation of the high purity of the initially prepared HD (very low specified H_2 and D_2 concentrations). This would not be possible if dissociation should occur during permeation into the target shells. We have thus tested polystyrene shells using a novel method which employs very pure ortho-D_2 as the test gas. An upper limit of 6×10^{-4} was deduced for the dissociation of D_2 upon room temperature permeation through an approximately 8 um wall of polystyrene, clearing the way for use of polystyrene target shells for ICF fusion experiments with spin-polarized hydrogens fuels.

INTRODUCTION

Molecular hydrogens fuel can be introduced into small (few hundred um diameter), thin-walled target shells for inertially confined fusion (ICF) via a diffusion process referred to as permeation[1]. If the shell material is ordinary glass, in order to insure a rapid enough permeation rate, the diffusion is carried out at temperatures of at least 300° C, and because of the elevated temperature, considerable dissociation may occur, with subsequent recombination back to the diatomic hydrogens. For certain fusion experiments where the molecular isotopic composition (or ortho-para symmetry species ratios) of the fuel mixture is of critical importance, such as is the case for one method of utilization of spin-polarized fuels[2], permeation into glass shells might thus be unacceptable. This is evident from consideration of the example of polarized D in HD, on which considerable progress has already been made[2,3]. The HD must be very pure, with less than 5×10^{-4} o-H_2 or p-D_2 present. Complete dissociation upon permeation would convert a properly prepared pure HD sample into one with an "equilibrium" mixture of 25% H_2, 25% D_2, and 50% HD, useless for the polarized nuclei application, and even a fraction of a percent dissociation would make application of the method much more time-consuming. Similar considerations hold for polarized pure o-D_2[4], and for polarized DT, under conditions where low T_2 concentration is mandatory[5]. Recently, progress has been made in producing very high quality plastic shells, for example of polystyrene[6,7] or parylene[8], into which hydrogens can be permeated to high pressures rapidly, even at room temperature. These shells are not as robust as the glass ones[8], but they can nevertheless support useful pressures for fusion experiments. Furthermore, cryo-condensed sample techniques have been proposed[9] by which the effective fuel densities are not limited by the shell construction material, and recent development of 4K cold-sample-transfer methods[10], necessary for polarized fusion experiments, provides a new basis for implementation of these condensed-fuels techniques. Of particular importance for our present concern is that in view of the low permeation temperature, it is quite likely that permeation will not be accompanied by dissociation, and thus these shells may be very well suited for fusion experiments with polarized fuels, as well as for other applications. The endeavor of this investigation is to test whether or not dissociation actually takes place during diffusion of diatomic molecular hydrogens into polystyrene shells. The experimental method, which is novel and fairly simple to employ, may also be quite useful for other situations in which one wishes to determine if hydrogens dissociation takes place during traversal of any type of material.

METHOD OF EXPERIMENT

The method utilizes very pure o-D_2, whose preparation is relatively staightforward due to recently developed techniques[4,11]. In the solid phase, at temperatures below 10K, the para to ortho conversion drives exponentially towards an equilibrium value of the p-D_2 concentration less than 10^{-4}, with a time constant[12,4] of about 80 days. Thus, during short term storage (about a day) of fairly pure o-D_2 at liquid helium temperatures, one expects little significant change of the p-D_2 concentration. The pure o-$_2$ is also relatively stable even at room temperature against back-conversion towards n-D_2 (67% o-D_2, 33% p-D_2) for periods of hours, depending on the care taken with the containment materials. A further attribute is that the concentration of p-D_2 can easily be determined to within about 1% accuracy with a thermal conduction cell, and to better than 10^{-4} with a nuclear magnetic resonance (NMR) spin-lattice relaxation time (T_1) measurement[4]. If complete dissociation were to occur for this gas during permeation, the o-D_2 would revert to normal-D_2, which has a 2:1 ratio of ortho/para molecules. In our case, very pure ortho-D_2 is initially prepared. This gas then undergoes a round-trip permeation-depermeation cycle into and out of a large number of polystyrene shells, after which the ortho-concentration is again measured. Use of D_2 in this manner as the working gas is preferable to HD gas in conjunction with subsequent isotopic analysis, because of the simplicity and accuracy of the method. Indeed, a stronger conclusion can be reached with the D_2 experiment because (in anticipation of the obtained negative result, i.e. little or no change in ortho-para ratio after permeation), the indication is that not only no dissociation, but also no conversion, occurs. With regard to our fusion-related inferences from these experiments, the assumption is made that the dissociation behaviors of D_2 and of HD (as well as of other isotopic hydrogen molecular combinations) are very nearly the same.

EXPERIMENTAL CONSIDERATIONS

The basic procedure of the experiment is to permeate gas into hollow polystyrene shells at a temperature where the equilibration time is relatively short, cool the permeation cell to a temperature where the equilibration time is very long (thus entrapping the gas within the shells), pump away the original fill gas, and then warm the cell, resulting in depermeating the gas from the shells. The resultant gas, which has undergone two passages through the shell walls, is then analyzed. The pressures used are limited by the mechanical resistance of the shells against implosion and explosion[8]. In the process of permeating, staged small differential pressures insure the cells against implosion, and a conservative value of the upper pressure was employed, for resistance to explosion after filling. Our aim was preservation of the integrity of all the shells rather than obtaining high pressures in a few surviving shells, as is sometimes the case. Permeation-filling was done at room temperature, where the equilibrating time constant for the least permeable shells of the distribution was calculated to be about 0.5 min, and liquid N_2 temperature was used for the shell sealing temperature, for its convenience and stability (equilibrating time of many days). Because of the need for substantial amounts of gas with our present analysis apparatuses, 2×10^{-4} moles for the thermal conductivity cell and about 3 times that quantity for the NMR relaxation time measurements at desirable signal/noise levels, a large number of shells was required. 6300 shells, made by the micro-encapsulation method, were employed, filling the entire volume of our permeation cell (0.35 cm^3), and these were loaded to a pressure of 6 atmospheres. The number of shells was determined by weighing the lot and characterizing three small representative samplings totaling 85 shells. Their diameters ranged from 260 to 600 um, their wall thicknesses from 5.3 - 9.5 um, and about 12% of the shells were defective (crushed, or apparently cracked walls). The most mechanically fragile shell (against explosion) of the distribution has the smallest wall thickness to radius ratio. In our limited sampling, this shell's ratio was 0.025, which from Fig. 5 of Ref. 8, implies survival with pressures up to 8 atmospheres. This is consistent with our observation of no loss of gas yield upon repeated permeation-depermeation cycles at 6 atmosphseres. Using the actual distributions, the effective total interior volume of all of our shells was calculated to be 1.98 cm^3, which accords satisfactorily (within 10%) with the experimentally measured value of the complete-cycle gas yield. With all shells filled to 6 atmospheres, the resultant single cycle total gas yield is still insufficient for our analysis instruments, so the depermeated gas was cryocondensed into a storage tube, and sufficient gas was then accumulated in successive cryocondensations of permeation-depermeation cycle yields. For the thermal conductivity apparatus, 4 cycles were employed, and for the NMR experiments, 11 cycles were utilized, with the entire latter process carried out in a period of about 8 hours.

The pure o-D_2 gas was prepared in a low-temperature grafoil cell[11], without special efforts to obtain a highest possible ortho-D_2 purity, since maximum purity was not essential to establish an upper limit of possible dissociation of 6 X 10^{-4} (2 X 10^{-4} p-D^2 concentration increase), which was our set goal. The actual sample was initially prepared[13] as 99.94% pure o-D_2, but after being used for other purposes, had the value 99.81% at the commencement of the permeation experiment.

The complete set-up for the experiment is shown in Fig. 1. All gas handling is via cryopumping. The shape of our glass sample containers allows direct insertion into the cryogenic NMR apparatus, and at the same time lends itself well to cryopumped gas transfer operations, fitting into virtually any available liquid helium storage vessel. Liquid helium filled portable dewars[14] on lab jacks provide convenient temperature reservoirs in the 4 - 30K region needed for cryocondensing and controlling the pressure of the D_2 gas. After the entire system is continuously pumped for a period of four hours, the pure o-D_2 gas in sample container A is introduced into liquid-helium-filled cryocondenser C_1 via valves V_2 and V_3. Closing V_3 and opening V_4 and V_5 allows the pressure in the permeation cell B, measured by G_1, to be brought to any value by adjustment of the height of liquid helium dewar C_1. We conservatively chose a maximum differential pressure of 2 atmospheres during permeation, and indeed this produced no shell destruction as was ascertained by the consistency of the gas yield in subsequent cycles. The room temperature permeation time constant, T_p, for the least permeable polystyrene shell of our distribution (262 um diameter, 8.0 um wall) is about 0.5 minutes[15]. Since factors other than permeation time were dominant in determining the total time of the experiment, we conservatively waited 4 minutes after each 2 atmosphere increment in the driving pressure. After reaching 6 atmospheres and equilibrating there, the small liquid-nitrogen-filled dewar (labeled N_2) was raised so as to immerse permeation cell B in liquid nitrogen. After about 10 minutes for temperature equilibration, all residual D_2 gas was pumped out, after which V_5 was closed and the liquid nitrogen bath removed. As the permeation cell and its contents rapidly warm with the aid of a directed-heat gun, the gas trapped in the shells depermeates, resulting in a cell filled with gas which has twice passed through polystyrene shell walls. This gas can now either be shared with the thermal conductivity analysis system D, cryopumped into a sample container of type A, or if of insufficient amount, cryoppumped into C_2 for storage. Subsequent similar cycles can build up the accumulated supply in C_2 to any desired amount, after which that gas can be conduited either to the thermal conductivity cell or to a sample container such as A, which is insertable directly into a low temperature NMR probe for T_1 analysis. Thermal conductivity cells for measuring ortho-para ratio similar in principle to ours have been described in the literature[16]. Ours is a home-built adaptation based on a glass-coated thermister[17]. The n-D_2 gas source depicted in the thermal conductivity unit is for calibration purposes. The NMR system consists of a crossed-coil probe in an exchange-gas-cooled shielding can immersed in a liquid helium cryostat. The sample is introduced through a vacuum lock arrangement.

RESULTS AND DISCUSSION

A first experiment with a 98% o-D_2 (2.0% p-D_2) sample[18] used a 4 cycle permeation accumulation, after which the ortho-para ratio was measured with the thermal conduction cell. The after-permeation p-D_2 concentration measurement was 2.2 +/- 1%, consistent with no conversion (or dissociation). This experiment illustrates that if only moderate precision is needed, very simple equipment suffices to implement the method. A second experiment utilized the 99.81% pure o-D_2 sample (0.0019 p-D_2 concentration). Ortho-para determinations in this case were made with the NMR method, but at the end of the experiment, were confirmed to be [0 +/- 1%] with the thermal conduction cell, to insure against possible ambiguity associated with the non-monotonic dependence at low temperatures of $T_1(D_2)$ on ortho-para ratio[4]. Care is taken to keep the sample at liquid helium temperatures during storage intervals, and to insure that residence times at room temperature, encountered while conveying the sample among the various apparatuses, are kept short to avoid excessive back conversion toward normal-D_2, as was discussed earlier. This time amounted to about 15 minutes in our experiment, during which time the p-D_2 concentration is estimated to have increased by 2×10^{-4}, based upon an independent measurement of back conversion on the particular sample flask used. Using Fig. 3 of Ref. 4, the p-D_2 concentration prior to permeation was deduced from the NMR T_1 measurement at 4.43 MHz and 1.2K, 15.2 +/- 1.0 seconds, to be 0.0019. After permeation, the T_1 measurement of 7.9 +/- 0.6 seconds yielded a p-D_2 concentration of 0.0025, giving a measured increase in p-D_2 concentration of 6 X 10^{-4}. Subtracting the p-D_2 concentration increase attributable to room-temperature back-conversion in the glass sample container, we obtain an upper limit on p-D_2 concentration increase associated with a round-trip permeation of 4 X 10^{-4}, or 2 X 10^{-4} for a single permeation. If p-D_2 concentration change is to be attributed to dissociation, this corresponds to an upper limit for dissociation of 6 X 10^{-4}, since 2/3 of dissociated D_2 presumably returns to the ortho state upon recombination. In addition to the small back- conversion from time spent at 300K, the sample spent about a half hour at room temperature in the stainless steel permeation chamber, and it is quite feasible that back conversion in that chamber accounts for the entire measured increase in p-D_2 concentration, and that the permeation-induced dissociation rate is zero. After completion of the permeation experiment, the resultant 99.75% o-D_2 sample was allowed to remain for a period of about 8 hours at room temperature at a pressure of 23 atmospheres in one of the thin stainless steel tubes used for cryocondensation. Upon remeasurement in the NMR apparatus, the p-D_2 concentration rose to 0.0056. This p-D_2 concentration increase of 0.0031 provides a rough estimate of the ortho-para conversion rate at high pressures, where there is otherwise very scant data. It is probable that this is still due to surface interactions, rather than to any intrinsic mechanism in the high pressure gas.

From the totality of measurements described above, we are able to conclude that consequent to permeation of D_2 gas through about 8 um thickness polystyrene walls at room temperature, neither dissociation nor conversion can result in an increase in p-D_2 concentration exceeding 2 X 10^{-4}. We also infer from the assumption that dissociative behavior of HD should be similar to that of D_2 that the compositional change of pure HD gas upon permeation is within acceptable limits for its use as a polarizable fusion fuel. After permeation-filling of polystyrene target shells, they must be kept near or below liquid N_2 temperatures to prevent gas leakage, and at temperatures near or below about 20K if high density condensed state targets are desired. For pure HD samples to serve as polarized fuel targets. the shells must remain even colder, at or below 4K, after polarization. This has been accomplished through 4K cold-transfer methods which the Syracuse University group has developed in order to permit insertion and retrieval of samples among various apparatuses at liquid helium temperatures without the sample ever warming appreciably above 4K[10]. These same 4K cold-transfer techniques are also effective for implementing the low temperature constraints which prevent target shell gas leakage and allow cryocondensation of the fuels. In the latter enterprise, the very high densities are build up in small differential increments after which condensation to the liquid or solid state allows their retention, at low pressure, until utilization. There is constant progress in shell development, such as the parylene coating[8] and special heat treatments of polystyrene[19] which result in mechanical strength greater than for ordinary polystyrene, but no improvement thus far permits densities approaching those obtainable with condensation and cold-transfer.

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<u>REFERENCES</u>:

1. D. E. Solomon and T. M. Henderson, J. Phys. D: Appl. Phys. <u>8</u>: L 85 (1975).
2. A. Honig, N. Alexander, and S. Yucel, in Muon Catalyzed Fusion, (Sanibel Island, 1988). Proceedings of the conference on Muon-Catalyzed Fusion, AIP Conf. Proc. No. 181, edited by Steven E. Jones, Johann Rafelski and Hendrik J. Monkhorst (AIP, New York, 1989).
3. N. Alexander, Y. Y. Yu, Q. Fan, X. Wei and A. Honig, Bull. Am. Phys. Soc. <u>35</u>, 925 (1990).
4. A. Honig, M. Lewis, Z.Z. Yu and S. Yucel, Phys. Rev. Lett. <u>56</u>, 1866 (1986).

5. P. C. Souers, E. M. Fearon and E. R. Mapoles, J. Vac. Sci. Technol. A4, 1118, (1986).

6. J. Kubo and H. Tsubakihara, J. Vac. Soc. Technol. A4, 1134 (1986).

7. L. A. Scott, R. G. Schneggenburger and P. R. Anderson, J. Vac Sci. Technol. A4, 1155 (1986).

8. R. Q. Gram, C. K. Immesoete, H. Kim and L. Forsley, J. Vac. Sci. Technol A6, 2998 (1988).

9. T. M. Henderson, D. L. Melmoth, D. C. Musinski, T. R. Pattinson and G. H. Wuttke, Adv. in Cryogenic Eng. 23, 699 (1978).

10. The cold-transfer (4K) system is reported in a paper by N. Alexander, J. Bardon, Q. Fan and A. Honig, which has been prepared for Rev. Sci. Instrum.

11. S. Yucel, N. Alexander, and A. Honig, Phys. Rev. B42, 820 (1990).

12. Yu. Ya Milenko and R. M. Sibileva, Fiz. Nizk. Temp. 1, 796 (1975). [Sov. J. Low Temp. Phys. 1, 382 (1975)].

13. Although not the highest purity obtainable with our new conversion method, this 99.94% o-D_2 sample is nevertheless the purest directly produced (without aging[4]) o-D_2 ever reported.

14. These are vapor-baffled glass helium dewars (no liquid N_2 requirement) manufactured by the former S. H. E. Corp. (now Biomagnetic Technologies, Inc.).

15. This value is approximately confirmed from the measured rate of pressure rise during depermeation.

16. E. R. Grilly, Rev. Sci. Instrum. 24, 72 (1953).

17. Our thermistor is Model CTFP14DE244R, made by THERMOMETRICS, 808 U.S. Highway 1, Edison, N.J. 08817.

18. o-D_2 of 98% purity can be produced very simply by catalysis of liquid D_2. [See, for example, I. F. Silvera, Rev. Mod. Phys. <u>52</u>, 393 (1980).]

19. H. Ito, T. Norimatsu, T. Takagi, S. Kobayashi, M. Yasumoto, K. A. Tanaka, T. Yamanaka and S. Nakai, "Development of Cryogenic Plasic Shell Targets for Laser Fusion", talk presented at Am. Vac. Soc. 37th Symposium, Oct 8 - 12, 1990, Toronto, Ontario.

FIGURE CAPTION

Fig. 1. Schematic of permeation apparatus using pure ortho-deuterium. A: Glass sample tube; B: Stainless steel permeation cell; C: Liquid helium cryo-condensers; N_2: Liquid nitrogen dewar; D: Thermal conduction system for measurement of D_2 ortho-para ratio; G: Pressure gauges; V: Valves.

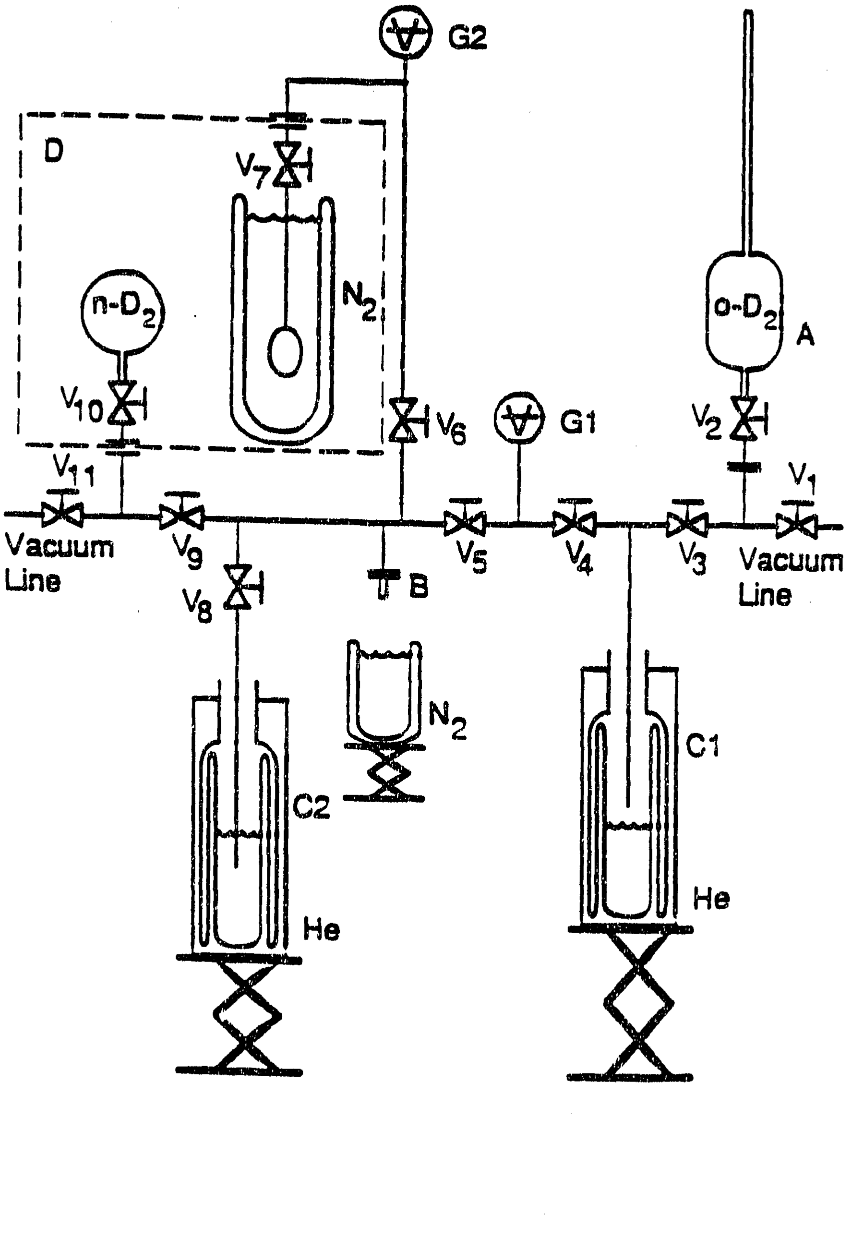
G2
D
V_7
N_2
$n\text{-}D_2$
V_{10}
V_6
G1
$o\text{-}D_2$
A
V_2
V_{11}
V_1
Vacuum Line
V_9
V_8
B
V_5
V_4
V_3
Vacuum Line
N_2
C2
He
C1
He

FIG. 1

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